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C−O Bond Cleavage of Alcohols via Visible Light Activation of Cobalt Alkoxycarbonyls

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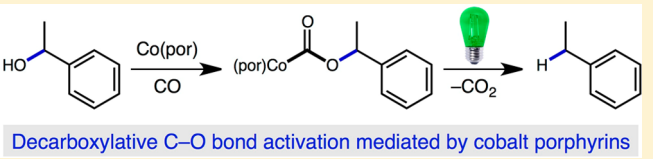
Supporting Information

ABSTRACT: A strategy for the activation of C−O bonds in alcohols via a carbonylation−homolysis−decarboxylation process is described. Using readily available cobalt(II) porphyrin precursors, carbonylation of simple alcohols provides access to alkoxycarbonyl cobalt(III) complexes. Spectroscopic, crystallographic, and computational methods are used to provide structural details and an estimate for the Co−C bond dissociation energy of an alkoxycarbonylcobalt(III) complex of 39.8 kcal/mol for the first time. Visible light irradiation in the presence of the radical trapping agent TEMPO and a thiol reducing agent demonstrates the cleavage of the alcohol C−O bond under oxidative and reductive conditions, respectively. Addition of a stoichiometric reducing agent allows the use of a catalytic amount of hindered thiol for the reduction of a benzylic alcohol to the corresponding hydrocarbon.



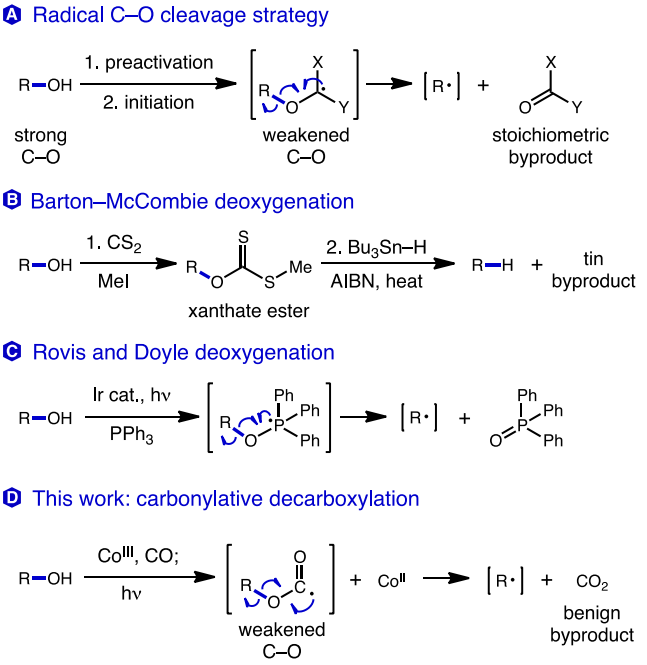
Decarboxylative C–O bond activation mediated by cobalt porphyrins

INTRODUCTION

Alcohols are one of the most abundant classes of organic molecules, with the hydroxyl group being prevalent in naturally occurring feedstocks such as sugars and complex natural products. Alcohols are also valuable synthetic intermediates, being readily introduced and converted to a myriad of other functional groups. Most transformations, however, require preactivation of the hydroxyl group due to the relatively inert nature of the C−OH bond.[1] In particular, radical chemistry relies on conversion to a halide or xanthate ester as a means to overcome the strong C−O bond, which can be weakened by the formation of an adjacent radical (Scheme 1A).[2] Transformations such as the Barton−McCombie deoxygenation facilitate cleavage of the strong C−O bond through the reaction of a xanthate ester with a tin radical species following the mechanistic pathway shown in Scheme 1B.[3] More recently, iridium photocatalysis were utilized to generate radical (or radical anion) intermediates that fragment[4] and in 2018, Rovis, Doyle, and co-workers reported a unique direct deoxygenation via C−O homolysis of phosphoranyl radicals (Scheme 1C).[5] It remains an important goal to identify systems that avoid stoichiometric preactivation and generate benign, low-molecular-weight byproducts. The ability to directly activate a wide variety of alcohols using an earth-abundant metal catalyst would represent a very valuable advance in the efficient use of alcohols in radical chemistry.

Coenzymes B_{12} (adenosylcobalamin, methylcobalamin, etc.) have been extensively studied for their ability to undergo reversible Co−C bond cleavage to generate carbon-centered radicals in numerous important enzymatic processes.[6] Many model systems have been developed to mimic this homolytic bond cleavage that are more synthetically available, such as cobalt complexes with salen, salophen, and dimethylglyoxime ligands.[7] Alkylcobalt derivatives of these complexes are typically synthesized from alkyl halides, and thermal- or

Scheme 1. Strategies for C−O Bond Activation of Alcohols Utilizing Cobalt Porphyrins



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light-driven homolysis[8] leads to radical cyclizations[9] and initiation of living radicals for polymerizations.[10,11] Pattenden and co-workers have demonstrated stoichiometric radical cyclizations[12] and intermolecular Michael additions with cobalt salophen pyridine complexes[13] while Carreira and co-workers used cobaloximes in a catalytic Heck-type coupling.[14]

While the synthesis and reactivity of the analogous *alkyl*cobalt porphyrin complexes have been studied,[15−17] including determining their Co−C bond dissociation energies,[18,19] much less is known about the *acyl* and *alkoxycarbonyl* complexes. Chan and co-workers reported isolable acyl Co(por) complexes (por = porphyrinato dianion) as intermediates in a photochemical C−C bond activation of ketones.[20] Only one alkoxycarbonyl derivative has been reported by Fu and co-workers for the initiation of living radical polymerization.[21] Development of a general synthesis of alkoxycarbonyl porphyrin complexes would facilitate further structure and reactivity studies.

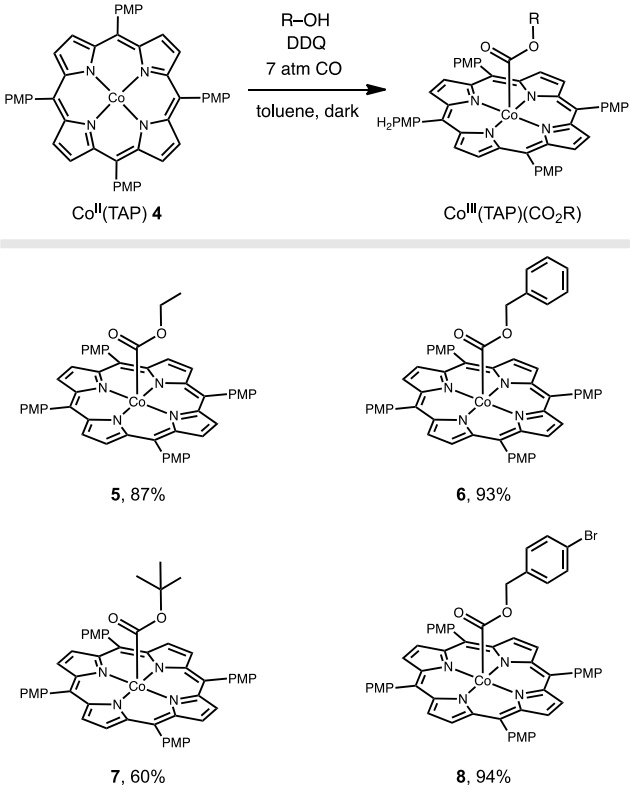
We envisioned that the C−O bond cleavage of alcohols could be achieved via decarboxylation of alkoxycarbonyl radicals generated via alcohol carbonylation (Scheme 1D).[22] In this way, a classic organometallic process could be merged with cobalt-mediated radical chemistry to ultimately develop a catalytic C−O bond cleavage via a polar/radical crossover process. Herein, we describe the efficient synthesis of porphyrin-derived cobalt alkoxycarbonyl complexes and the study of the radical generation with visible light. This strategy enables the C−O bond activation of alcohols and alkyl radical generation with carbon dioxide as the only byproduct and establishes the fundamental processes for a cobalt-mediated C−O bond activation strategy.

RESULTS AND DISCUSSION

We first turned our attention to the synthesis of alkoxycarbonyl cobalt porphyrin complexes with representative alcohols. Fu and co-workers have demonstrated the synthesis of a methoxycarbonylcobalt tetramesitylporphyrin (TMP) using methanol and silver(I) triflate under CO.[21] Unfortunately, this synthesis was not effective with more complex alcohols in our hands, giving only undesired side products. As such, we have developed a method informed by previous work from our group on the carbonylation of salen and salophen cobalt complexes and other related reports.[22−24] Both methods are quite general, tolerating a wide range of alcohols and ligand substitution patterns.

We first evaluated the oxidant required for this transformation, finding many inorganic oxidants and weaker benzoquinones ineffective. A strong oxidant such as DDQ was optimal for the in situ oxidation without interfering with the carbonylation process. As shown in Table 1, optimized conditions using 1 equiv of DDQ and 5 equiv of alcohol produced complexes **5**−**8** in good yields following purification by recrystallization. This method was efficient for 1°, 2°, and 3° alcohols. These complexes are air stable at room temperature for months; however, they are highly labile on either silica gel or alumina, resulting in decomposition to the Co(II) porphyrin starting material. This method of carbonylation was then tested on a wider range of porphyrin ligands with differing electronics (Table 2). Oxidation/carbonylation of 1-phenethanol with electron-rich porphyrin systems such as TAP, TPP, and OEP gave excellent conversion to complexes **9**−**11**, respectively. The same transformation with the electron-deficient porphyrin TFP was achieved, albeit in lower yield (**12**, 56%).

Table 1. Oxidative Carbonylation of a PMP-porphyrin Complex[a]



[a]Reaction conditions: Co(por) (0.25 mmol), alcohol (1.25 mmol), DDQ (0.25 mmol), toluene (20 mL), 7 atm of CO, room temperature. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Structural and Spectroscopic Studies. In order to obtain detailed structural information, we carried out X-ray diffraction studies. Crystals of complex **9** were grown by slow diffusion of pentane into $CHCl_3$, resulting in long thin red crystals with the complex adopting a square-pyramidal geometry (Figure 1). This pentacoordinate form is commonly observed in similar porphyrin systems that contain acyl[20] and vinyl[25] substituents. The alkoxycarbonyl complex has a slightly shorter Co−C1 bond length in comparison to the acyl substituents (1.906 Å vs 1.922−1.926 Å) and comparable Co−N bond lengths. The cobalt is displaced above the porphyrin plane toward the apical carbonyl group (C1), which is also observed in the other acyl and amine[26] complexes but not in the instance with an apical vinyl group. This may result from a greater degree of back-bonding into the π^* orbital of the alkoxycarbonyl substituent that is less pronounced in the vinyl counterpart.

The C−Co bond dissociation energies (BDE) of a variety of alkyl cobalt complexes have been measured experimentally through the extensive studies of Halpern and others, and more recently DFT calculations have provided estimates for many more complexes.[27−29] The C−Co BDEs for alkoxycarbonyl complexes, on the other hand, have not been reported to the best of our knowledge. We calculated complex **9**'s C−Co BDE using the BP86 functional that was found to correctly predict BDEs for alkyl C−Co BDEs (see the Supporting Information for more details).[19,30,31] The predicted structure using DFT

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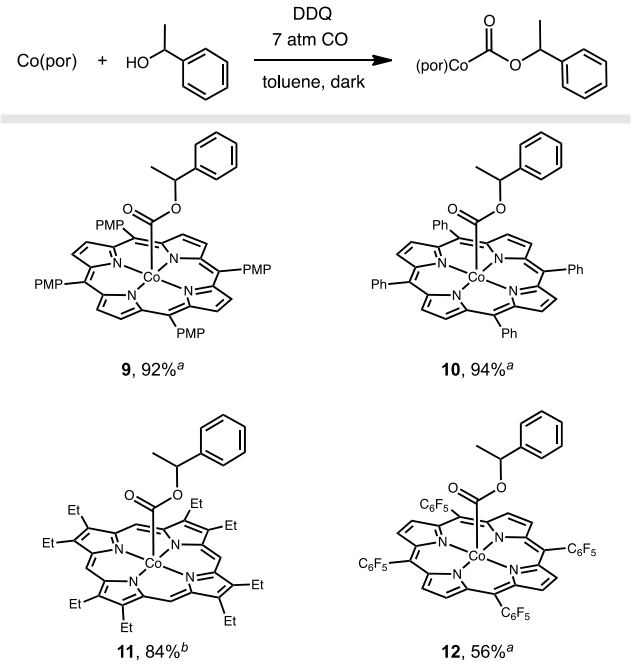
Table 2. Oxidative Carbonylation with Substituted Porphyrins



[a]Reaction conditions: Co(por) (0.25 mmol), alcohol (1.25 mmol), DDQ (0.25 mmol), toluene (20 mL), 7 atm of CO, room temperature. [b]Reaction conditions: Co(OEP) (0.25 mmol), alcohol (0.75 mmol), DDQ (0.25 mmol), toluene (15 mL), 7 atm of CO, room temperature. Reduced amount of alcohol to facilitate isolation.

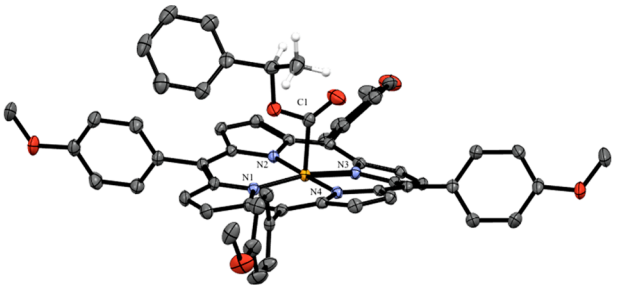


Figure 1. X-ray crystal structure of **9** with thermal ellipsoids at the 50% probability level. The compound crystallizes as a racemate; only one enantiomer is shown for clarity. Selected bond lengths (Å) and angles (deg): Co−C1 1.906(2), Co−N1 1.963(2), Co−N2 1.958(2), Co−N3 1.945(2), Co−N4 1.956(2); C1−Co−N3 95.45, C1−Co−N4 88.17, C1−Co−N1 96.45, C1−Co−N2 90.87, N3−Co−N4 89.79, N4−Co−N1 90.41, N3−Co−N2 89.76, N1−Co−N2 90.32.

showed excellent agreement with the crystal structure (Figure 2) with a calculated C−Co bond length of 1.892 vs 1.906 Å in the crystal structure. In comparison to other Co−alkyl complexes, the calculated bond dissociation energy was fairly high at 39.8 kcal/mol.

With the structure of the alkoxycarbonyl complexes confirmed, we further examined their spectroscopic characteristics. The UV−vis absorption spectrum for compound **9** (Figure 3) exhibited a strong Soret band at 424 nm and another maximum at 540 nm. The absorption maxima are well-suited for photochemical activation using green or violet light (vide infra). Excitation at either band gave no measurable fluorescence for compound **9**.

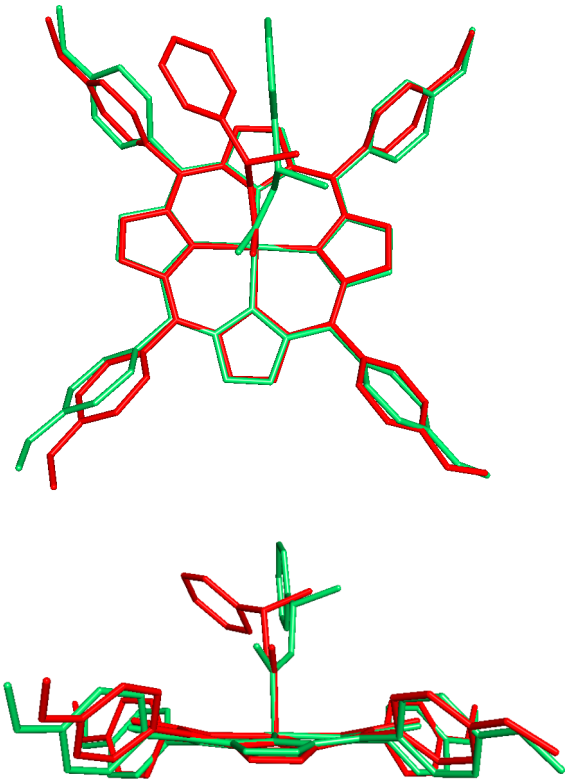


Figure 2. Overlay of the optimized structure at the BP86/LanL2DZ level of theory (green) and X-ray crystal structure of compound **9** (red).

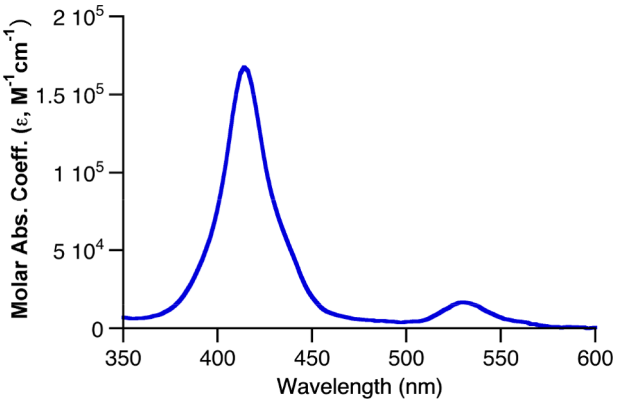


Figure 3. Absorption spectra of **9** in $CHCl_3$.

Reactivity Studies. We next examined the reactivity of the alkoxycarbonyl compounds under activation with visible light to determine if they retain behavior similar to that of vitamin B_{12} and their alkylcobalt counterparts. We anticipated that visible light corresponding to the absorption bands above would be sufficient to homolyze the Co−C bond. To compare, the energy of green photons at the emission maximum of a simple LED source (515 nm) is 55.5 kcal/mol, more than sufficient to cleave the C−Co bond.

Radical trapping experiments were performed with benzylic alcohol derivatives, TEMPO, and various light sources (Table 3).[32] On the basis of studies by Newcomb and Pattenden, we expected to observe the decarboxylated products due to the rapid formation of stabilized benzylic radicals from the intermediate acyl radical.[33,34] Efficient radical generation could be achieved with a 390 nm LED source, and green

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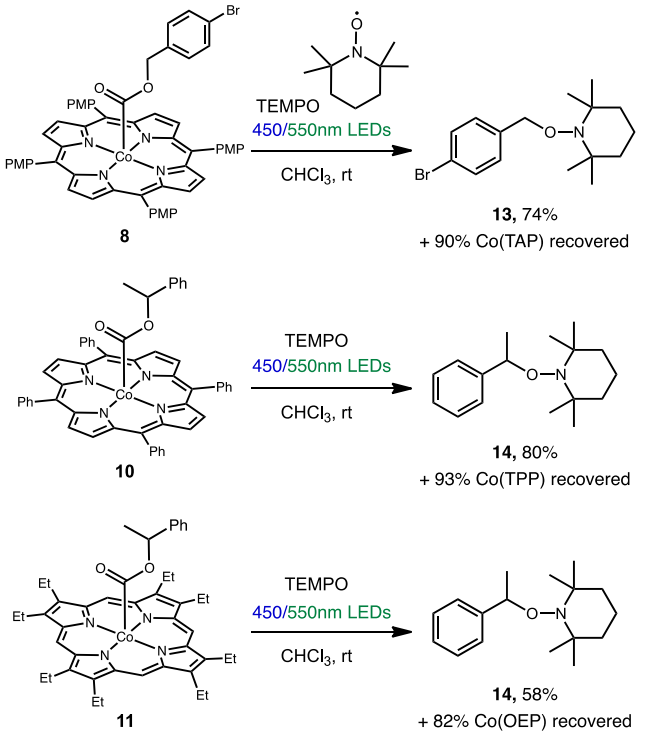
Table 3. TEMPO Trapping Experiments[a]



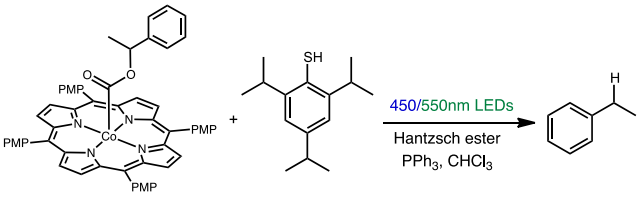
[a]Reaction conditions: **8**, **10**, or **11** (0.02 mmol), TEMPO (0.04 mmol), $CHCl_3$ (2 mL), room temperature. TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

LEDs (510−520 nm) also gave full conversion, however with a longer reaction time (16 h). A higher intensity LED lamp with emission maxima at 450 and 550 nm achieved the same conversion in 4 h.[35] Some homolysis was observed with 440 and 456 nm light sources; however, these mismatched wavelengths were much less effective, as expected from the observed absorption spectra.

Under these conditions, efficient homolysis and loss of CO_2 occurred and TEMPO adducts **13** and **14** were isolated in 58−80% yield (Table 3); as expected, only decarboxylated products were observed. Co(TAP), Co(TPP), and Co(OEP) were also isolated from these reactions, indicating that no major decomposition of the Co-porphyrin complexes took place under these reaction conditions. Interestingly, when the *p*-bromobenzyloxycarbonyl compound was subjected to irradiation conditions, the TEMPO-trapped product was isolated without loss of the bromine atom. This outcome demonstrates that this method of radical generation tolerates aryl bromides, a reactive source of radicals under traditional initiation conditions.

To further explore the utility of this strategy to deoxygenation, irradiation in the presence of a hydrogen atom donor was performed. We focused on thiols on the basis of the favorable thermodynamics of H atom transfer between thiols and the transient benzylic radical (S−H BDE = 82 kcal/mol for thiophenol, C−H BDE = 86 kcal/mol for ethylbenzene).[36−39] Initial studies found that the thiophenol underwent rapid dimerization to disulfide under our reaction conditions; therefore, more sterically hindered thiols were examined (Table 4). Introducing methyl or isopropyl substituents at the ortho positions slowed dimerization and increased the yield of ethylbenzene (entry 1, 43% yield). Even

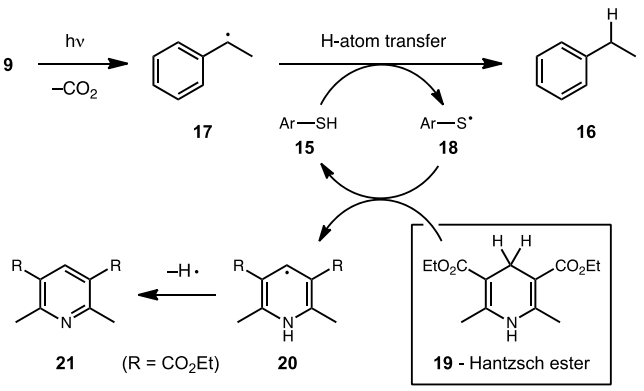
Table 4. Hydrogen Atom Transfer Studies Using a Sterically Hindered Thiol



Entry	Thiol **15**	Hantzsch Ester	Yield **16**
1	2 equiv	–	43%
2	2 equiv	2 equiv	94%
3	0.5 equiv	2 equiv	86%

with an excess of hindered thiol **15**, only moderate yields were achieved along with full consumption of thiol to disulfide. We explored Hantzsch ester **19** as a stoichiometric reducing agent to regenerate the thiol from the thiyl radical **18** (Scheme 2),

Scheme 2. Proposed Turnover of Thiol with Hantzsch Ester 19



which could address the issue of disulfide formation. Gratifyingly, inclusion of Hantzsch ester increased the yield of ethylbenzene to 94% (entry 2). Although Hantzsch ester was not effective in the absence of thiol (<5% yield), it was highly efficient at turning over the thiyl radical and allowed the H atom donor to be reduced to substoichiometric quantities, providing ethylbenzene in 86% yield (entry 3). These studies demonstrate that decarboxylation and reductive radical trapping can be achieved with these complexes under mild conditions.

CONCLUSIONS

We have synthesized several new alkoxycarbonyl complexes of cobalt porphyrins and examined their structure and reactivity. Alcohols undergo efficient carbonylation with Co-porphyrins to produce alkoxycarbonyl cobalt species featuring different substitution patterns. These complexes are estimated to have Co−C BDEs of 39.8 kcal/mol by computational methods and absorb visible light to produce acyl radicals that readily decarboxylate. Trapping of the alkyl radicals with TEMPO and a thiol reducing agent provides a proof of concept for decarboxylation and reduction protocols in the presence of cobalt porphyrins. This approach enables the C−O bond activation of alcohols via alkyl radical generation with carbon dioxide as the only byproduct and establishes the fundamental

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processes for a cobalt-mediated C−O bond activation strategy. Efforts to extend this carbonylation−homolysis−decarboxylation process to a catalytic method analogous to the Barton−McCombie deoxygenation are ongoing and will be reported in due course.

EXPERIMENTAL SECTION

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance Neo 400 MHz spectrometer unless otherwise indicated and were internally referenced to residual protio solvent signal (note: DMSO-d_6 referenced at δ 2.50 and 39.52 ppm, respectively; $CDCl_3$ referenced at δ 7.26 and 77.16 ppm, respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ, ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, app = apparent), and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift, and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer. Exact masses were recorded on an Agilent LCTOF instrument using direct injection of samples in methanol into the electrospray source (ESI) with positive ionization. LEDs were purchased from Kessil (http://www.kessil.com/photoredox/Products.php).

General Methods. All reactions were carried out in oven-dried or flame-dried glassware charged with a magnetic stir bar, were prepared under an inert nitrogen atmosphere, and were subsequently degassed with carbon monoxide. Solvents were dried by passage through alumina columns. Commercially available alcohols were distilled from calcium hydride prior to use. Co(II) porphyrins were prepared according to known literature procedures or purchased and used as received.[40−43]

General Procedures. *Procedure A.* To a mixture of Co(II) porphyrin and DDQ were added 20 mL of toluene and the respective alcohol. The reaction mixture was degassed and pressurized to 7 atm of CO using a Parr pressure vessel and stirred for the indicated time, in the dark, at room temperature. Upon completion of the reaction, the solvent was removed and the crude reaction mixture was recrystallized from CH_2Cl_2 and heptane. The red precipitate was filtered through Celite and washed several times with heptane to remove excess unreacted alcohol. Subsequent washing with 2/1 hexanes/CH_2Cl_2 separated the product from the remaining Co(II) starting material. The red Co(III) filtrate was concentrated to yield a red solid. No further purification was required.

Procedure B. To a mixture of alkoxycarbonylcobalt(II) porphyrin and TEMPO was added 1.5 mL of $CHCl_3$, and the reaction mixture was degassed by three cycles of freeze−pump−thaw. The reaction mixture was stirred for 4 h at room temperature and irradiated by 450/550 nm LEDs. Upon completion, the Co(II) product was precipitated by addition of heptane. Filtration through Celite on washing several times with heptane separated the TEMPO-trapped product, and subsequent washing with CH_2Cl_2 isolated the Co(II) porphyrin. Concentration of the filtrates gave the desired products with no further purification required.

Ethoxycarbonylcobalt *meso*-(4-Methoxyphenyl)porphyrin (5). This compound was prepared according to the general procedure A using 198 mg of cobalt *meso*-(4-methoxyphenyl)porphyrin (0.25 mmol, 1 equiv), 73 μL of ethanol (1.25 mmol, 5 equiv), and 56.7 mg of DDQ (0.25 mmol, 1 equiv). After 16 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a red solid (189 mg, 0.22 mmol, 87%): IR (film) 2931, 1691, 1570, 1287, 1001 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 8H, por-H), 8.04 (d, J = 8.0 Hz, 8H, PMP), 7.25 (d, J = 8.4 Hz, 8H, PMP), 4.07 (s, 12H, OCH_3), 1.64 (q, J = 7.0 Hz, 2H, CH_2CH$_3$), −0.74 (t, J = 7.0 Hz, 3H, CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 145.9, 134.8, 134.3, 132.7, 121.8, 112.48, 62.67, 55.68, 13.01; HRMS (ESI) m/z calcd for $C_{51}H_{42}CoN_4O_6$ (M+ H)$^+$ 865.2431, found 865.2453.

Benzyloxycarbonylcobalt *meso*-(4-Methoxyphenyl)-porphyrin (6). This compound was prepared according to the general procedure A using 198 mg of cobalt *meso*-(4-methoxyphenyl)-porphyrin (0.25 mmol, 1 equiv), 130 μL of benzyl alcohol (1.25 mmol, 5 equiv), and 56.7 mg of DDQ (0.25 mmol, 1 equiv). After 16 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a red solid (215 mg, 0.23 mmol, 93%): IR (film) 2933, 1688, 1606, 1246, 1025 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 8H, por-H), 7.92 (s, br, 8H, PMP), 7.24 (d, J = 8.0 Hz, 8H, PMP), 7.03 (t, J = 7.4 Hz, 1H, Ph), 6.86 (t, J = 7.5 Hz, 2H, Ph), 5.34 (d, J = 7.5 Hz, 2H, Ph), 4.07 (s, 12H, OCH_3), 2.63 (s, 2H, OCH_2Ph); ^{13}C NMR (10 MHz, $CDCl_3$) δ 159.4, 145.9, 134.7, 134.3, 132.7, 127.8, 127.2, 126.3, 121.8, 112.4, 67.9, 55.7; HRMS (ESI) m/z calcd for $C_{56}H_{43}CoN_4O_6$ M$^+$ 926.2509, found 926.252

***tert*-Butyloxycarbonylcobalt *meso*-(4-Methoxyphenyl)-porphyrin (7).** This compound was prepared according to the general procedure A using 198 mg of cobalt *meso*-(4-methoxyphenyl)-porphyrin (0.25 mmol, 1 equiv), 119 μL of *tert*-butyl alcohol (1.25 mmol, 5 equiv), and 56.7 mg of DDQ (0.25 mmol, 1 equiv). After 16 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a red solid (134 mg, 0.15 mmol, 60%): IR (film) 2928, 1692, 1507, 1247, 1027 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 8H, por-H), 8.03 (s, 8H, PMP), 7.25 (d, J = 8.8 Hz, 8H, PMP), 4.07 (s, 12H, OCH_3), −0.75 (s, 9H, *t*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 145.6, 134.7, 134.4, 132.5, 121.0, 112.3, 55.6, 25.8; HRMS (ESI) m/z calcd for $C_{53}H_{45}CoN_4NaO_6Na$ (M + Na)$^+$ 915.2569, found 915.2567.

4-Bromobenzyloxycarbonylcobalt *meso*-(4-Methoxyphenyl)porphyrin (8). This compound was prepared according to the general procedure A using 198 mg of cobalt *meso*-(4-methoxyphenyl)porphyrin (0.25 mmol, 1 equiv), 234 mg of 4-bromobenzyl alcohol (1.25 mmol, 5 equiv), and 56.7 mg of DDQ (0.25 mmol, 1 equiv). After 16 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a red solid (226 mg, 0.23 mmol, 94%): IR (film) 2954, 1671, 1607, 1247, 1001 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 8H, por-H), 7.89 (s, br, 8H, PMP), 7.23 (d, J = 8.8 Hz, 8H, PMP), 6.97 (d, J = 8.2 Hz, 2H, Ph), 5.19 (d, J = 8.2 Hz, 2H, Ph), 4.07 (s, 12H, OCH_3), 2.53 (s, 2H, OCH_2Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 145.8, 134.7, 134.4, 134.1, 132.8, 130.9, 128.3, 121.8, 112.5, 67.0, 55.7; HRMS (ESI) m/z calcd for $C_{56}H_{42}BrCoN_4ONa^+$ 1027.1512, found 1027.1534.

1-Phenethyloxycarbonylcobalt *meso*-(4-Methoxyphenyl)-porphyrin (9). This compound was prepared according to the general procedure A using 198 mg of cobalt *meso*-(4-methoxyphenyl)-porphyrin (0.25 mmol, 1 equiv), 151 μL of 1-phenylethanol (1.25 mmol, 5 equiv), and 56.7 mg of DDQ (0.25 mmol, 1 equiv). After 16 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a red solid (216 mg, 0.23 mmol, 92%): IR (film) 2957, 2833, 1690, 1504, 1241, 996 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.76 (s, 8H, por-H), 7.90 (s, br, 8H, PMP), 7.33 (d, J = 8.8 Hz, 8H, PMP), 6.85 (t, J = 7.4 Hz, 1H, Ph), 6.70 (t, J = 7.7 Hz, 2H, Ph), 4.95 (d, J = 7.3 Hz, 2H, Ph), 4.03 (s, 12H, OCH_3), 2.90 (q, J = 6.2 Hz, 1H, OCHCH$_3$), −0.75 (d, J = 6.5 Hz, 3H, OCHCH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.8, 143.8, 143.7, 141.5, 134.5, 133.9, 132.1, 127.1, 126.1, 123.2, 119.0, 112.4, 69.2, 55.4, 21.3; HRMS (ESI) m/z calcd for $C_{57}H_{45}CoN_4O_6Na$ (M + Na)$^+$ 963.2563, found 963.2533.

1-Phenethyloxycarbonylcobalt *meso*-Tetraphenylporphyrin (10). This compound was prepared according to the general procedure A using 167 mg of cobalt tetraphenylporphyrin (0.25 mmol, 1 equiv), 151 μL of 1-phenylethanol (1.25 mmol, 5 equiv) and 56.7 mg of DDQ (0.25 mmol, 1 equiv). After 16 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a red solid (232 mg, 0.23 mmol, 94%): IR (film) 3055, 2925, 1693, 1599, 1351, 1003 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (s, 8H, por-H), 8.14 (s, br, 4H, meso-Ph), 7.98 (s, br, 4H, meso-Ph), 7.79−7.74 (m, 12H, meso-Ph), 6.85 (t, J = 7.4 Hz, 1H, Ph), 6.70 (t, J = 7.7 Hz, 2H, Ph), 4.97 (d, J = 7.2 Hz, 2H, Ph), 2.92 (q, J = 6.4 Hz, 1H, OCHCH$_3$), −0.73 (d, J = 6.5 Hz, 3H, OCHCH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.5, 143.4, 141.6, 133.5, 132.2, 127.7, 127.1, 126.9, 126.1, 123.2, 119.4, 69.4, 21.2;

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HRMS (ESI) m/z calcd for $C_{53}H_{37}CoN_4O_6Na^+$ 843.2141, found 843.2127.

1-Phenethyloxycarbonylcobalt Octaethylporphyrin (11). This compound was prepared according to the general procedure A using 59 mg of cobalt octaethylporphyrin (0.1 mmol, 1 equiv), 24 μL of 1-phenylethanol (0.2 mmol, 2 equiv), and 22.7 mg of DDQ (0.1 mmol, 1 equiv). After 16 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a red solid (62.2 mg, 0.08 mmol, 84%): IR (film) 2964, 2870, 1697, 1263, 1021 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 4H, meso), 6.79 (t, J = 7.4 Hz, 1H, Ph), 6.67 (t, J = 7.6 Hz, 2H, Ph), 4.96 (d, J = 7.4 Hz, 2H, Ph), 4.17−3.97 (m, 16H, por-CH_2CH_3), 2.96 (q, J = 6.4 Hz, 1H, $OCHCH_3$), 1.93 (dd, J = 12.7, 7.4 Hz, 24H, por-CH_2CH_3), −0.82 (d, J = 6.5 Hz, 3H, $OCHCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.9, 143.1, 141.1, 127.1, 126.2, 123.6, 99.3, 72.3, 20.9, 20.1, 18.6; HRMS (ESI) m/z calcd for $C_{45}H_{53}CoN_4O_2Na$ $(M + Na)^+$ 763.3393, found 763.3426.

1-Phenethyloxycarbonylcobalt Tetrakis-(pentafluorophenyl)porphyrin (12). This compound was prepared according to the general procedure A using 257 mg of cobalt *meso*-tetrakis(pentafluorophenyl)porphyrin (0.25 mmol, 1 equiv), 53 μL of 1-phenylethanol (0.5 mmol, 2 equiv), and 56.7 mg of DDQ (0.25 mmol, 1 equiv). After 16 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a red solid (165 mg, 0.14 mmol, 56%): IR (film) 2928, 1648, 1476 1217, 1007 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 7.3 Hz, 8H, por-H), 6.76 (d, J = 7.8 Hz, 1H, Ph), 6.63 (t, J = 7.6 Hz, 2H, Ph), 5.05 (d, J = 7.7 Hz, 2H, Ph), 3.22 (q, J = 6.5 Hz, 1H, $CHCH_3$), −0.57 (d, J = 6.5 Hz, 3H, $CHCH_3$); ^{19}F NMR (400 MHz, $CDCl_3$) δ −133.93, −137.47, −151.50; HRMS (ESI) m/z calcd for $C_{53}H_{17}CoN_4O_2F_{20}$ Na $(M)^+$ 1180.0364, found 1180.0408.

1-((4-Bromobenzyl)oxy)-2,2,6,6-tetramethylpiperidine (13). This compound was prepared according to the general procedure B using 20 mg of **8** (0.02 mmol, 1 equiv) and 6.2 mg of TEMPO (0.04 mmol, 2 equiv). After 4 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a clear oil (4.8 mg, 0.015 mmol, 74%): IR (film) 2928, 1508, 1264, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.4 Hz, 2H, Ar), 7.16 (d, J = 8.5 Hz, 2H, Ar), 4.69 (s, 2H, CH_2Ar), 1.17 (d, J = 12.6 Hz, 12H), 1.07 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 131.3, 129.1, 121.2, 78.0, 60.0, 39.7, 33.1, 29.7, 20.3, 17.1); HRMS (ESI) m/z calcd for $C_{16}H_{25}BrNO$ $(M + H)^+$ 326.1120, found 326.1118.

2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (14). This compound was prepared according to the general procedure B using 18.8 mg of **8** (0.02 mmol, 1 equiv) and 6.2 mg of TEMPO (0.04 mmol, 2 equiv). After 4 h, the reaction mixture was worked up as outlined in the general procedure. The reaction afforded a clear oil (4 mg, 0.016 mmol, 80%): IR (film) 2924, 2136, 1966, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.27 (m, 4H, Ph), 7.22 (m, 1H, Ph), 4.78 (q, J = 6.7 Hz, 1H, $CHCH_3$), 1.48 (d, J = 6.7 Hz, 3H, $CHCH_3$), 1.21 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 128.1, 127.3, 101.5, 59.9, 59.3, 39.6, 32.9, 29.5, 20.1, 17.0, 0.85; HRMS (ESI) m/z calcd for $C_{17}H_{28}NO$ $(M + H)^+$ 262.2165, found 262.2164.

Computational Methods. Density functional theory (DFT) calculations were performed using the Gaussian 09 suite.[44] All calculations were done using the generalized gradient approximation (GGA) density functional BP86, which combines Becke's 1988[45] exchange functional and Perdew's 1986[46] correlation functional. Geometry optimization and frequency calculations were performed in the gas phase and at the default temperature of 298.15 K. The resulting outputs were verified to be free of imaginary frequencies to ensure that the optimized structures were local minima. The Co−C bond dissociation energy was calculated as the subtraction of $\Delta_fH°$ for compound **9** from the sum of $\Delta_fH°$ for the appropriate homolytic dissociation products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00552.

Description of crystallographic methods and spectroscopic data (PDF)

Cartesian coordinates of DFT structures (XYZ)

Accession Codes

CCDC 1946972 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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