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Cobaltporphycenes as Catalysts. The Oxidation of Vinyl Ethers via the Formation and Dissociation of Cobalt−Carbon Bonds

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Cobalt(III) porphycenes, structural isomers of cobalt(III) porphyrins, catalyze the addition of alcohols to vinyl ethers in a toluene−dioxane solution containing alcohol and Et_3N as well as the autoxidation of the resultant metal-bound adduct; this produces two acetals, namely, those of β-formylacetaldehyde and β-hydroxyacetaldehyde, with a total turnover number of 34−77 after 21 h at 20 °C. Under identical reaction conditions, analogous cobalt-(III) porphyrins were found to undergo rapid decomposition. A salient feature of this catalytic process is the formation of an alkylcobalt(III) complex, a species that was characterized using ^{1}H NMR and UV−vis spectroscopic methods. The pseudo-first-order rate constants for the addition of n-butyl vinyl ether to the chloride adducts of octaethylporphycene cobalt-(III) and octaethylporphyrin cobalt(III) complexes were determined to be 8.8×10^{-4} and 1.9×10^{-4} s^{-1} at 20 °C, respectively. Irradiating a solution of the alkylcobalt(III) complex resulting from the addition of vinyl ether to a tetra-n-propylporphycene cobalt(III) complex under aerobic conditions yielded an alkylperoxocobalt(III) species as the result of insertion of dioxygen into the cobalt−carbon bond. This intermediate species was characterized by the presence of diagnostic proton resonances, ascribed to the axial ligand, in the upfield region of the ^{1}H NMR spectrum; specifically, the Co−CH_2 and Co−OOCH_2 proton resonances appear at −3.91 and −1.22 ppm, respectively, in toluene-d_8 at −40 °C. Breakdown of the alkylperoxocobalt(III) intermediate, via O−O bond homolysis, produces the two observed acetal products. The exact product ratio of these acetals, aldehyde/alcohol, depends on the viscosity of the solution. This result is taken as support for the idea that alkoxy radicals that diffuse away from the cobalt complex give the alcohol, whereas the aldehyde is produced as the result of oxidation occurring within a solvent cage. The Co(III) complex that results after (1) O−O bond homolysis and then (2) hydrogen atom abstraction from the medium is a five-coordinate species that is capable of continuing the reaction cycle in the presence of excess vinyl ether. As a consequence, the starting octaethylporphycene cobalt(III) complex acts as an efficient catalyst for the oxidation of vinyl ethers.

Introduction

Alkylcobalt(III) porphyrins have attracted considerable interest in recent years both as reactivity models for coenzyme B_{12} and as simplified systems wherein key aspects of cobalt−carbon (Co−C) bond chemistry may be readily studied.[1,2] Over the last two decades, a variety of σ-bonded organometalloporphyrins have been synthesized to evaluate their stability and reactivity.[3] As a result of these studies, it is now appreciated that photolysis or thermolysis of a porphyrin-stabilized Co−C bond gives rise to useful radical species.[4,5] While much remains to be done in terms of exploiting these radicals in, for example, catalysis, we have considered that additional insights into the underlying chemistry could come from changing the basic tetrapyrrolic framework. Toward this end, we focused on a study involving the use of Co(III) porphycene,[6−8] an isomer of Co(III) por-

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(4) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, 116, 7943−7944.
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phyrin, as the supporting ligand framework for Co–C bond formation[9] and lysis. As detailed below, we have found that, in contradistinction to the corresponding porphyrin species, (OEPc)Co^{III}Cl[10] is a good catalyst for the conversion of electron-rich olefins such as ethyl vinyl ether (**1**) or *n*-butyl vinyl ether (**2**) into two different corresponding acetals, namely, β-formylacetaldehyde acetal (RO)$_2$CHCHO (**a**) and β-hydroxyacetaldehyde acetal (RO)$_2$CHCH$_2$OH (**b**) under aerobic conditions. In this paper, we wish to report the characteristics of cobalt porphycenes as catalysts toward the oxidation of vinyl ethers and discuss the mechanism of this reaction.

(OEPc)Co^{III}Cl   (OEP)Co^{III}Cl

(TPrPc)Co^{III}Cl   (EtioPc)Co^{III}Cl
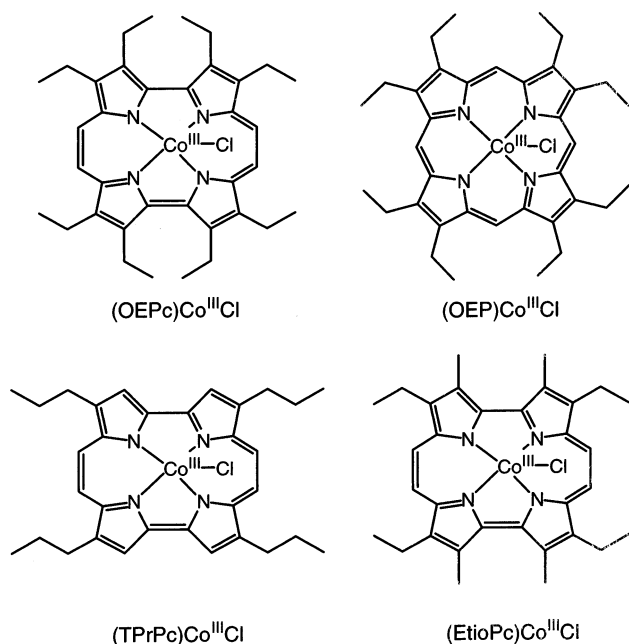
Results and Discussion

Co–C Bond Formation and Dissociation. It has been understood for some time that the reaction of (OEP)Co^{III}Cl and (TPP)Co^{III}Cl with **1** serves to generate the corresponding alkyl complexes, (OEP)Co^{III}(CH$_2$CH-(OEt)$_2$) and (TPP)Co^{III}(CH$_2$CH(OEt)$_2$), respectively, in the presence of ethanol.[11] We have recently found that cobalt(III) porphycenes, such as (OEPc)Co^{III}Cl, (TPrPc)-Co^{III}Cl, and (EtioPc)Co^{III}Cl, can react with **1** in the presence of ethanol in analogy with what is observed for cobalt(III) porphyrins. The result of this reaction is a cobalt-linked acetal species that displays resonances in the upfield region of the ^{1}H NMR spectrum as shown in Figure 1A. For instance, the methylene and methine protons of the alkyl groups coordinated to (TPrPc)Co^{III}-Cl are observed at −3.91 and −2.25 ppm, respectively, findings that are consistent with a bound −CH$_2$CH-
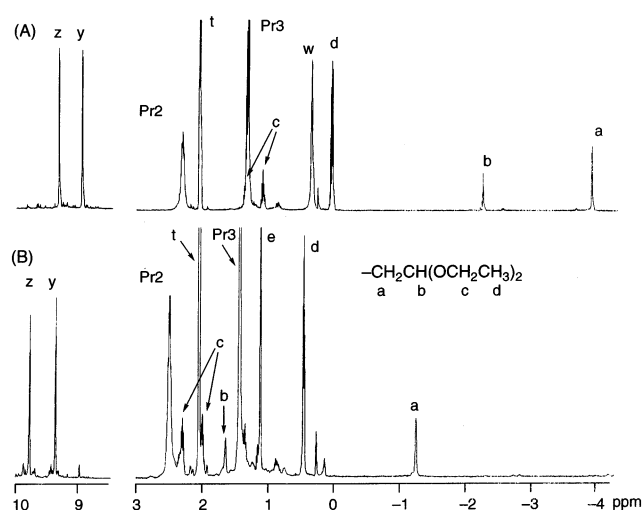
(7) Sessler, J. L.; Weghorn, S. J. *Expanded, Contracted and Isomeric Porphyrins*; Pergamon: Wiltshire, 1997.
(8) D'Souza, F.; Boulas, P.; Aukauloo, A. M.; Guilard, R.; Kisters, M.; Vogel, E.; Kadish, K. M. *J. Phys. Chem.* **1994**, *98*, 11885−11891.
(9) The first synthesis of an organocobalt(III) porphycene was reported by Kadish, Vogel, Guilard, and their co-workers. Kadish, K. M.; Boulas, P. L.; Kisters, M.; Vogel, E.; Aukauloo, A. M.; D'Souza, F.; Guilard, R. *Inorg. Chem.* **1998**, *37*, 2693−2700.
(10) Abbreviations for tetrapyrrole dianion ligands: EtioPc, 2,7,-12,17-tetraethyl-3,6,13,16-tetramethylporphycene; OEP, octaethylporphyrin; OEPc, 2,3,6,7,12,13,16,17-octaethylporphycene; TPP, tetraphenylporphyrin; TPrPc, 2,7,12,17-tetra-*n*-propylporphycene.
(11) Sugimoto, H.; Nagano, M.; Yoshida, Z.-i.; Ogoshi, H. *Chem. Lett.* **1980**, 521−524.

Figure 1. ^{1}H NMR spectra (500 MHz, −40 °C, in toluene-d_8) of (TPrPc)Co^{III}(CH$_2$CH(OEt)$_2$) (spectrum A) and (TPrPc)-Co^{III}(OOCH$_2$CH(OEt)$_2$) (spectrum B) after irradiation for 10 min in the presence of ethanol-d_6. Resonances a−d are due to alkyl groups. Protons y and z are ascribed to β-pyrrole-H and ethylene-H protons, whereas Pr3 and Pr2 denote signals arising from the methyl and methylene protons of the peripheral *n*-propyl groups. Residual proton signals of toluene-d_8 and ethanol-d_6 are assigned as peak t and e, respectively. The broad peak marked w is due to H$_2$O. These assignments were confirmed by 2D NMR spectroscopic analyses.
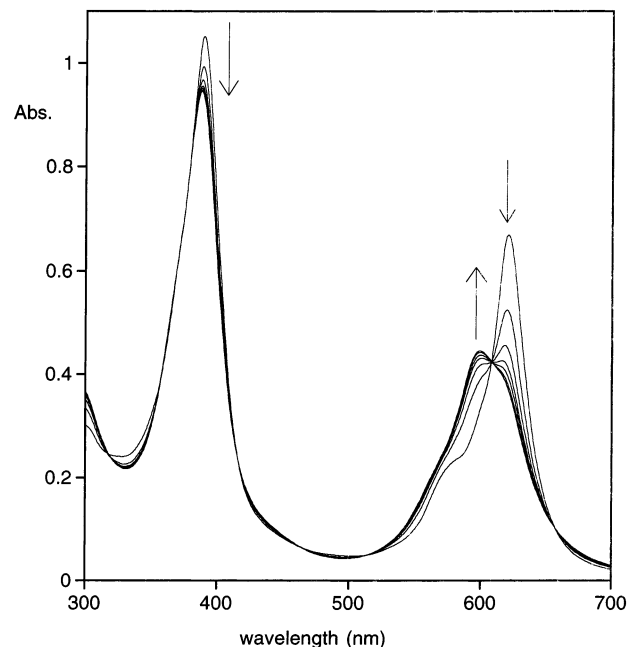

Figure 2. UV−vis spectral changes in the reaction of (TPrPc)Co^{III}Cl (1.9 × 10^{-5} M) with **2** (0.33 M) in toluene containing *n*-BuOH (0.15 M) and Et$_3$N (3.1 × 10^{-4} M) at 20 °C. The spectra were recorded 0, 15, 30, 45, 60, 90, and 120 min after mixing.

(OEt)$_2$ fragment. Support for the formation of this type of organocobalt(III) porphycene moiety also comes from the observation of a characteristic UV−vis spectrum as shown in Figure 2; for instance, the λ_{max} value of the Q-band at 621 nm, observed in the starting material, (TPrPc)Co^{III}Cl, was found to be shifted to 599 nm in the species assigned as (TPrPc)Co^{III}(CH$_2$CH(OEt)$_2$). By contrast, the corresponding Q-band of cobalt(III) por-

Table 1. Comparison of Cobalt Porphycenes and Porphyrins as Catalysts for the Oxidation of 2

entry	cobalt complex	initial rate[a−c]	total turnover number[a,c,d]
1	$(OEPc)Co^{III}Cl$	0.080	77
2	$(TPrPc)Co^{III}Cl$	0.042	45
3	$(EtioPc)Co^{III}Cl$	0.030	34
4	$(OEP)Co^{III}Cl$	0.037	12
5	$(TPP)Co^{III}Cl$	nd	<1

[a] [Co(III) complex] = $(1.2−1.3) \times 10^{-4}$ M, **[2]** = 1.9 M, [n-BuOH] = 2.7×10^{-1} M, [Et$_3$N] = 1.7×10^{-4} M, [dioxane] = 1.7 M in toluene (0.65 mL) at 20 °C under aerobic conditions. Irradiation with a 500 W tungsten lamp from a distance of 10 cm. [b] The unit for initial rate is turnover per minute. [c] Errors are <10%. [d] The data were obtained after 21 h.

phyrins showed only slight variations when exposed to a mixture of vinyl ether and ethanol.

Irradiation of the alkylated cobalt(III) porphycenes with visible light, provided by a 500 W tungsten lamp, was found to produce a species analogous or identical to the starting complexes (e.g., $(TPrPc)Co^{III}X$, X = Cl or OH) under aerobic conditions. Furthermore, the alkylcobalt(III) intermediate was regenerated by adding vinyl ether and alcohol to the reaction mixture in the dark in the presence of Et$_3$N.[12] Support for this conclusion came from chemical analyses as well as the finding that these possibly distinct cobalt(III) porphycene complexes were both capable of catalyzing a reaction between vinyl ether and alcohol. In the presence of light and air, visible light irradiation produces two different acetal products, $(n$-BuO)$_2$CHCHO (**3a**) and $(n$-BuO)$_2$-CHCH$_2$OH (**3b**), from **2**. Here, the relevant aerobic reactions were performed in a toluene−dioxane solution containing n-BuOH and Et$_3$N at 20 °C, with the products being identified by a combination of GC−MS and NMR spectroscopic analyses.

Catalytic Reaction. Table 1 and Figure 3 allow the catalytic features of cobalt(III) porphycenes and cobalt-(III) porphyrins to be compared. From the data in this table and figure, it can be inferred that (i) the catalytic reaction mediated by $(OEPc)Co^{III}Cl$ is clearly faster than that observed for other cobalt complexes of porphycenes and porphyrins. The initial rates for catalysis effected by $(TPrPc)Co^{III}Cl$ and $(EtioPc)Co^{III}Cl$ are almost the same as those for $(OEP)Co^{III}Cl$-mediated catalysis. (ii) The total turnover numbers depend on the choice of catalyst. In the presence of $(OEPc)Co^{III}Cl$, **2** is oxidized to its acetal products with a turnover number of 77 after 21 h, whereas its isomeric congener, $(OEP)Co^{III}Cl$, catalyzes the analogous oxidation with an effective turnover number of only 12. This latter observation, which serves to underscore a key difference between porphyrin and porphycene, reflects the fact that the porphyrin skeleton is seen to undergo decomposition during the course of the reaction (as evidenced by porphyrin chromophore bleaching). (iii) $(TPP)Co^{III}Cl$ did not give products with any kind of reasonable turnover or yield; rather, this putative catalyst was found to undergo reduction in the presence of Et$_3$N. (iv) It is found that other cobalt complexes, such as cobalt salen or vitamin B$_{12}$ derivatives, do not work as catalysts for this transformation (data not shown). Taken together,

(12) Et$_3$N quenches acid generated during the reaction. In the absence of Et$_3$N, various acetal and vinyl ether products undergo acid-catalyzed solvolysis in alcohol to yield simple acetal, (RO)$_2$CHCH$_3$.
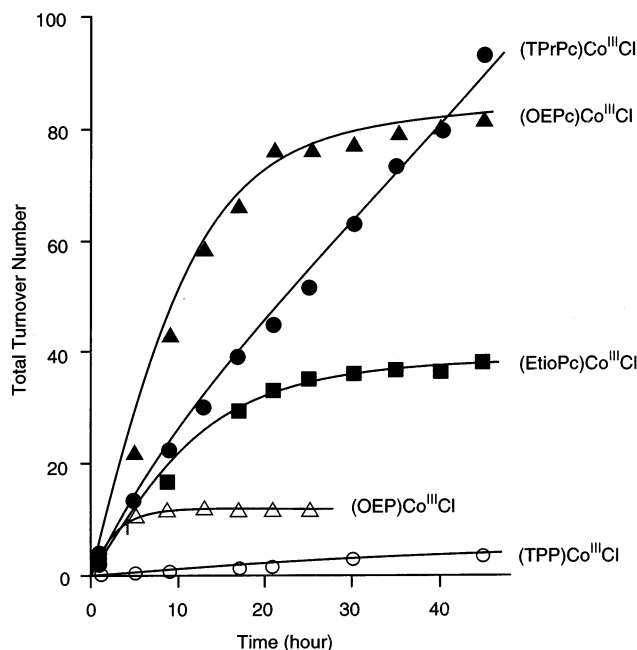

Figure 3. Comparison of catalytic behavior of cobalt(III) porphyrins and porphycenes toward vinyl ether oxidation. Total turnover number (**a** + **b**), which was determined by gas chromatography analysis, was plotted on the ordinate. [Cobalt(III) complex] = $(1.1−1.2) \times 10^{-4}$ M, **[2]** = 1.9 M, [n-BuOH] = 2.7×10^{-1} M, [Et$_3$N] = 1.7×10^{-2} M, [1,4-dioxane] = 1.7 M in toluene at 20 °C under aerobic condition with a 500 W tungsten lamp.

Scheme 1. Plausible Mechanism of the Catalytic Reaction to Yield Two Acetals, a and b, from Vinyl Ether 1 or 2, by Cobalt(III) Porphycenes in the Presence of Alcohol and Et$_3$N under Aerobic Conditions
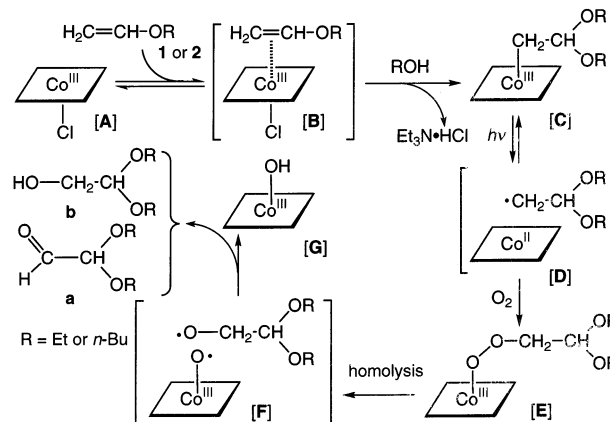
these findings demonstrate that cobalt(III) porphycenes, especially $(OEPc)Co^{III}Cl$, are good catalysts for the oxidative conversion of vinyl ethers into acetals, being markedly superior to the corresponding cobalt(III) porphyrin complexes.

Mechanistic Studies of the Vinyl Ether Oxidation Catalyzed by Cobalt Porphycenes. Scheme 1 outlines a proposed mechanism for the catalytic reaction chemistry described above. The first step in the sequence involves the addition of a vinyl ether to the starting cobalt(III) complex [**A**] via what is presumably a π-complex intermediate [**B**] and follow-up reaction

Table 2. Pseudo-First-Order Rate Constants for Co−C Bond Formation at 20 °C under N_2 Atmosphere with Complete Exclusion of Extraneous Light[a]

cobalt complex	Co−C bond formation (s^{-1})[b]
(OEPc)Co^{III}Cl	8.8×10^{-4}
(TPrPc)Co^{III}Cl	2.2×10^{-4}
(EtioPc)Co^{III}Cl	2.7×10^{-4}
(OEP)Co^{III}Cl	1.9×10^{-4}
(TPP)Co^{III}Cl	2.7×10^{-5}

[a] [Co(III) complex] = 1.8×10^{-4} M, **[2]** = 0.33 M, [*n*-BuOH] = 0.16 M, [Et$_3$N] = 3.1×10^{-4} M, [dioxane] = 0.27 M in toulene (3.0 mL). [b] Errors are <10%.

with an alcohol.[13] The pseudo-first-order rate constants for the formation of this organometallic species [**C**] are depicted in Table 2. These kinetic parameters are consistent with the contention that (OEPc)Co^{III}Cl is more reactive in terms of Co−C bond formation than other cobalt(III) porphycenes: $k_{obs} = 8.8 \times 10^{-4}$ s^{-1} for (OEPc)Co^{III}Cl and $k_{obs} = 2.2 \times 10^{-4}$ s^{-1} for (TPrPc)Co^{III}-Cl at 20 °C. These same rate constants also support the conclusion that the Co−C bond-forming addition of **2** to cobalt(III) porphyrins is even slower: $k_{obs} = 1.9 \times 10^{-4}$ s^{-1} for (OEP)Co^{III}Cl (see Experimental Section).

The next step in the presumed catalytic sequence involves insertion of O_2 into the Co−C bond, a transformation that is triggered by photolysis with visible light. Here, an important finding was that, after irradiation of the alkylcobalt(III) species [**C**], analysis of the UV−vis spectrum in toluene solution failed to provide any evidence for the formation of a cobalt(II) species under aerobic conditions. On the other hand, upon irradiation, the axial ligand resonances ascribed to the pre-photolysis (TPrPc)Co^{III}(CH$_2$CH(OEt)$_2$) species in the upfield region of the ^{1}H NMR spectrum were found to decrease in intensity. Meanwhile, a new set of resonances developed as shown in Figure 1B. 2D NMR spectroscopic analyses led to the conclusion that the new resonances, seen at −1.22 and 1.66 ppm, are due to the methylene and methine protons of the coordinated peroxide ligand of (TPrPc)Co^{III}(OOCH$_2$CH(OEt)$_2$), respectively. These NMR spectroscopic results are thus comparable to what is observed upon photolysis of (TPrPc)Co^{III}(*n*-Bu), a reaction that produces (TPrPc)-Co^{III}(OO*n*-Bu) under aerobic conditions.[14] Given these findings, it is thought that this step in the catalytic cycle proceeds to produce an acetal-functionalized alkylperoxocobalt(III) complex [**E**] as the result of insertion of O_2 into the Co−C bond via an intermediate [**D**]. Consistent with this conclusion is the finding that photolysis of the species [**C**] under anaerobic conditions yielded cobalt(II) porphycene and a simple acetal product, CH$_3$-CH(OEt)$_2$, via homolytic cleavage of the Co−C bond.

The final step in the process is the thermal homolysis of the O−O bond of the above alkylperoxocobalt(III) (complex [**E**]).[15] This produces an unstable Co(III)−O• species [**F**] and an alkoxy radical, •O−CH$_2$CH(OR)$_2$, as the initial products. Products **a** and **b** presumably derive
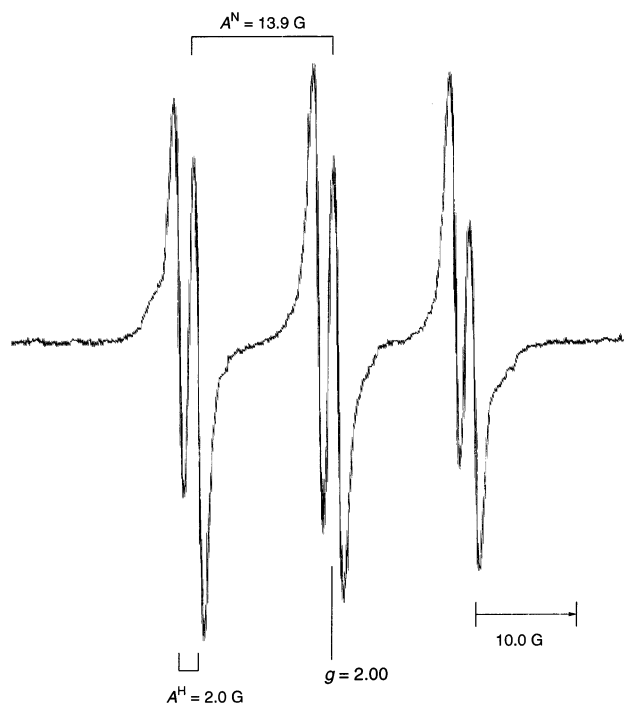

Figure 4. EPR spectrum of the spin adduct generated by the catalytic reaction in the presence of PBN upon irradiation under aerobic conditions at room temperature.

from this latter species. We suggest that when this alkoxy radical diffuses away from the initial solvent cage in which it and the cobalt radical, Co(III)−O•, are formed, hydrogen atom abstraction from the medium produces the alcohol product **b** (as well as separately a more stable cobalt hydroxide complex, Co(III)−OH [**G**]). By contrast, when the initial alkoxy radical remains trapped within the solvent cage, direct hydrogen atom abstraction by the neighboring Co−O• radical produces aldehyde **a**.[16] Consistent with this thinking is the finding that the product ratio, **a/b**, depends on the temperature and viscosity of the solution.[17,18] Furthermore, when *N-tert*-butyl-α-phenylnitrone, PBN, was added as a spin-trapping agent, not only were characteristic spin adducts observed by EPR spectroscopy (Figure 4) but it was also found that the only product of the catalytic reaction was aldehyde **a**. This, we suggest, means the extracage alkoxy radical gets trapped completely by PBN under these conditions.

Conclusion

The present results serve to illustrate a new way in which metalloporphyrin species can act as catalysts, since the organometallic reactions catalyzed by porphyrins via initial Co−C bond formation have been quite rare. They also provide one of the first reports wherein

(13) Silverman, R. B.; Dolphin, D. *J. Am. Chem. Soc.* **1976**, *98*, 4626−4633.

(14) A resonance at −4.47 ppm is observed in CD$_2$Cl$_2$ at −40 °C that is ascribed to the α-methylene protons of a coordinated Co−C*H$_2$*− subunit of (TPrPc)Co^{III}(*n*-Bu). A peak is also observed at −2.06 ppm that is assigned to Co−OOC*H$_2$*− protons of (TPrPc)Co^{III}(OO*n*-Bu). Hayashi, T.; Okazaki, K.; Shimakoshi, H.; Tani, F.; Naruta, Y.; Hisaeda, Y. *Chem. Lett.* **2000**, 90−91.

(15) It was found that CoO−OR species prepared at low temperature in an NMR tube rapidly undergoes thermal bond homolysis under dark conditions.

(16) Balch, A. L.; Cornman, C. R.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 2963−2969.

(17) Product ratios of the reaction catalyzed by (TPrPc)Co^{III}Cl (1.1 × 10^{-4} M), **3a/3b**, were 2.8 (η = 0.61 cP) and 1.3 (η = 0.37 cP) at 20 and 45 °C, respectively, in a toluene solution (0.65 mL volume) containing **2** (1.9 M), *n*-BuOH (0.27 M), and Et$_3$N (0.017 M). Upon addition of 95 mL of dioxane (η = 0.68 cP), the ratio was 3.8 at 20 °C.

(18) Garr, C. D.; Finke, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 10440−10445.

catalysis is mediated by a porphyrin isomer complex[19] and the first where a porphyrin isomer has proved superior to a porphyrin in terms of enhancing a chemical transformation of any kind. This work serves to underscore how small changes in ligand size, shape, and structure can have an important effect on the chemistry of cyclotetrapyrroles.[20]

Experimental Section

General Procedures and Methods. NMR spectra were collected on Bruker AMX-500 (500 MHz) NMR spectrometers. ^{1}H NMR chemical shift values are reported in ppm relative to the residual solvent resonances (^{1}H NMR δ 2.09 for toluene-d_8). UV−visible experiments were conducted on a Hitachi U-3300 double beam spectrophotometer. GC−MS data were obtained on an HP 5890A gas chromatograph equipped with a DB-1 (J & W Scientific) capillary column (30 m) and a JEOL JMS-AM120 mass spectrometer. GC data were collected on a Shimadzu GC-9A gas chromatograph equipped with a Silicone DC-550 (Shimadzu, Japan) packed column (3 m × 5 mm).

Materials. All reagents and chemicals were obtained from commercial sources and used as received unless otherwise indicated. Solvents were dried and distilled under N_2 immediately before use. Cobalt(III) porphyrins and porphycenes were prepared according to literature procedures.[8,9,21]

Preparation and Characterization of (TPrPc)Co^{III}-(CH$_2$CH(OEt)$_2$). To 1 mL of a dry CH$_2$Cl$_2$ solution containing ethanol (0.46 M), ethyl vinyl ether (0.93 M), and Et$_3$N (1.3 × 10^{-2} M) was added 2.95 mg (5.16 × 10^{-6} mol) of (TPrPc)Co^{III}-Cl. The solution was stirred at room temperature for 8 h in the dark. After Co−C bond formation was essentially complete, as inferred from UV−visible spectroscopic analysis, the solvent was removed by flashing with N_2. The resulting residue was washed with petroleum ether and dried in vacuo to give the alkyl complex as a powder (ca. 30% yield): ^{1}H NMR (toluene-d_8, 25 °C, 500 MHz) δ −3.91 (d, $J = 5$ Hz, 2H), −2.25 (t, $J = 5$ Hz, 1H), 0.07 (m, 6H), 1.09 (t, $J = 5$ Hz, 2H), 1.33 (m, 14H), 2.32 (m, 8H), 3.85 (m, 8H), 8.99 (s, 4H), 9.35 (s, 4H) ppm; UV−visible (CH$_2$Cl$_2$) λ_{max} 384, 591 nm.

Aerobic Cleavage of the Co−C Bond of (TPrPc)Co^{III}-(CH$_2$CH(OEt)$_2$) at Low Temperature. A toluene-d_8 solution (0.5 mL) of (TPrPc)Co^{III}(CH$_2$CH(OEt)$_2$) (1.5 × 10^{-6} mol) containing ethanol-d_6 (50 mL) was sealed in an NMR tube and cooled to −40 °C. The solution was irradiated with a 500 W tungsten lamp from a distance of 10 cm for 15 min. The ^{1}H

NMR spectrum of the solution at −40 °C provides support for the conclusion that the alkylcobalt complex had been converted to the corresponding alkylperoxo species under these conditions. The new species displayed resonances at δ −1.22 (b, 2H), 0.47 (b, 6H), 1.45 (b, 12H), 1.66 (b, 1H), 2.07 (b, 2H), 2.31 (b, 2H), 2.50 (b, 8H), 4.14 (b, 8H), 9.38 (s, 4H), 9.78 (s, 4H) ppm.

Determination of the Pseudo-First-Order Rate Constant Associated with Co−C Bond Formation. A 3 mL dry toluene solution of the cobalt complex in question, either porphycene or porphyrin (1.8×10^{-4} M), n-butanol (0.16 M), dioxane (0.27 M), Et$_3$N (3.1×10^{-4} M), and n-butyl vinyl ether (0.33 M) was made up in a cuvette and analyzed immediately using UV−visible spectroscopy. The experiment was conducted at 20 °C under N_2 atmosphere with complete exclusion of extraneous light. The spectrum of the Co(III) species was seen to change drastically under these conditions. However, isosbestic points were observed, and a new absorption assigned to an organocobalt(III) species was seen to grow in with time. For kinetic analyses the absorbance at 420−434 nm for cobalt-(III) porphyrin and at 616−624 nm for cobalt(III) porphycene was monitored over 200 min. The pseudo-first-order rate constant of Co−C bond formation was determined from the exponential decay of the spectral intensity assigned to the initial Co(III) species.

Aerobic Oxidation of Vinyl Ether Catalyzed by Cobalt(III) Porphyrin or Porphycene Complexes. A 0.65 mL toluene solution of cobalt complex ($1.2−1.3 \times 10^{-4}$ M), n-butanol (0.27 M), dioxane (1.7 M), Et$_3$N (1.7×10^2 M), and n-butyl vinyl ether (1.9 M) was made up in a 5 mL vial equipped with a stirring bar and rubber septum. It was then stirred at 20 °C under these aerobic conditions. The solution was then irradiated with a 500 W tungsten lamp from a distance of 10 cm without any filter. The progress of the reaction was monitored every 2 h by gas chromatographic analysis. The total turnover number was calculated on the basis of changes in peak area as a function of time using n-dodecane as an internal standard. The initial rate (turnover per minute) was determined from the total number of turnovers observed after 4 h. This could be done safely, since the total turnover number for each catalyst increased linearly with reaction time for at least the first 4 h. The two main products, β-formylacetaldehyde dibutyl acetal and β-hydroxyacetaldehyde dibutyl acetal, were independently isolated and characterized by ^{1}H NMR and mass spectrometry using know reference standards to validate the analyses.[22]

(19) To our knowledge, there is only one other report of a reaction catalyzed by a metalloporphycene. In this paper, the cyclopropanation of olefins by ruthenium porphycenes is described. However, the characteristics of the active metalloporphycene were not detailed. Lo, W.-C.; Che, C.-M.; Cheng, K.-F.; Mak, T. C. W. *Chem. Commun.* **1997**, 1205−1206.

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