

# Catalytic Dioxygen Activation by (Nitro)(*meso*-tetrakis(2-*N*-methylpyridyl)porphyrinato)cobalt(III) Cation Derivatives Electrostatically Immobilized in Nafion Films: An Experimental and DFT Investigation

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Complexes of the (nitro)(*meso*-tetrakis(2-*N*-methylpyridyl)porphyrinato)cobalt(III) cation, [LCoTMPyP(2)(NO<sub>2</sub>)]<sup>4+</sup>, in which L = water or ethanol have been immobilized through ionic attraction within Nafion films (Naf). These immobilized six-coordinate species, [LCoTMPyP(2)(NO<sub>2</sub>)/Naf], have been found to catalyze the oxidation of triphenylphosphine in ethanol solution by dioxygen, therefore retaining the capacity to activate dioxygen catalytically without an additional reducing agent as was previously observed in nonaqueous solution for the non-ionic (nitro)cobalt porphyrin analogs. Heating these immobilized six-coordinate species under vacuum conditions results in the formation of the five-coordinate nitro derivatives, [CoTMPyP(2)(NO<sub>2</sub>)/Naf] at 85 °C and [CoTMPyP(2)/Naf] at 110 °C. The catalytic oxidation of gas-phase cyclohexene with O<sub>2</sub> is supported only by the resulting immobilized five-coordinate nitro complex as was previously seen with the corresponding solution-phase catalyst in dichloromethane solution. The simultaneous catalytic oxidation of triphenylphosphine and cyclohexene with O<sub>2</sub> in the presence of the Nafion-bound six-coordinate ethanol nitro complex is also observed; however, this process is not seen for the CoTPP derivative in dichloromethane solution. The oxidation reactions do not occur with unmodified Nafion film or with Nafion-supported [BrCo(III)TmPyP]/Naf or [Co(II)TmPyP]/Naf, indicating the necessity for the nitro/nitrosyl ligand in the oxidation mechanism. The existence of a second reactive intermediate is indicated because the two simultaneous oxidation reactions depend on two distinct oxygen atom-transfer steps having different reactivity. The absence of homogeneous cyclohexene oxidation by the six-coordinate (H<sub>2</sub>O)CoTPP(NO<sub>2</sub>) derivatives in the presence of Ph<sub>3</sub>P and O<sub>2</sub> in dichloromethane solution indicates that the second reactive intermediate is lost by an unidentified route only in solution, implying that the immobilization of it in Nafion allows it to react with cyclohexene. Although direct observation of this species has not been achieved, a comparative DFT study of likely intermediates in several catalytic oxidation mechanisms at the BP 6-31G\* level supports the possibility that this intermediate is a peroxy-nitro species on the basis of relative thermodynamic accessibility. The alternate intermediates evaluated include the reduced cobalt(II) porphyrin, the dioxygen adduct cobalt(III)-O<sub>2</sub><sup>-</sup>, the oxidized cobalt(II) π-cation radical, and the nitrito complex, cobalt(III)-ONO.

## Introduction

Development of robust heterogeneous catalysts for activation of molecular oxygen is important for a wide range of applications including environmentally benign synthesis, water purification, and the oxygen reduction reaction in fuel-cell technology.<sup>1</sup> Many heterogeneous catalysts based on metalloporphyrins that are effective in electrocatalytic and photocatalytic oxidations with dioxygen have been studied,

and porphyrin-catalyzed oxidation reactions using peroxides, *N*-oxides, and other oxidants or co-reductants are also well known.<sup>2</sup> A relatively small subset of these metalloporphyrin systems carries out catalytic oxidation reactions with molecular oxygen as the oxidant in the absence of a co-reductant; although some of these have been shown to occur by auto-oxidation radical-chain mechanisms.<sup>3</sup> The use of metalloporphyrin catalysts in supported heterogeneous systems<sup>4,5</sup> and in microporous porphyrin assemblies<sup>6</sup> has also been widely investigated.<sup>1</sup>

The reactivity of five-coordinate (nitro)cobaltporphyrins in the catalytic oxidation of alkenes, apparently through secondary oxo-transfer from the coordinated nitro ligand, was

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previously studied in dichloromethane solution.<sup>7</sup> The reduced cobalt(II) nitrosyl porphyrin product that was observed by visible and IR spectroscopy in the absence of oxygen, is able to react with molecular oxygen and to be reoxidized ultimately to the cobalt(III) nitro complex in solution. It was suggested that this proceeds through the formation of a peroxynitro intermediate that disproportionates in a reaction with the unreacted nitrosyl complex in solution, although direct observation of the intermediate has not been possible.<sup>7,8</sup> Indeed, the original syntheses of the (nitro)(pyridyl)-cobalt tetraphenylporphyrin complex, CoTPP(py)(NO<sub>2</sub>), made use of the this reaction in the presence of pyridine and oxygen gas.<sup>9</sup>

Six-coordinate derivatives of the (nitro)cobalt porphyrins with nitrogen-bound<sup>7</sup> or oxygen-bound ligands trans to the nitro ligand are not reactive with alkenes, due to unfavorable oxo-transfer thermodynamics.<sup>10</sup> However, derivatives with weakly bound sixth ligands are capable of alkene oxidation under appropriate conditions due to the five-coordinate nitro species that exists in equilibrium in solution.<sup>10</sup> All of the solution-phase six-coordinate derivatives with nitrogen- and oxygen-bound ligands studied so far in solution share the ability to oxidize triphenylphosphine, Ph<sub>3</sub>P, catalytically due to the great stability of the product, triphenylphosphine oxide, Ph<sub>3</sub>PO, and the ability of the intermediate nitrosyl complexes to be reoxidized to the corresponding nitro complex by dioxygen. Triphenylphosphine itself also functions as a sixth ligand in competition with solvent when it is present at high enough concentrations,<sup>11</sup> but the resulting six-coordinate (Ph<sub>3</sub>P)(nitro)cobalt(III) complex does not continue to transfer an oxygen atom from the nitro ligand to Ph<sub>3</sub>P in solution, disrupting the oxygen-activation catalysis. Photochemical dissociation of the nitro and Ph<sub>3</sub>P ligands that provide additional reaction pathways have been investigated in addition to the thermal oxo-transfer reactions we have studied.<sup>11</sup>

Similar oxo-transfer reactivity of sublimed thin films of CoTPP(NO<sub>2</sub>) with gas phase trimethylphosphine has also been observed recently.<sup>12</sup> The reoxidation of the resulting CoTP-

P(NO) product to CoTPP(NO<sub>2</sub>) by O<sub>2</sub>, however, is known to proceed slowly in these immobilized porphyrin systems, so they have not been seen as effective oxygen-activation catalysts. Also, these sublimed films are soluble in organic solvents, so the use of high concentrations of solution-phase reactants is not possible with them. Their microporous structures are unstable under elevated temperatures, so despite the wealth of information they have provided regarding structure and reactivity for heterogeneous reactions with gas phase dioxygen,<sup>13</sup> nitric oxide,<sup>14</sup> nitrogen dioxide,<sup>15</sup> their use as catalysts currently faces practical limitations in the simple form produced by sublimation of CoTPP. An oligomeric cross-linked derivative, however, has a more robust structure and similar coordination chemistry.<sup>16</sup>

Immobilization of water-soluble porphyrins onto ionically charged polymers (ionomers) has been explored for two decades for potential use as heterogeneous catalysts. The use of cross-linked Nafion 117 as a substrate is particularly attractive in catalytic systems due to the stability imparted by its fluorinated structure. Nafion-bound neutral and cationic porphyrins, and CoTPyP, CoTAPP, and CoTMAP were first investigated for electrocatalytic hydrogen evolution by Spiro, et al. in the mid-1980s.<sup>17,11</sup> All of these derivatives have been studied for their electrocatalytic reduction of molecular oxygen.<sup>18–21</sup>

In this work, we have prepared Nafion-bound derivatives of [LCoTmPyP(2)(NO<sub>2</sub>)]<sup>4+</sup>, where L = water, ethanol, or no added ligand, to explore their potential use as heterogeneous catalysts for dioxygen activation through the ligand in the nitro–nitrosyl couple. We have observed the solution-phase catalytic oxidation of both triphenylphosphine and cyclohexene by dioxygen, a unique result for this heterogeneous catalyst. This is significant because it would be consistent with the existence of a second oxo-transfer intermediate that is formed as a result of the reduction with triphenylphosphine, and subsequent reaction with O<sub>2</sub>. An unstable peroxynitro complex is suggested as this second intermediate.

Generation of the electrostatically immobilized reactive five-coordinate (nitro)cobalt porphyrin derivative has also been pursued and the catalytic reactivity of the tentatively assigned product in the oxidation of cyclohexene by dioxygen observed.

Although peroxynitrite complexes have been implicated in the scavenging of nitric oxide by oxy-hemoglobin in a

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process called nitric oxide dioxygenation;<sup>22</sup> coordination through the nitrogen atom has not been indicated in that case. The formation of a stable peroxyntro complex has been claimed by Wick et al.,<sup>23</sup> but definite characterization has remained elusive.<sup>24</sup> The high reactivity of such a species toward O-atom transfer and comproportionation has made it difficult to isolate, especially in solution. The report of a nitrogen-bound peroxyntro intermediate that results from the reaction of O<sub>2</sub> with a rhenium nitrosyl complex both in the solution and the solid state is explained by a single electron-transfer reaction from the nitrosyl complex to the oxygen molecule, followed by formation of a dimeric species bridged by the two oxygen atoms in a transient N<sub>2</sub>O<sub>4</sub> arrangement, that undergoes comproportionation and rearrangement to the nitrosyl and nitrate complexes.<sup>25</sup> Reactions of ionomer-immobilized [CoTMpyP(NO)]/Naf with molecular oxygen have therefore been carried out now in an attempt to observe this species with minimal opportunities for decomposition by comproportionation.

A computational evaluation of the thermodynamic stability of possible intermediates in the catalysis has been undertaken with these porphyrin complexes, using DFT calculations at the BP 6-31G\* level. Thermodynamic accessibility of the peroxyntro and other possible intermediates has been evaluated in this way and supports that the N-bound peroxyntro intermediate could be formed from the direct interaction of dioxygen with the cobalt(II) nitrosyl complex. The likelihood for the observed catalytic oxidation reactions to occur by a traditional auto-oxidation radical-chain mechanism was also considered from this perspective because such a route could be initiated by the substitution of an NO<sub>2</sub> or NO ligand by O<sub>2</sub>, or by outer-sphere electron transfer, leading to the formation of a superoxide radical chain initiator.<sup>26</sup> Other routes involving ligand rearrangements were also considered. These include the formation of the nitrito derivatives and loss of NO to form an oxo-complex, and rearrangements of the proposed N-bound peroxyntro intermediate to the O-bound peroxyntro complex Co–O–O–N=O, which has precedent as an intermediate in the single-domain hemoglobin that functions as a nitric oxide dioxygenase. This intermediate promotes the isomerization to nitrate,<sup>27,28</sup> and a DFT study by those authors suggests that several mechanisms may be involved.<sup>29</sup> Attempts to observe a new immobilized intermediate in the oxidation of CoTMpyP(NO) with O<sub>2</sub> have been made without success, however. While a mechanism involving secondary oxo-transfer from cobalt-

bound NO<sub>2</sub><sup>-</sup> followed by an inner sphere reaction with O<sub>2</sub> and its activation as a part of bound ONOO<sup>-</sup> is still not confirmed, the additional positive evidence warrants continued study.

## Experimental Section

**Preparation of Films.** Nafion 117 films (0.05 mm thickness) were obtained from Aldrich in the sodium form and were used as received. Formation of immobilized [XCo(III)TMpyP(2)]/Naf (**1**) (X = Cl or Br) was achieved by soaking the films in aqueous solutions of [ClCo(III)TMpyP(2)]Cl<sub>4</sub> (Midcentury Chemicals) or [BrCo(III)TMpyP(2)]Br<sub>4</sub> prepared by literature procedures.<sup>19</sup> The loading of porphyrin in the films was loosely controlled by concentration of the porphyrin solution and the time of soaking, but has not been studied quantitatively. In general, films were exposed to ~1 mM solutions for 1–2 min at room temperature to acquire ion-paired porphyrin-Nafion films with measurable and visible absorbance values (0.1–1.0 au) for bands in the Soret region corresponding to 1 × 10<sup>-9</sup> to 1 × 10<sup>-8</sup> mol porphyrin/cm<sup>2</sup> film. Longer soaking times can result in opaque films. The irreversibility of the binding is evident by the unchanging absorbance values in films that are soaked in pure water, although boiling in dilute nitric acid can remove the immobilized porphyrins.

Conversion of **1** to [(H<sub>2</sub>O)Co(III)TMpyP(2)(NO<sub>2</sub>)]/Naf (**2**) was carried out by washing **1** with deionized water and then soaking the films in ~0.1 M solutions of sodium nitrite for several hours. The resulting films were again washed, placed between pieces of flat glass to avoid curling, and dried at 80 °C in an oven.

Conversion of **2** to [(CH<sub>2</sub>CH<sub>3</sub>OH)Co(III)TMpyP(2)(NO<sub>2</sub>)]/Naf (**3**) was carried out by soaking **2** in absolute ethanol solvent for several hours.

Conversion of **1** to [Co(II)TMpyP(2)]/Naf (**4**) was carried out in several ways: (a) Oven-dried samples of **1** were taken into the glovebox and were treated with dichloromethane or ethanol solutions of excess tetrabutylammonium borohydride (Aldrich) under the oxygen-free nitrogen atmosphere for several hours. (b) Samples of **1** were reduced with aqueous NaBH<sub>4</sub> (Aldrich) under nitrogen for more rapid in situ preparation of EPR samples, described below. (c) Samples of **2** and **3**, were converted to **4** by heating at 115 °C for several hours under vacuum conditions. The films were very air-sensitive and sample (b) was determined to be paramagnetic by EPR spectroscopy.

Conversion of **2** or **3** to [Co(II)TMpyP(2)(NO)]/Naf (**5**) takes place upon their reaction with Ph<sub>3</sub>P dissolved in ethanol under nitrogen atmosphere.

Formation of five-coordinate [Co(III)TMpyP(2)(NO<sub>2</sub>)]/Naf (**6**) was attempted by heating of the film **2** to 105 °C under a vacuum of ~0.1 torr for several hours. A similar approach was used with film **3** to prepare **6** by heating to 85 °C under vacuum conditions for about the same duration. Prolonged heating under vacuum (days) or the use of higher temperatures (115 °C) resulted in the eventual loss of NO<sub>2</sub> and apparent formation of **4** as described above. Addition of water or ethanol to product **6** at room temperature resulted in rapid reversal of the spectral changes. Addition of low pressure NO or NO<sub>2</sub> gas to **4** results in formation of **5** or **6**, respectively.

Addition of O<sub>2</sub> gas at 1 atm to **5**, CoTMpyP(NO)/Naf, in contact with ethanol, results in a fast but subtle shift in the Soret band position at 417 to 419 nm, suggesting the relatively rapid formation of **6**. The similarity of these visible spectra make the assignments inconclusive. However, longer exposure to oxygen and ethanol

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solvent (2–3 h) resulted in the formation of **3** with a gradual shift of the Soret band position to 425 nm, consistent with the formation of **3**.

**Spectroscopic Methods.** Solution and film-immobilized UV–vis and visible spectra were recorded under nitrogen atmosphere using screw-capped 1-cm path length cells with a Hewlett-Packard 8453 diode array spectrometer or in a Vacuum-Atmospheres Glove Box with an Ocean Optics PC1000 fiber optics spectrometer controlled by OOIBASE32 operating software. This system was periodically calibrated with a holmium oxide filter to ensure precise wavelength determination.

Experiments involving the heating of films under vacuum used a stainless-steel gas cell with a 10 cm path length, heating jacket, and quartz windows (International Crystal Laboratories). A GlassCol MantleMinder II was used to regulate the cell temperature with its integrated thermocouple. A film holder for use inside this cell was constructed from ordinary zinc-plated steel washers and springs. Spectroscopic measurements of the films held in this cell were carried out using the Ocean Optics PC1000 by means of a home-built cell holder.

The EPR spectrum of air sensitive samples of **4** were obtained by anaerobic reduction of small pieces (ca. 2–3 mm wide) of **1** with aqueous  $\text{NaBH}_4$  inside a quartz EPR tube before removing the solvent by cannula. Data was collected at ambient laboratory temperature of 23 °C with a Resonance Instruments Model 8400 X-band EPR spectrometer at 9.448 GHz.

**Reaction Studies.** The reactions of ethanol solutions of  $\text{Ph}_3\text{P}$  with **3** were carried out in two ways: 1) Under an atmosphere of nitrogen in the glovebox so as to limit reoxidation of the resulting air-sensitive product, and 2) Under 1 atm  $\text{O}_2$ , maintained with oxygen-filled latex balloons. In this experiment, 3.5 mL of 0.1 mM  $\text{Ph}_3\text{P}$  in absolute ethanol (Aldrich) was allowed to react at room temperature in a quartz cuvette with a 1 cm path length. The loss of  $\text{Ph}_3\text{P}$  was monitored by UV spectral changes over 12 h. Reactions of cyclohexene with the films of **6** were carried out in the gas phase at 85 °C in the stainless-steel optical cell. Product analyses of the cyclohexene reactions were carried out by GC-MSD using a Hewlett-Packard Model 6890 gas chromatograph with a Model 5973 mass selective detector. Cyclohexene (Aldrich) was purified by reflux over sodium metal for 12 hours, followed by fractional distillation and analysis for possible oxidized contaminants by GC-MSD. The products of the gas-phase reactions in the heated stainless-steel optical cell were collected by cooling, disassembling and rinsing the inside of the cell with HPLC-grade acetone. These samples were concentrated by evaporation before analysis. The simultaneous oxidation of cyclohexene and triphenylphosphine was carried out in the presence of **3** as described above for the reaction of triphenylphosphine but with cyclohexene as the solvent. The products of the simultaneous oxidation of cyclohexene and triphenylphosphine were separated by distillation to avoid injection of the high-boiling triphenylphosphine oxide into the GC-MSD system.

**Computational Studies.** Computational modeling was carried out using *Spartan '06* running on a PC for all the porphyrin derivatives with different ligand systems corresponding to compounds **1–6** and intermediates discussed below. DFT methods at the BP 6-31G\* level were used for geometry optimization and harmonic vibrational frequency determination for all the compounds to verify that the structures corresponded to minima on the potential energy surfaces. Determination of the thermodynamics parameters of the compounds was then carried out for each of these structures with the *Spartan '06 Properties* program. In all cases except where noted, the calculations were carried out with models having all of the *N*-methyl-2-pyridyl moieties on the same side of the porphyrin

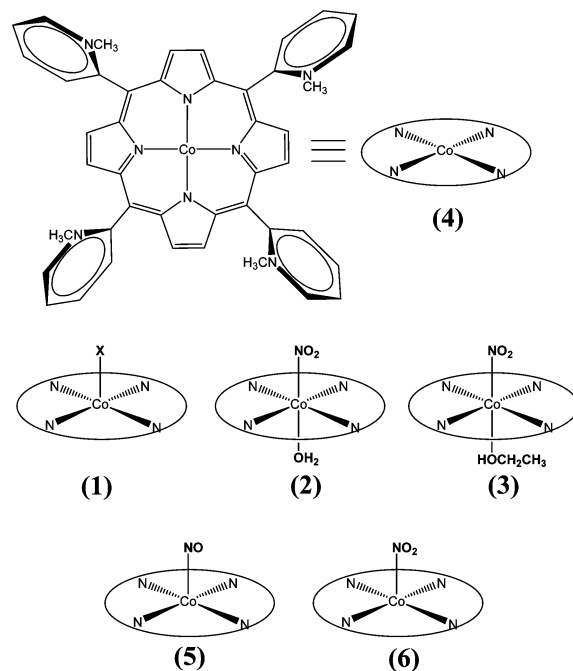


Figure 1. Schematic structures of **1–6**.

as the nitro ligand and its variations and do not include any solvation energies. The use of this porphyrin geometry was arbitrary and is a simplification of the actual distribution of isomers. It is not known if the ion-pairing interaction with Nafion has any bearing on the geometry of the porphyrin complex or the position in which the nitro ligand is oriented during the preparation of the nitro complexes. Calculation of the transition-state energy for the reaction of dioxygen with  $[\text{CoTMpyP}(\text{2})(\text{NO})]^{4+}$  was simplified by use of a semiempirical (PM3) calculation of the transition-state geometry followed by DFT BP 6-31G\* determination of the thermodynamic parameters for this structure. DFT methods were not successful for the calculation of the transition-state geometry in this case.

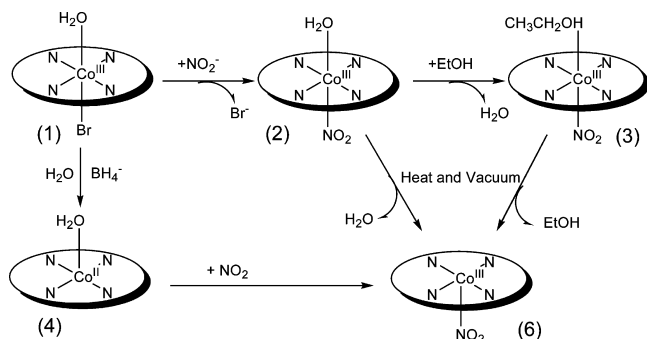
## Results Section

**Synthesis.** Structures of **1–6** are depicted in Figure 1 and their corresponding visible spectral characteristics in Table 1. Visible spectra of these are shown in parts a–f of Figure S1 in the Supporting Information. The Soret-band positions are quite similar to previously reported values of solution-phase or immobilized analogues that were also characterized by IR spectroscopy, as summarized in Table 1.<sup>7</sup> Reactions of the six-coordinate derivatives **2** and **3** by heating under a vacuum to form the five-coordinate species **6** are accompanied by shift in the Soret band to 417 nm. Although this removal of the solvent ligand is reversible, the similarity of this visible spectrum to other derivatives makes the assignment inconclusive. Prolonged heating or higher temperatures result in a further shift of the Soret band to 408 nm, consistent with the results for the borohydride reduction to cobalt(II). That reduction of **1** by borohydride in aqueous solution was confirmed by EPR spectroscopy, as shown in Figure S2 in the Supporting Information, and was therefore likely to be the aqua complex of the cobalt(II) porphyrin. Observation of an EPR spectrum of the heat-reduced species has not been feasible thus far. As shown in part g of Figure S2 in the Supporting Information, direct addition of  $\text{NO}_2$

**Table 1.** Visible Spectral Data of Porphyrin Derivatives in Nafion Films and Solution<sup>b,c</sup>

porphyrin complex	phase/solvent	$\lambda$ , nm <sup>a</sup>	ref.
(1) [XCo(III)TMpyP(2)]/Naf	film/Nafion	429, 548	this work
[XCo(III)TMpyP(2)] <sup>4+</sup>	solution/water	432	
(2) [(H <sub>2</sub> O)Co(III)TMpyP(2)(NO <sub>2</sub> )]/Naf	film/Nafion	428, 549	this work
[(H <sub>2</sub> O)Co(III)TMpyP(2)(NO <sub>2</sub> )] <sup>4+</sup>	water	432, 546, 570	33
(3) [(EtOH)Co(III)TMpyP(2)(NO <sub>2</sub> )]/Naf	film/Nafion	424, 545	this work
(4) [Co(II)TMpyP(2)]/Naf	film/Nafion	408	this work
(5) [Co(II)TMpyP(2)(NO)]/Naf	film/Nafion	417, 548	this work
[(H <sub>2</sub> O)Co(II)TMpyP(2)(NO)] <sup>4+</sup>	solution/water	412, 540	33
(6) [Co(III)TMpyP(2)(NO <sub>2</sub> )]/Naf	film/Nafion	417, 552	this work
Co(III)TPP(NO <sub>2</sub> )	solution/CH <sub>2</sub> Cl <sub>2</sub>	417	7
[Co(II)TMpyP(2)(H <sub>2</sub> O)] <sup>4+</sup>	solution/water	416, 530, 560	33
Co(II)TPP(NO)	solution/CH <sub>2</sub> Cl <sub>2</sub>	414	7

<sup>a</sup> Loading of porphyrin into the films and corresponding molar absorptivities were not assessed quantitatively in this work. The absorbance values vary significantly with the level of solvent content of the films. Weaker spectral features were obscured by broadening and background absorbance from the Nafion matrix. <sup>b</sup> Prepared by anaerobic reduction of **1** with aqueous NaBH<sub>4</sub> or Bu<sub>4</sub>NBH<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Prepared by heating **3** under vacuum conditions.

**Figure 2.** Summary of the conversions of **1–4** and **6** on Nafion films.

gas at  $\sim 1$  Torr to the cobalt(II) complex, **4**, however results in a spectral shift consistent with the formation of the five-coordinate nitro complex, with a shoulder at 430 nm, indicating the presence of a small amount of a six-coordinate complex, such as **2** from the presence of contaminant water. The sequence of transformations is summarized in Figure 2.

Attempts to collect reliable FTIR spectra of the immobilized porphyrins using a Bomem Michelson spectrometer with ATR attachment have not been successful due to the IR absorbance of the Nafion and its tendency to shrink or expand under the varying states of hydration/solvation, thereby making background spectral subtraction problematic.

The EPR spectrum of the reduced [(H<sub>2</sub>O)CoTMpyP(2)]/Naf, **4** shown in S2 shows a broad signal at room temperature with the isotropic  $g$  value of 2.067 with no observable hyperfine coupling. Earlier reports of the solution-phase species at 77 K give values for anisotropic  $g_{\perp} = 2.338$  and  $g_{\parallel} = 2.060$  that predict the isotropic  $g$  value of 2.25.<sup>18,30</sup>

Five-coordinate low-spin cobalt(II) species have isotropic  $g$  values close to 2,<sup>31</sup> and the coordination of a water ligand is assumed in this preparation that was in contact with an aqueous solution. The broadness of the signal may be attributed to spin–lattice relaxation effects in the solid, but may also indicate spin–spin relaxation by adjacent porphyrin complexes. The broad spectrum is very similar in appearance to the room-temperature (19 °C) spectrum obtained for the five-coordinate *N*-methylimidazole complex of a cobalt(II) picket-fence porphyrin, which reversibly binds O<sub>2</sub>.<sup>32</sup> Like our solid samples,<sup>59</sup>Co hyperfine splittings were not observed for the broad signals measured for these systems. Unlike other films used for visible spectra, these EPR samples were opaque and dark-reddish brown due to the high concentration of porphyrin. Exposure of the samples to air resulted in loss of the EPR signal, indicating oxidation to cobalt(III), as has been observed for the closely related [Co(II)TMpyP(4)]<sup>4+</sup> in solution by Anson and co-workers.<sup>21</sup> This air-sensitivity arises from the relatively less-positive reduction potential compared with other cobalt porphyrins and proceeds by electron-transfer from the cobalt(II) species to the Co–O<sub>2</sub> adduct that forms in low proportions to produce hydrogen peroxyide in the presence of water. The metal-centered Co(III/II) reduction potentials are pH independent and for the 4-*N*-methylpyridyl cation, [CoTMpyP(4)]<sup>4+</sup>, it was reported as  $-0.66$  V versus Ag/AgCl in aqueous solution. The value for the 2-*N*-methylpyridyl derivative, [CoTMpyP(2)]<sup>4+</sup>, has a reported value of  $-0.59$  V versus Ag/AgCl.<sup>11,21</sup>

**Oxo-Transfer Reaction Chemistry.** Under a nitrogen atmosphere, the oxo-transfer reaction between **2** and Ph<sub>3</sub>P in ethanol results in a shift of the Soret band in part b of Figure S1 in the Supporting Information from 428 to 417 nm in part e of Figure S1 in the Supporting Information, attributed to formation of [CoTMpyP(2)(NO)]/Naf, (**5**) that was reported in solution.<sup>33</sup> For the reaction of **3** with Ph<sub>3</sub>P under dioxygen atmosphere, the IR spectra of the isolated solid product shows emergence of the phosphorus–oxygen stretching band,  $\nu_{\text{P=O}}$ , at  $\sim 1200$  cm<sup>-1</sup>. The GC-MS study also revealed the characteristic mass spectrum of Ph<sub>3</sub>PO. Monitoring the reaction of 3.5 mL of 0.10 mM Ph<sub>3</sub>P in the presence of **3** under 1 atm oxygen by UV–vis spectra showed the conversion to Ph<sub>3</sub>PO at a constant rate of reaction  $\sim 0.01$  mM/hour. The original film-immobilized porphyrin had a Soret absorbance maximum of 0.53 that corresponds to  $\sim 2.6 \times 10^{-9}$  mol porphyrin/cm<sup>2</sup>. With a film area of 2 cm<sup>2</sup>, the constant reaction rate corresponds to a turnover frequency of 5.5 mol Ph<sub>3</sub>P/(mole porphyrin hour). This is consistent with the 10–15 min reaction time for conversion of **3** to **5** observed under nitrogen atmosphere if the oxo-transfer from the nitro complex is rate limiting. The number of reaction cycles or turnover number, TN, was 66 moles

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Ph<sub>3</sub>P/mol porphyrin for this experiment at room temperature and 1 atm O<sub>2</sub>, and the visible spectrum of the resulting film showed a Soret shift to 432 nm. There was no indication that catalytic activity had ceased in the quantitative reaction. Addition of triphenylphosphine oxide to **3** results in the same Soret peak position, suggesting the formation of the triphenylphosphine oxide complex in which Ph<sub>3</sub>PO is an O-donor ligand. Experiments involving increased pressures of O<sub>2</sub>, increased loadings of porphyrin, other alkenes, and with temperature variation are in progress.

The combination of **3** with allyl bromide or cyclohexene under nitrogen atmosphere showed no change in the visible spectrum of **3**. No evidence of oxidation of the alkenes was observed in GC-MS analysis of the solutions kept in contact with **3** under oxygen atmosphere for 1 week.

Addition of gas-phase cyclohexene to the tentatively assigned film-immobilized five-coordinate nitro complex, **6**, at 85 °C in the absence of oxygen results in the slight shift of the Soret position of 419 to 417 nm within 10–15 min. The addition of oxygen gas at ~1 atm to this system over 12 h results in formation of several oxidized products, including cyclohexene oxide (7-oxa-bicycloheptane) (23%), 2-cyclohexene-1-one (14%), and 2-cyclohexene-1-ol (62%) as determined by GC-MS analysis. The simultaneous oxidation of Ph<sub>3</sub>P and cyclohexene by oxygen in the presence of **3** resulted in oxidized cyclohexene products similar to the gas-phase reaction with cyclohexene alone but with shifted distribution toward the ketone: cyclohexene oxide (7-oxa-bicycloheptane) (27%), 2-cyclohexene-1-one (70%), and 2-cyclohexene-1-ol (2%). In contrast, when a similar experiment was carried out with CoTPP(NO<sub>2</sub>)(2,6-lutidine) in CH<sub>2</sub>Cl<sub>2</sub>, with cyclohexene (1 mM) and Ph<sub>3</sub>P (1 mM), under 1 atm O<sub>2</sub>, only the oxidation of triphenylphosphine occurred, as assessed by GCMS analysis.

**Computational Studies.** Table S1 in the Supporting Information lists the thermodynamic parameters (298.15 K) for both five-coordinate derivatives of [CoTMpyP(2)]<sup>4+</sup> and six-coordinate derivatives having a water ligand in the sixth position. To investigate some of the key reactions involving these complexes, the thermodynamic parameters for NO, NO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O were also determined by the same computational methods, that is, at the BP 6-31G\* level of theory. The results of calculations individual species are listed in Table S1 in the Supporting Information, and the results for the standard free energy changes are listed in Table 2. These results are also illustrated in parts A–C of Figure 3, and in the following results and discussion sections these standard free energy values will be used for comparisons. Part A of Figure 3 focuses upon the formation of several possible intermediates that could arise from simple mechanistic steps from the reactive five-coordinate complex [CoTMpyP(NO<sub>2</sub>)]<sup>4+</sup>. The sequence on the left in part A of Figure 3 shows the free-energy change for the loss of the nitrogen dioxide ligand to form the four-coordinate cobalt(II) species with a standard free-energy change of +191.9 kJ/mol. Rearrangement of the nitro ligand to the O-bound nitrito ligand is calculated to be slightly favorable at –9.24 kJ/mol. The nitrite-ligand orientation preferred by the geometry

optimization was unusual in that the unbound oxygen atom is directed inward toward the porphyrin plane. The energy of the nitrito complex with the usual outward orientation was also determined and found to be less stable than the nitro form by +13.6 kJ/mol. The more-stable inward nitrite orientation was observed to be more stable only when all of the *N*-methyl-(2)-pyridyl positions also oriented on the same side as the nitrito ligand. In modeling, the case in which the nitrite ligand was placed on the opposite side of the porphyrin plane, the usual nitrite geometry with the unbound oxygen atom extending outward was determined to be less stable than the nitro complex by +136 kJ/mol, and the inward pointing nitrito complex was even less stable. Further reaction of the nitrito species described first by bond breakage between the metal-bound oxygen atom and the nitrogen atom to yield the oxo-cobalt species and free nitric oxide requires +203.58 kJ/mol. The oxo-cobalt species, however, has not been observed experimentally by anyone to our knowledge, with peroxy and hydroperoxy species the dominant oxidation intermediates. However, it has been proposed as a hydroxylating intermediate in a high-valence electron-deficient porphyrin complex in the oxidation of alkanes by peroxybenzoic acid.<sup>34,35</sup> The calculation of the oxo-species was only successful when it was allowed to run with a quartet multiplicity, suggesting a high-spin cobalt(II),  $\pi$ -cation radical in the porphyrin ring system. This is consistent with the M.O. orbital surfaces determined by the calculation. The calculation failed to converge when this was run as a doublet state.

The central scheme in part A of Figure 3 involves the slightly unfavored initial oxygen-atom transfer half-reaction step (+14.92 kJ/mol) to form the reduced nitrosyl complex [CoTMpyP(NO)]<sup>4+</sup> and 1/2 O<sub>2</sub>. We earlier suggested the possibility that the interaction of this species with O<sub>2</sub> could be the dioxygen activation step via the formation of an N-bound peroxy-nitro complex by way of bond formation between the bound nitrogen atom and an O<sub>2</sub> molecule. Part A of Figure 3 illustrates that the free-energy change for this reaction is calculated to be +111.11 kJ/mol. The transition-state free energy for the formation of this species was calculated as a slightly higher +118.85 kJ/mol. The calculation of the free-energy change for rearrangement of the N-bound peroxy-nitro complex to Co–O–O–N=O showed that this isomer is more stable by –43.5 kJ/mol in the singlet state, and an additional –3.4 kJ/mol more stable in the triplet state.

Part B of Figure 3 includes free-energy changes involving the coordination and loss of a water ligand to the complexes discussed above. One difference in the results in this series of calculations compared to the five-coordinate complexes was that the six-coordinate (aqua)(oxo)cobalt porphyrin species was only able to be determined in the low-spin doublet state. The calculation failed to converge in the high-

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**Table 2.** Thermodynamics of Reactions Determined from Calculated Values Listed in Table S1 in the Supporting Information at 298.15 K<sup>a</sup>

reaction	$\Delta H^\circ$ , kJ/mol	$\Delta S^\circ$ , J/mol-K	$\Delta G^\circ$ , kJ/mol (298.15 K)
Part A of Figure 3			
[CoTMpyP(2)(NO <sub>2</sub> )] → [CoTMpyP(2)(NO)] + 1/2O <sub>2</sub>	39.7	83.2	14.9
[CoTMpyP(2)(NO <sub>2</sub> )] → [CoTMpyP(2)] + NO <sub>2</sub>	162.6	-98.3	191.9
[Co(II)TMpyP(2)] + NO → [CoTMpyP(2)(NO)]	-252.1	-115.0	-217.8
[CoTMpyP(2)(NO)] + O <sub>2</sub> → [CoTMpyP(2)(NO <sub>2</sub> O)]	76.5	-116.0	111.1
[CoTMpyP(2)(NO <sub>2</sub> O)] → [CoTMpyP(2)(O-O-N=O)] (singlet)	-51.1	-25.5	-43.5
[CoTMpyP(2)(O-O-N=O)] (singlet) → [CoTMpyP(2)(O-O-N=O)] (triplet)	-5.1	-6.5	-3.1
[CoTMpyP(NO <sub>2</sub> O)] → [CoTMpyP(NO <sub>2</sub> )] + 1/2O <sub>2</sub>	-116.3	32.8	-126.0
[CoTMpyP(2)(NO <sub>2</sub> )] → [CoTMpyP(2)(ONO)]	-9.0	0.7	-9.2
[CoTMpyP(2)(ONO)] → [CoTMpyP(2)(O)] + NO	240.5	123.8	203.6
[CoTMpyP(2)(O)] + NO → [CoTMpyP(2)] + NO <sub>2</sub>	60.4	73.7	38.4
[CoTMpyP(2)] + O <sub>2</sub> → [CoTMpyP(2)(O <sub>2</sub> )]	-163.5	-66.8	-133.7
Text Only			
[CoTMpyP(NO <sub>2</sub> O)] + [CoTMpyP(2)(NO)] → 2[CoTMpyP(NO <sub>2</sub> )]	-156.0	-50.4	-141.0
[CoTMpyP(2)(NO)] + O <sub>2</sub> → {[CoTMpyP(2)(NO)]-O <sub>2</sub> } transition state	80.4	-129.1	118.9
Part B of Figure 3			
[CoTMpyP(2)(NO <sub>2</sub> )] + H <sub>2</sub> O → [CoTMpyP(2)(NO <sub>2</sub> )(H <sub>2</sub> O)]	-138.8	-189.1	-82.4
[CoTMpyP(2)(NO)] + H <sub>2</sub> O → [CoTMpyP(2)(NO)(H <sub>2</sub> O)]	-89.0	-179.0	-35.6
[CoTMpyP(2)(NO <sub>2</sub> )(H <sub>2</sub> O)] → [CoTMpyP(2)(NO)(H <sub>2</sub> O)] + 1/2O <sub>2</sub>	89.5	93.4	61.7
[CoTMpyP(2)(NO)(H <sub>2</sub> O)] + O <sub>2</sub> → [CoTMpyP(2)(NO <sub>2</sub> O)(H <sub>2</sub> O)]	57.6	-148.7	102.0
[CoTMpyP(2)(NO <sub>2</sub> O)(H <sub>2</sub> O)] → [CoTMpyP(2)(NO <sub>2</sub> O)] + H <sub>2</sub> O	107.9	211.7	44.7
[CoTMpyP(2)(NO <sub>2</sub> O)(H <sub>2</sub> O)] → [CoTMpyP(2)(NO <sub>2</sub> )(H <sub>2</sub> O)] + 1/2O <sub>2</sub>	-163.7	-151.4	-169.2
[CoTMpyP(2)(NO <sub>2</sub> )] → [CoTMpyP(2)(NO)] + 1/2O <sub>2</sub>	-116.3	32.8	-126.0
Part C of Table 3			
[CoTMpyP(2)(NO <sub>2</sub> )(H <sub>2</sub> O)] → [CoTMpyP(2)(H <sub>2</sub> O)(NO <sub>2</sub> )]	6.1	11.5	2.7
[CoTMpyP(2)(NO <sub>2</sub> )(H <sub>2</sub> O)] → [CoTMpyP(2)(NO <sub>2</sub> )] + H <sub>2</sub> O	138.8	189.1	82.4
[CoTMpyP(2)(NO <sub>2</sub> )(H <sub>2</sub> O)] → [CoTMpyP(2)(H <sub>2</sub> O)] + NO <sub>2</sub>	97.9	-13.7	102.0
[CoTMpyP(2)(H <sub>2</sub> O)(NO <sub>2</sub> )] → [CoTMpyP(2)(NO <sub>2</sub> )] + H <sub>2</sub> O	51.3	223.4	-15.3
[CoTMpyP(2)(H <sub>2</sub> O)(NO <sub>2</sub> )] → [CoTMpyP(2)(H <sub>2</sub> O)] + NO <sub>2</sub>	121.7	-78.7	145.1

<sup>a</sup> The change in free energy values are illustrated in parts A–C of Figure 3.

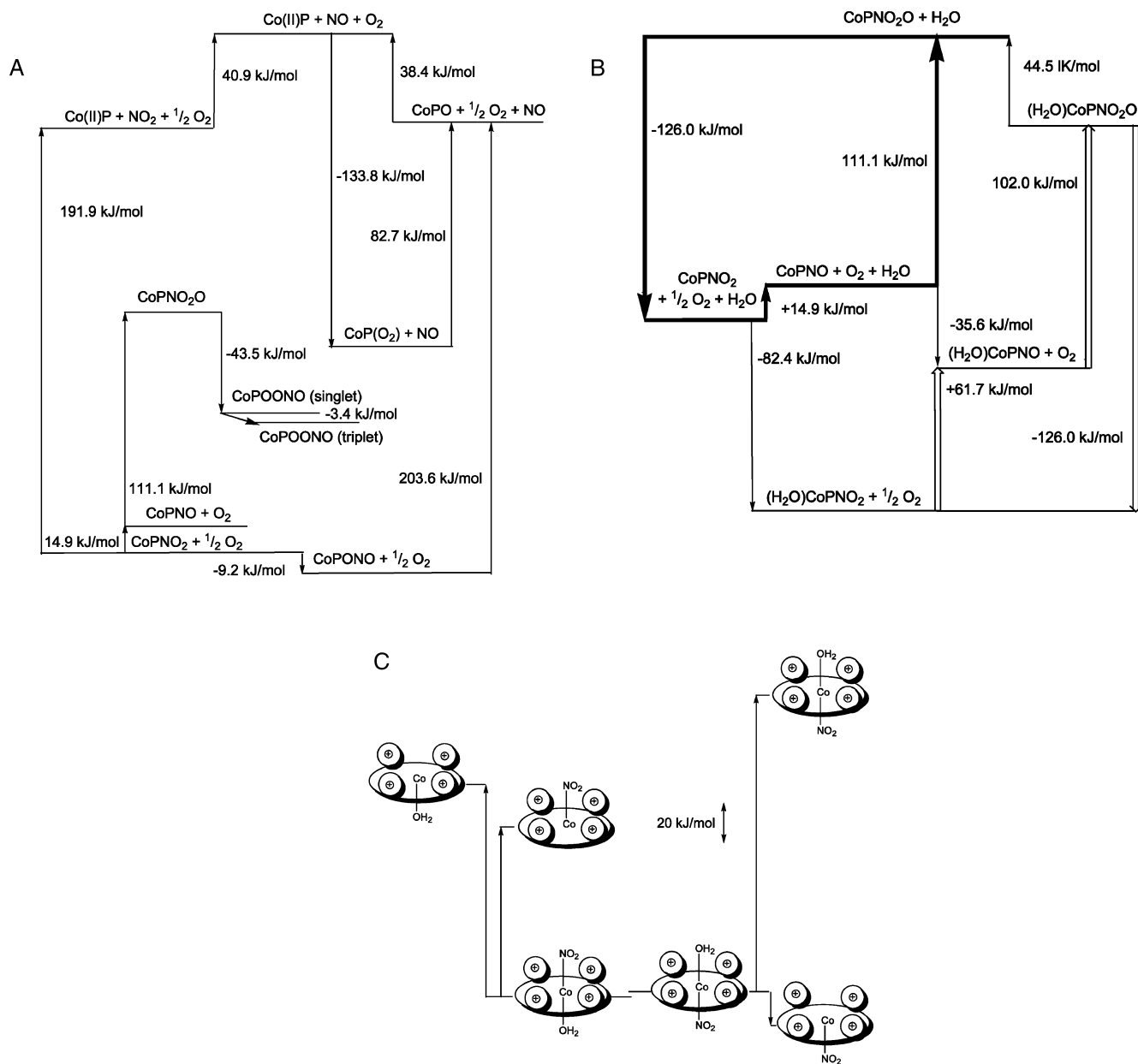
spin state, consistent with an expected increase of the ligand field strength with the addition of the water ligand.

The relative stability of the five-coordinate (aqua)cobalt(III) species and the (nitro)cobalt(III) species that would result from the loss of NO<sub>2</sub> or H<sub>2</sub>O from the six-coordinate [CoTMpyP(2)(NO<sub>2</sub>)(H<sub>2</sub>O)]<sup>4+</sup> is summarized in part C of Figure 3. The loss of water is less energetically demanding (82.40 kJ/mol) than the loss of the nitro ligand (101.99 kJ/mol), which is consistent with our assignment of species **6**, the product of heating [CoTMpyP(2)(NO<sub>2</sub>)(H<sub>2</sub>O)]/Naf to form [CoTMpyP(2)(NO<sub>2</sub>)]/Naf rather than the penta-coordinate aqua complex. It turns out that the orientation of the two ligands with respect to the pyridyl substituents has a surprisingly large role in determining the relative stability of these complexes. As mentioned, the calculations summarized in parts A and B of Figures 3 and Table S1 in the Supporting Information arbitrarily used the orientation of the pyridyl substituents on the same side of the porphyrin and held the nitrogen or oxygen bound dioxygen or oxo ligand on that same side of the porphyrin ring. Even though placing the nitro group on the opposite side of the porphyrin from the pyridyl groups in the six-coordinate aqua complex results in a complex that is only 2.7 kJ/mol less stable than the first isomer, in the five-coordinate nitro complex, the isomer with the nitro ligand on the opposite side from the pyridyl groups is -95 kJ/mol more stable. As a result, the reaction involving the loss of the water ligand in this orientation is actually *favorable* in this case (-15.3 kJ/mol), that is, the penta-

ordinate nitro complex is more stable than the hexacoordinate complex. The loss of the NO<sub>2</sub> ligand to form the five-coordinate (aqua)cobalt(II) complex requires input of +145.1 kJ of free energy. This result is also consistent with our assignment of water loss preceding NO<sub>2</sub> loss in the heating sequence to form **6**. The presumed random distribution of isomers in the compound would likely lead to a distribution of products from the heating process, and perhaps in other reactions as well, and this analysis suggests that significant control over intermediates may be imparted by preparing pure isomers of [CoTRpyP]<sup>4+</sup>, where R are bulkier alkyl groups than methyl, so that they are incapable of rearrangement.

## Discussion Section

**Preparation of Films.** The formation of Nafion-immobilized six-coordinate [LCoTMpyP(2)(NO<sub>2</sub>)/Naf] where L is water or ethanol appears to be straightforward, and the visible spectra of the various derivatives are consistent with those observed in the solution phase. Soret bands are observed at 428 nm for the (aqua)(nitro)cobalt(III) species and 426 nm for the ethanol derivative. These two differ in thermal stability, explained below. Because of the electrostatic attraction between the cationic porphyrin and the anionic sulfonate groups in the Nafion structure, it may be assumed that the porphyrins are localized in the hydrophilic regions of the Nafion film. Recent investigations into the distribution of ionic porphyrins in Nafion have shown localization of the porphyrin near the surface of the films,



**Figure 3.** A. Plotted values of standard free energy changes (at 298 K, determined by DFT BP 6-31G\* methods) for conversion of five-coordinate  $[\text{CoTMpyP}(\text{NO}_2)]^{4+}$  to some possible intermediates in the oxygen activation catalysis. The nitro ligand as well as its derivatives are oriented on the same side of the porphyrin plane as all the *N*-methylpyridyl moieties in these calculations. The graph is approximately to scale. B. Plotted values of standard free energy changes (at 298 K, determined by DFT BP 6-31G\* methods) for possible catalytic dioxygen activation by  $[\text{CoTMpyP}(\text{NO}_2)]^{4+}$  and its aqua complexes. The nitro ligand as well as its associated ligands is oriented on the same side of the porphyrin plane as all the *N*-methylpyridyl moieties. The graph is drawn approximately to scale. C. Plotted values of standard free energy changes (at 298 K, determined by DFT BP 6-31G\* methods) illustrating the relative stability of five- and six-coordinate complexes with water and nitrite as ligands, and the effect of the orientation of the *N*-methylpyridine substituents. All other calculations in this work assume the orientation on the left-hand side of the figure. The actual orientations of the *N*-methylpyridine substituents were not controlled, so the compound is likely a mixture of all the possibilities. The graph is drawn approximately to scale.

and this is likely in this case as well.<sup>36</sup> The six-coordinate nitro cobalt complexes have visible spectra that appear to be unchanged from the solution phase.

Comparison of the visible spectra of **4**, **5**, and **6** to their solution-phase analogues shows very minor differences, however. Species **4**, the reduced cobalt(II) form shows variation in the Soret peak position that may be attributable to the availability of coordinating solvent water or ethanol, and the loading into the film. The five-coordinate aqua complex observed by Cheng and Su in solution<sup>33</sup> had a clear EPR spectrum at 77 K, indicating the coordination of the fifth ligand and a Soret peak position at 415 nm. Our EPR

data were collected under conditions that favored coordination of water also. The conditions of some of our reduction reactions, however, avoided water and may have resulted in formation of four-coordinate species with the Soret peak position at 408 nm. The possibility of dimer formation is greater at higher loadings into the Nafion films and may explain the slight variation observed in the Soret peak position. There are other reports of shifts in the visible spectra of porphyrins upon immobilization in Nafion films that are attributed to dimerization of four-coordinate species.<sup>37</sup>

The Soret peak position of the Nafion-bound nitrosyl species, **5**, is also different from the spectrum reported in



aqueous solution by Cheng and Su.<sup>33</sup> The spectrum of the film obtained by reacting the ethanol-solvated (nitro)cobalt porphyrin, **3**, with Ph<sub>3</sub>P dissolved in ethanol under nitrogen atmosphere has a Soret peak maximum at 417 nm, compared with the position of 412 nm reported in solution phase [CoTMpyP(NO)]<sup>4+</sup>.<sup>33</sup> Our observed peak at 417 nm is more similar to our earlier experiments with CoTPP(NO) in dichloromethane solution in which the Soret peak position was observed at 414 nm.<sup>7</sup>

The tentatively assigned five-coordinate nitro species **6** only has counterparts in non-ionic porphyrins in non-coordinating solvents. Our earlier observation of the CoTPP(NO<sub>2</sub>) Soret peak at 417 nm is the same as the 417 nm position that we now observe for the Nafion-bound system produced by thermal dissociation of the sixth solvent ligand, but also similar to the spectrum of [Co(II)TMpyP(H<sub>2</sub>O)]<sup>4+</sup> previously reported.<sup>32</sup> Without the possibility of investigating this species by IR spectroscopy due to the overlapping IR absorbance by the Nafion film, we are limited to the circumstantial reactivity evidence for this assignment. Beyond the preparative measures, that evidence lies primarily in the reversible reactivity with solvent and in the oxo-transfer reaction with oxophiles. If samples of **6** are exposed to water or ethanol, the spectra of **2** and **3**, respectively, are obtained and the reactions are reversible. Reduction of **6** by an O-atom acceptor to form [CoTMpyP(NO)]<sup>4+</sup> would be inconclusive with visible spectroscopy because the known spectra are so similar. Because the catalytic oxidation of cyclohexene by oxygen is also supported by this species, we conclude it is most likely to be the reactive five-coordinate nitro complex instead of the five-coordinate cobalt(II) complex, [CoTMpyP(2)(H<sub>2</sub>O)]<sup>4+</sup>. The formation of **6** by heating under vacuum takes several hours, but this process may also lead to complete reduction to **4** if the films are heated excessively, so it is possible that a mixture of products is present as a result of heating. It is noteworthy, however, that the films that are either not heated sufficiently or heated to excess have not shown evidence of supporting catalytic oxidation of cyclohexene.

**Catalysis.** Carrying out the catalytic oxidation of triphenylphosphine under oxygen atmosphere indicated catalytic oxygen activation in the conversion of  $3.5 \times 10^{-7}$  mol of Ph<sub>3</sub>P to Ph<sub>3</sub>PO over the course of 12 h. For the 2 cm<sup>2</sup> film loaded to  $2.6 \times 10^{-9}$  mol porphyrin/cm<sup>2</sup>, the catalytic turnover number of 66 and a turnover frequency of 5.5 h<sup>-1</sup> at room temperature with 1 atm O<sub>2</sub> present. The reoxidation of (nitrosyl)cobalt(II) porphyrins to the (nitro)cobalt(III) form by dioxygen has been observed for a number of solution-phase porphyrins and also slowly in sublimed thin films under oxygen atmosphere. This is the first evidence of the reoxidation reaction occurring in immobilized cobalt nitrosyl porphyrins at an appreciable rate, and is significant because the mechanism of the oxidation is still in question. The

possible transient formation of a peroxy-nitro complex that can quickly undergo a comproportionation reaction with another nitrosyl complex in solution<sup>8</sup> cannot currently be ruled out for the Nafion-bound system because it could occur if there is mobility of some of the porphyrin molecules within the matrix or if the immobilized porphyrins are close enough to allow it. The calculated free-energy change for this reaction from our DFT analysis is -140.97 kJ/mol at 298 K (Table 2). Carrying out the dual oxidation reaction in solution by using a six-coordinate LCoTPP(NO<sub>2</sub>) complex for comparison resulted in loss of the cyclohexene oxidation reaction. This could be explained in several ways. (i) A comproportionation reaction takes place more rapidly than a cyclohexene oxidation. (ii) Under the conditions of the experiment, triphenylphosphine reacts more rapidly with the intermediate than cyclohexene. (iii) The six-coordinate intermediate peroxy-nitro complex with the stronger N-donor ligand, 2,6-lutidine instead of the O-donor ethanol, deactivates the intermediate so that oxidation of the alkene does not occur.<sup>10</sup> More systematic variation of reaction conditions will be required to understand this discrepancy.

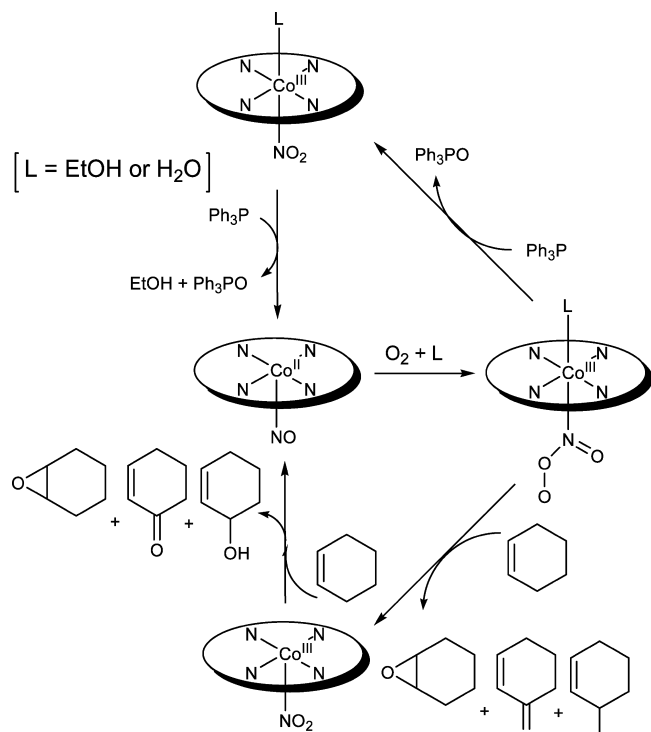
Another possibility is that the oxidation occurs through the loss of the NO ligand from the complex. The free nitric oxide could be oxidized by oxygen and then re-coordinate as NO<sub>2</sub>, so this could be used to explain why the nitro complex is observed at the end of the catalytic reaction. Considering the very large stability constant of  $1.3 \times 10^{13}$  M<sup>-1</sup>, that was measured for nitric oxide coordination for a similar water soluble porphyrin, [CoTPPS]<sup>4+</sup>, this mechanism is less likely.<sup>38</sup> The possibility of a photochemically promoted dissociation<sup>11</sup> followed by the gas-phase reaction with O<sub>2</sub> and coordination of NO<sub>2</sub> cannot be dismissed, but no intentional irradiation of the system has been pursued in our work. The shift of the Soret band to 432 nm that takes place after oxidation of Ph<sub>3</sub>P suggests coordination by either Ph<sub>3</sub>P or Ph<sub>3</sub>PO to make a six-coordinate nitro complex under these conditions and that this complex is able to support continued catalysis. The spectrum of CoTPP(NO<sub>2</sub>)(Ph<sub>3</sub>P) has been reported to have a Soret peak at 450 nm and is unreactive with respect to oxygen atom transfer to uncoordinated Ph<sub>3</sub>P.<sup>11</sup> Our direct addition of Ph<sub>3</sub>PO to samples of **3** resulted in the expected shift to 432 nm, so these three observations indicate that the sixth ligand in this case is O-bound Ph<sub>3</sub>PO and that this complex retains the ability to oxidize Ph<sub>3</sub>P. Whereas the turnover frequency is a modest value of 5.5 h<sup>-1</sup> at room temperature, this system may be capable of operating under high O<sub>2</sub> pressures and temperatures, with expected increases in turnover frequency.

The mechanism illustrated in Figure 4 that involves the formation of a reactive N-bound peroxy-nitro complex appears to account for catalytic oxidation of Ph<sub>3</sub>P by six-coordinate complexes having water or ethanol as a ligand, L, but also for the catalytic oxidation of cyclohexene alone only by the five-coordinate complex. It also illustrates how cyclohexene can be oxidized by the six-coordinate complex in the presence of Ph<sub>3</sub>P because only the more reactive peroxy-nitro intermediate would react with cyclohexene.

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**Figure 4.** Proposed catalytic pathways involving the reactive peroxy-nitro intermediate.

The lack of direct observation of a peroxy-nitro intermediate at this point makes the claim for its existence tenuous, and determination of its structure even more so. Other mechanisms involving low concentrations of other species bear examination. The possible formation of a five-coordinate nitrito complex that undergoes bond dissociation to result in NO and a reactive oxo-cobalt species can be envisioned. The resulting NO would, of course be reactive with O<sub>2</sub>, again forming NO<sub>2</sub>. The DFT analysis of the formation of the nitrito species followed by breaking of the bond between the metal-bound oxygen atom and the nitrogen atom to make the oxo-cobalt derivative suggest this is not a favorable route. Part A of Figure 3 and data in Table 2 show the relative energy changes involved are over 200 kJ/mol for the formation of the oxo-cobalt derivative compared to the formation of the peroxy-nitro intermediate at +111 kJ/mol. The latter has a transition-state energy of +118.85 kJ/mol. Loss of the NO<sub>2</sub> ligand and NO ligand to form the four-coordinate cobalt(II) complex have free energy values of +192 kJ/mol and +218 kJ/mol, respectively, at 298.15 K, according to the DFT results.

Because intramolecular rearrangement of the N-bound peroxy-nitro complex to an O-bound isomer is plausible (reviewer's suggestion), the relative energy of the Co—O—O—N=O form was also computed. This type of coordinated has been characterized for iron-heme systems that involve coordinated O<sub>2</sub> reacting with free NO, forming the O-bound intermediate. This peroxy-nitro species then undergoes a rapid isomerization reaction to produce coordinated nitrate. Formation of this type of intermediate could give rise to a CoO<sub>2</sub> complex with the loss of NO, or to Co=O with the loss of NO<sub>2</sub>. The DFT thermodynamics calculations for both singlet

and triplet states and both five-coordinate and six-coordinate complexes (with water as the sixth ligand) were carried out, and the results listed in Table S1 in the Supporting Information. The singlet-state five-coordinate Co—O—O—N=O complex is more stable thermodynamically than the N-peroxy-nitro complex by  $-43.47$  kJ/mol at 298 K. Further speculation about the likelihood of the ensuing bond breakage and loss of NO<sub>2</sub> or NO as a mechanistic path for the catalysis is tempting but unwarranted without further experimental evidence.

A corresponding set of calculations for the CoTPP analogues has also been pursued for comparison. These data are listed in Table S2 in the Supporting Information. The reactions  $\text{CoTPP}(\text{NO}_2) \rightarrow \text{CoTPP}(\text{NO}) + \frac{1}{2}\text{O}_2$  and  $\text{CoTPP}(\text{NO}) + \text{O}_2 \rightarrow \text{CoTPP}(\text{NO}_2\text{O})$  in that series have standard free-energy change values calculated as +57 and +105 kJ/mol, respectively. The loss of NO<sub>2</sub> from  $\text{CoTPP}(\text{NO}_2)$  requires +186 kJ/mol. The conversion of  $\text{CoTPP}(\text{NO}_2)$  to the nitrito complex and its loss of NO to form the high spin oxo complex,  $\text{CoTPP}(\text{O})$ , have standard free-energy values of +52 and +127 kJ/mol, respectively. So, whereas the peroxy-nitro intermediate,  $\text{CoTPP}(\text{NO}_2\text{O})$ , again appears to be the most accessible intermediate, the formation of the high-spin  $\text{CoTPP}(\text{O})$  species is not so difficult as in the  $\text{CoTMpyP}$  case. The lower energy for the formation of the nitrosyl product in the presence of oxo-atom acceptors, of course, would favor the subsequent formation of the peroxy-nitro intermediate rather than  $\text{CoTPP}(\text{O})$ .

The possibility of the interaction of water or other oxygen-donors with the five-coordinate complexes to make six-coordinate complexes has been shown to lower the oxygen atom transfer reactivity of the resulting nitro complexes for a number of cobalt porphyrins. The data in Table 2, represented in part B of Figure 3 support this earlier observation on thermodynamic grounds, as we determined with simpler computational models. Calculations involving the water ligand show a slight thermodynamic advantage in the formation of the aqua complex  $[\text{CoTMpyP}(\text{NO}_2\text{O})\text{-(H}_2\text{O)}]^{4+}$  from  $[\text{CoTMpyP}(\text{NO})(\text{H}_2\text{O})]^{4+}$  (+102 kJ/mol for aqua complex vs +111 kJ/mol for the five-coordinate complex) as determined for at 298.15 K. The formation of six-coordinate cobalt nitrosyl complexes that exist at low temperatures and only decompose as they approach  $-20$  °C has recently been presented.<sup>39</sup> Assuming the change in enthalpy and entropy are unchanged from the values determined at 298.15 K, the thermodynamic stability of the (aqua)(peroxy-nitro)cobalt(III) complex relative to the corresponding reactants is even greater at lower temperatures, approaching +69 kJ/mol for the aqua complex at 77 K versus +85 kJ/mol for the five-coordinate complex at 77 K. Future attempts to isolate and characterize such a complex, perhaps by resonance Raman spectroscopy or EPR spectroscopy, may be more fruitful at low temperatures starting with a six-coordinate (aqua)(nitrosyl)cobalt porphyrin because the energy for the formation of the complex will be smaller ( $\Delta G$  calculated as +69 kJ/mol at 77 K for the reaction of

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CoTMpyP(2)(NO)(H<sub>2</sub>O) with  $^{1/2}$ O<sub>2</sub>) even though the stability of the six-coordinate peroxyntro complex would be less than the five-coordinate complex ( $\Delta G$  calculated for loss of  $^{1/2}$ O<sub>2</sub> at 77 K for [CoTMpyP(2)(NO<sub>2</sub>O)(H<sub>2</sub>O)]<sup>4+</sup> is  $-151$  kJ/mol). However, to have the best chance of isolating such a species, it would have to be immobilized in a matrix, such as Nafion or a sublimed thin film to prevent the strongly favored comproportionation reactions between the peroxyntro complex and the nitrosyl complex to form two nitro complexes. The calculated  $\Delta G$  for the comproportionation reaction of the five-coordinate species is  $-141$  kJ/mol as shown in Table 2 but is calculated as  $-234$  kJ/mol for the six-coordinate water complex at 77 K. Work to isolate and spectroscopically observe a peroxyntro intermediate is in progress.

## Conclusion

Formation of the Nafion-bound six-coordinate (nitro) cobalt porphyrin complexes, **2** and **3**, catalytically oxidize triphenylphosphine by dioxygen and moreover can simultaneously catalytically oxidize triphenylphosphine and cyclohexene. Because cyclohexene cannot be oxidized by this system alone, this stands as evidence for production of a second reactive intermediate proposed to be a peroxyntro complex. DFT calculations have been used to evaluate possible candidates for this intermediate based on thermodynamic calculations. Although the experimental results are not conclusive, the apparent loss of ethanol from **3** at 85

°C suggests that oxygenated hydrocarbon ligands can be removed from the six-coordinate nitro complexes simply by heating under vacuum conditions, creating the reactive five-coordinate species. Ensuing catalysis by the immobilized porphyrin further indicates formation of a peroxyntro intermediate. The use of DFT thermodynamic calculations supports the argument for the formation of a (peroxyntro)-cobalt(III) porphyrin species by comparison of its thermodynamic accessibility to other expected oxidation intermediates.

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**Supporting Information Available:** Visible spectra of Nafion-bound **1–6**, room-temperature EPR spectrum of [(H<sub>2</sub>O)Co(II)-TMpyP(2)]/Naf (**4**) collected at 9.448 GHz, thermodynamic parameters of [CoTMpyP]<sup>4+</sup> derivatives calculated with DFT BP 6-31G\* methods at 298.15 K, and thermodynamic parameters for the reaction intermediates of the CoTPP derivatives calculated from DFT BP 6-31G\* methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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