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# Communications

## Preparation and Characterization of (Alkylperoxo)cobalt(III) Porphyrins: First Direct Evidence for Metal–Carbon Bond Homolysis in Dioxygen Insertion Reactions

*Sir:*

It has recently been reported[1] that a stable (acylperoxo)iron(III) complex could be prepared from a sterically hindered iron(III) porphyrin, providing a synthetic analogue for the alkylperoxo intermediate in the catalytic cycles of cytochrome P-450 and the peroxidases.[2] We describe here an alternate route to (alkylperoxo)metalloporphyrins, without the use of sterically hindered porphyrins, via dioxygen insertion into the metal–carbon bonds of organocobalt(III) porphyrins and provide evidence that the reaction proceeds via metal–carbon bond homolysis.

**Scheme I**

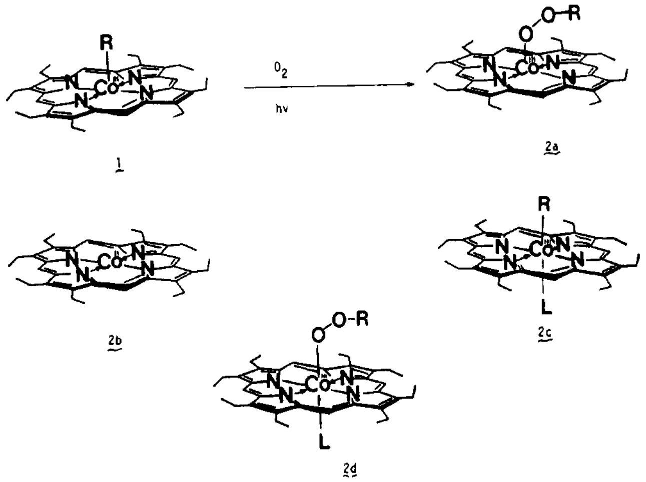

**Table I.** $^1$H NMR (200 MHz) Spectral Properties of Metalloporphyrins Isolated[a]

| complex | chem shift for proton resonances of coordinated alkyl ligand, ppm |
|---|---|
| $(TPP)Co^{III}(CH_3)(py)$ | −4.85 (s, 3 H) |
| $(TPP)Co^{III}(C_2H_5)(py)$ | −3.61 (q, 2 H), −4.80 (t, 3 H) |
| $(TPP)Co^{III}(CH_2C_6H_5)$ | −2.55 (s, 2 H), 3.42 (d, 2 H), 5.88 (t, 2 H); 6.74 (t, 1 H) |
| $(OEP)Co^{III}(CH_3)$ | −5.20 (br, s, 3 H) |
| $(OEP)Co^{III}(C_2H_5)$ | −4.08 (br, 2 H), −5.47 (t, 3 H) |
| $(OEP)Co^{III}(CH_2C_6H_5)$ | −2.67 (br, 2 H), 3.15 (2 H), 5.56 (2 H), 7.09 (s, 1 H) |
| $(OEP)Co^{III}(OOCH_2C_6H_5)$ | −0.45 (s, 2 H), 5.50 (d, 2 H), 6.75 (m, 2 H), 6.81 (m, 1 H) |
| $(TPP)Co^{III}(OOCH_2C_6H_5)(py)$ | −0.13 (s, 2 H), 5.51 (d, 2 H), 6.78 (m, 2 H), 6.85 (m, 1 H) |
| $(OEP)Co^{III}(OOCH_2C_6H_5)(PPh_3)$ | −0.43 (br, 2 H), 3.40 (d, 2 H), 5.75 (t, 2 H), 6.80 (t, 1 H) |
| $(OEP)Co^{III}(OOC_2H_5)(PPh_3)$ | −2.01 (2 H), −3.43 (t, 3 H) |
| $(OEP)Co^{III}(OOCH_3)(PPh_3)$ | −2.81 (s, 3 H) |

[a] Spectra were recorded in $C_6D_6$ (29 °C), with tetramethylsilane added as internal reference. [b] Porphyrin ligand proton resonances were found at 1.96–2.01 ppm (q, 16 H), 3.98–4.03 ppm (t, 24 H), and 9.91–10.00 (s, 4 H) for OEP derivatives; for the TPP derivatives, similar chemical shifts were found as in ref 4.

The reaction of $Co^{III}OEP(R)$,[3] $Co^{III}OEP(R)(L)$,[4] or $Co^{III}TPP(R)(L)$[5] (R = $CH_3$, $C_2H_5$, $CH_2C_6H_5$; L = pyridine, 1-methylimidazole, $PR_3$; OEP = octaethylporphyrin dianion; TPP = tetraphenylporphyrin dianion) at 5 °C in the presence of 355-nm light in oxygen-saturated $CH_2Cl_2$ was found to be slow. After 24 h at 5 °C, this reaction gave a new species with a visible spectrum typical of a Co(III) porphyrin ($\lambda_{max}$ = 422 nm).[6] In a typical synthesis (Scheme I), this reaction proceeded cleanly through isosbestic changes from $Co^{III}OEP(R)$ to **2a**. As shown in Figure 1, **2a** is spectrally distinct from both the $Co^{III}OEP(R)$ starting material (**1**) and $Co^{II}OEP$ (**2b**).[6] During the course of the reaction, the presence of a Co(II) intermediate was detected by UV–visible spectrophotometry.[7] The Co(II) porphyrin generated is photostationary under the experimental conditions noted. The 200-MHz $^1$H NMR spectra of **2a** and **2d** were typical for diamagnetic Co(III) porphyrins (see Table I).[8] The effective diamagnetic ring current of the porphyrin macrocycle shifts the

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(5) Peree-Fauret, M.; Gaudemer, A.; Boucly, P.; Devynek, *J. Organomet. Chem.* **1976**, *120*, 439–451. We have obtained satisfactory C, H, and N elemental analyses for all the compounds listed in Table I. Typical yields for the insertion reactions range from 54 to 63%.

(6) UV–visible data for products and starting materials (benzene), $\lambda_{max}$, nm (log $\epsilon$): $Co^{II}OEP$, 393 (5.71), 520 (4.11), 550 (4.50); $Co^{III}TPP(CH_3)$, 400 (5.00), 519 (4.00), 542 (4.41); $Co^{III}TPP(C_2H_5)$, 400 (4.88), 521 (4.10), 540 (4.50); $Co^{III}OEP(CH_3)$, 393 (5.30), 519 (4.00), 522 (4.41); $Co^{III}OEP(C_2H_5)$, 393 (5.30), 519 (4.00) 552 (4.35); $Co^{III}OEP(CH_2C_6H_5)$, 393 (5.05), 519 (4.01), 552 (4.42); $Co^{III}TPP(OOCH_2C_6H_5)(py)$, 430 (4.88), 551 (4.21), 520 (sh); $Co^{III}OEP(OOCH_2C_6H_5)$, in $CH_2Cl_2$, 420 (5.43), 539 (3.89); $Co^{III}OEP(OOC_2H_5)$, 422 (5.40), 538 (3.90); $Co^{III}OEP(OOC_2H_5)(PPh_3)$, 455 (4.21), 356 (3.87); $Co^{III}OEP(OOCH_2C_6H_5)(PPh_3)$, 458 (4.71), 358 (3.71); $Co^{III}OEP(OOCH_2C_6H_5)(P\text{-}n\text{-}Bu_3)$, 455 (4.35), 355 (3.83); $Co^{III}OEP(OOCH_2C_6H_5)(PEtPh_2)$, 456 (4.31), 357 (3.85); $Co^{II}OEP(PPh_3)$, 455 (4.30), 358 (4.23).

(7) The $Co^{II}P$ and $Co^{II}P(L)$ complexes exhibit the same $\lambda_{max}$ values as the $Co^{III}P(R)$ and $Co^{III}P(R)(L)$ complexes. The molar absorptivities for the Co(II) complexes are higher than those of the corresponding Co(III) complexes.

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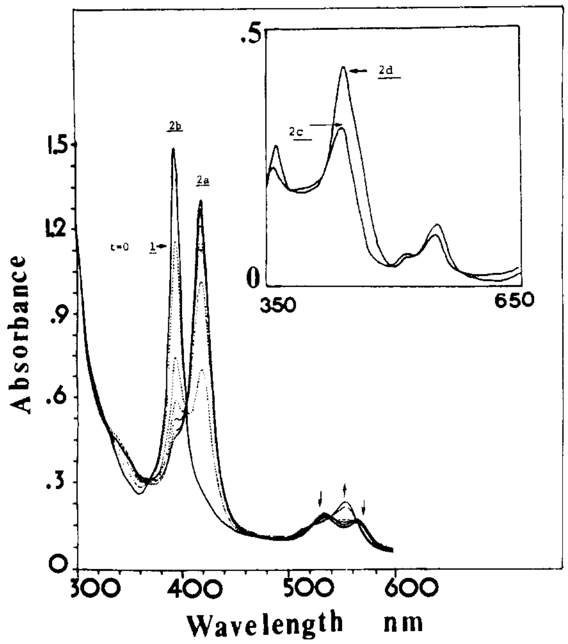

**Figure 1.** Reaction of 1.0 × $10^{-5}$ M CoOEP($CH_2C_6H_5$) with oxygen in toluene at 50 °C. The reaction was monitored every 30 min, starting with complex **1** and then quenching an aliquot from the reaction mixture to room temperature. With time, species **2b** ($Co^{II}$) appears, followed by the appearance of the (alkylperoxo)cobalt(III) porphyrin, **2a**. Inset: comparison of CoOEP($OOCH_2C_6H_5$)($PPh_3$) (8.6 × $10^{-6}$ M; **2d**) and CoOEP($CH_2C_6H_5$)($PPh_3$) (1.9 × $10^{-5}$ M; **2c**).

protons on the coordinated –R or –OOR linkage to high fields.[9] The closer these protons are to the porphyrin ring, the stronger is the effect of shifting the proton resonances to higher field.[10] Thus, in the dioxygen-inserted products, $Co^{III}$(P)(OOR)(L) (P = porphyrin), because the alkyl protons are now presumably at a greater distance from the porphyrin rings than in the parent $Co^{III}$(P)(R)(L) complexes, the protons on –OOR are shifted to lower fields.

In contrast, attempts to isolate (alkylperoxo)cobalt(III) porphyrins by additions of alkylhydroperoxides to $Co^{III}$TPP(Cl), $Co^{III}$OEP(Cl), or $Co^{III}$OEP(OH) failed in our hands, as products were detected typical of isoporphyrins, where the alkylhydroperoxide has attacked the porphyrin ring itself analogous to the work of Bruice et al.[11]

In addition to $^1H$ NMR results, further evidence that dioxygen has inserted into the cobalt–carbon bond of these organocobalt porphyrins comes from IR spectra of the isolated (alkylperoxo)cobalt(III) porphyrins. Moderate $\nu_{O-O}$ stretching frequencies were found for each (alkylperoxo)cobalt(III) porphyrin isolated in the 835–880-$cm^{-1}$ region, typical of coordinated –OOR complexes.[12]

Previous attempts to isolate and characterize (alkylperoxo)cobalt(III) porphyrins resulted in complexes that were apparently contaminated with starting material.[4] In order to ensure the formation of the six-coordinate $Co^{III}$(P)(OOR)(L) complexes in high yield, excess L must be present. Recent work has demonstrated the crucial role that L plays in modulation of the Co–C bond strength in $Co^{III}$(P)(R)(L) complexes.[3] As will be demonstrated below, homolysis of the Co–C bond is an important step in the dioxygen insertion reaction; therefore, modulation of this bond strength is important.

We have measured the rate of dioxygen insertion into the Co–C bond[13] for a series of $Co^{III}$OEP(R)(L) complexes[3] where L = $PR_3$, or no ligand, and R = $CH_2C_6H_5$ and have found that the observed rate constants for dioxygen insertion correlate with the Co–C bond dissociation energies of such complexes, which have been determined previously[3] (see Figure 2). On the basis of our results described herein and the fact that Co(II) can be detected as an intermediate in the insertion of dioxygen into the Co–C bond of organocobalt porphyrins, we postulate the following mechanism for the overall insertion reaction:

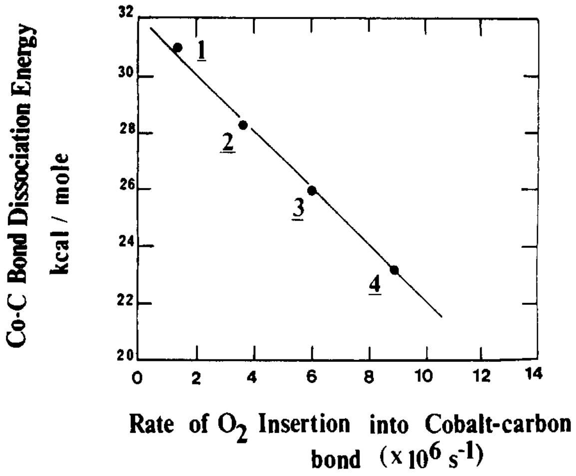

**Figure 2.** Plot of Co–C bond dissociation energy versus $k_{obsd}$ (50 °C, toluene) for dioxygen insertion into CoOEP(R) and CoOEP(R)($PR_3$) complexes; (R = $CH_2C_6H_5$): (1) CoOEP($CH_2C_6H_5$); (2) CoOEP($CH_2C_6H_5$)(P-*n*-$Bu_3$); (3) CoOEP($CH_2C_6H_5$)(PEt$Ph_2$); (4) CoOEP($CH_2C_6H_5$)($PPh_3$).

$$\mathrm{Co^{III}(P)(R)(L)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Co^{II}(P)(L)} + \mathrm{R^{\bullet}} \tag{1}$$

$$\mathrm{R^{\bullet}} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{ROO^{\bullet}} \tag{2}$$

$$\mathrm{Co^{II}(P)(L)} + \mathrm{ROO^{\bullet}} \xrightarrow{k_3} \mathrm{Co^{III}(P)(OOR)(L)} \tag{3}$$

$$\text{net: } \mathrm{Co^{III}(P)(R)(L)} + \mathrm{O_2} \rightarrow \mathrm{Co^{III}(P)(OOR)(L)}$$

We are currently extending our studies to include kinetic verification of the preceding mechanism as well as to explore the use of these complexes as catalysts for the oxidation of hydrocarbons.

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Department of Chemistry
University of Alabama
Tuscaloosa, Alabama 35487-9671

**Maureen J. Kendrick***
**Walid Al-Akhdar**

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[13] The rate constant for dioxygen insertion into the cobalt–carbon bond was measured spectrophotometrically, by following the increase in absorbance with time of the band absorption with the $Co^{III}$(P)(OOR) or $Co^{III}$(P)(OOR)(L) complex. At 50 °C, the following rate constants, ($s^{-1}$) were measured for dioxygen insertion into Co–R bonds (toluene solvent): $Co^{III}$OEP($OOCH_2C_6H_5$), 0.000 001 65; $Co^{III}$OEP($OOCH_2C_6H_5$)(P(*n*-$C_4H_9$)$_3$), 0.000 003 30; $Co^{III}$OEP($OOCH_2C_6H_5$)(P($C_2H_5$)($C_6H_5$)$_2$), 0.000 005 91; $s^{-1}$; $Co^{III}$OEP($OOCH_2C_6H_5$)(P($C_6H_5$)$_3$), 0.000 009 07.

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## New Monomeric and Binuclear Hydride- and Alkyl-Substituted Platinum(II) Complexes Having Unsubstituted Terminal or Bridging Amide Ligands

*Sir:*

Despite recent interest in the activation of C–H bonds by low-valent transition-metal complexes,[1] little work has been

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