Light-induced O_2-dependent aliphatic carbon-carbon (C-C) bond cleavage in bipyridine-ligated Co(II) chlorodiketonate complexes

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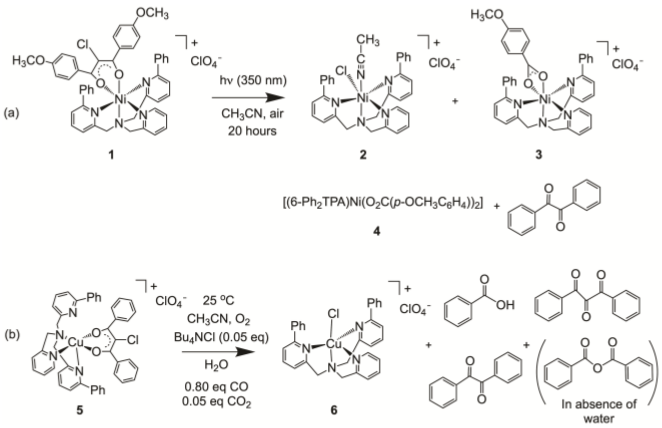
Mononuclear bipyridine (bpy)-ligated Co(II) chlorodiketonate complexes $[(bpy)_2Co(R\text{-}PhC(O)C(Cl)C(O)R\text{-}Ph)]ClO_4$ (R = -H (**8**), $-CH_3$ (**9**), and $-OCH_3$ (**10**)), were prepared, characterized and investigated for O_2-dependent aliphatic C-C bond cleavage reactivity. Complexes **8**-**10** have a distorted psuedo-octahedral geometry. ^1H NMR spectra of **8**-**10** in CD_3CN show signals for the coordinated diketonate moiety, and signals suggesting ligand exchange reactivity leading to the formation of a small amount of $[(bpy)_3Co](ClO_4)_2$ (**11**) in solution. While **8**-**10** are air stable at room temperature, illumination at 350 nm results in oxidative cleavage reactivity within the diketonate moiety leading to the formation of 1,3-diphenylpropanetrione, benzoic acid, benzoic anhydride, and benzil. Illumination of **8** under $^{18}O_2$ results in a high level of ^{18}O incorporation (>80%) in benzoate anion. The product mixture, high level of ^{18}O incorporation, and additional mechanistic studies suggest a reaction sequence wherein light-induced reactivity leads to the formation of a triketone intermediate that undergoes either oxidative C-C bond cleavage or benzoyl migration promoted by a bipyridine-ligated Co(II) or Co(III) fragment.

Introduction

Oxidative aliphatic carbon-carbon bond cleavage reactions mediated by first-row transition metals involving O_2 as the terminal oxidant are of current interest for synthetic applications. Examples involving iron and copper salts are the most common.[1,2] Related to such systems are model complexes for metalloenzyme-catalyzed O_2-dependent aliphatic C-C bond cleavage reactions. These include synthetic complexes of relevance to O_2-dependent flavonol, acireductone and diketone-cleaving enzymes.[3-5] It is important to note that flavonols and acireductones exhibit enhanced reactivity with O_2 as compared to simple diketones. In fact, there very few well-characterized first-row metal diketonate complexes that are known to exhibit reactivity with O_2 and undergo aliphatic C-C bond cleavage.[5,6] To date, a Co(II) diketonate complex which undergoes O_2-dependent aliphatic C-C bond cleavage within the diketonate moiety has not been reported.

As an approach for investigating the O_2 reactivity of metal diketonate complexes, our laboratory has pursued studies of first-row metal divalent metal chlorodiketonate complexes.[6] A mononuclear Ni(II) *p*-methoxy-substituted chlorodiketonate complex (**1**, Scheme 1(a)) supported by an aryl-appended tris(2-pyridylmethyl)amine ligand is stable with respect to O_2 under ambient conditions. However, oxidative C-C bond cleavage occurs within the diketonate unit upon illumination with UV light (350 nm) under aerobic conditions.[6a] The products identified included Ni(II) chloride and carboxylate complexes and benzil (Scheme 1(a)). Mechanistic studies suggest that illumination of **1** results in intramolecular redox to produce a diketonate radical and a Ni(I) species which lead to O_2 activation and the production of superoxide (O_2^-). The involvement of superoxide in the reaction pathway is supported by the results of an independent reaction between **1** and KO_2 (in the presence 18-crown-6) which also yields anisic acid as the major β-diketonate derived product. Labelling studies involving $^{18}O_2$ showed 36% incorporation of a labelled oxygen in the carboxylic acid product. The formation of benzil as a minor organic product in the reaction pathway suggests the involvement of a triketone intermediate. In support of this proposal, α-I-β-diketones have been reported to undergo reaction with O_2 under illumination to produce 1,3-diphenylpropanetrione, PhC(O)C(O)C(O)Ph).[7] Notably, analogs of **1** having *p*-methyl or *p*-H chlorodiketonate



Scheme 1 Examples of O_2-reactive divalent metal chlorodiketonate complexes.

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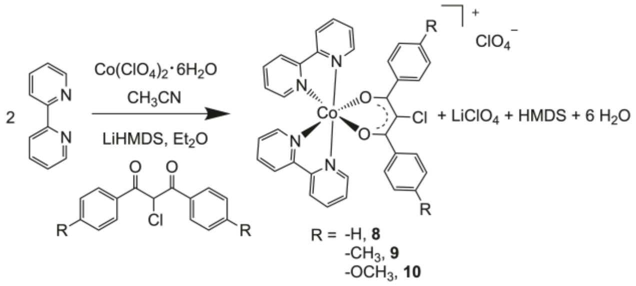
Electronic Supplementary Information (ESI) available: X-ray crystallographic data; Spectroscopic data for characterization; spectra of reaction and product mixtures. See DOI: 10.1039/x0xx00000x ligands exhibit significantly lower levels of oxidative C-C bond cleavage reactivity, indicating that the electronic structure of the diketonate ligand has an impact on the photoinduced reactivity in this system.[6a]

A Cu(II) chlorodiketonate complex supported by the same 6-Ph_2TPA ligand (**5**, Scheme 1) exhibits thermal O_2-mediated C-C bond cleavage reactivity in the presence of added chloride anion at room temperature.[6b-c] The oxidative C-C bond cleavage products generated in this reaction are similar to those generated from **1** under illumination conditions, indicating that a change in the metal center enables enhanced thermal reactivity. Exposure of the Cu(II) chlorodiketonate complex [(6-Ph_2TPA)Cu(PhC(O)C(Cl)C(O)Ph)]ClO_4 (**5**) to $^{18}O_2$ results in the formation of benzoic acid containing ~60% of one labelled oxygen atom.[6b] Under dry conditions, benzoic anhydride is formed and quantitative ^{18}O incorporation is found in a 1,3-diphenylpropanetrione intermediate. We note that a bipyridine-ligated Cu(II) chlorodiketonate complex, [(bpy)Cu(PhC(O)C(Cl)C(O)Ph)]ClO_4 (**7**), is also reactive with O_2 under ambient conditions.[6c] Notably, use of the tetradentate tris(2-pyridylmethyl)amine supporting ligand in a Cu(II) chlorodiketonate complex results in a non-redox, water-dependent retro-Claisen pathway becoming more prevalent for aliphatic C-C cleavage.[6d]

Examples of Co(III) chloroacetoacetonate complexes supported by amine ligands have been previously reported.[8] However, Co(II)-containing chlorodiketonate complexes akin to **1**, **5** or **7** have not been previously reported. With an interest in further understanding reactions of first row metal complexes with O_2 leading to aliphatic C-C bond cleavage in diketonate ligands, we outline herein the preparation, characterization, and O_2 reactivity of a series of Co(II) complexes [$(bpy)_2$Co(R-PhC(O)C(Cl)C(O)Ph-R)]ClO_4, R = -H (**8**), -CH_3 (**9**), and OCH_3 (**10**). These complexes exhibit UV light-induced oxidative aliphatic C-C bond cleavage to give reaction products similar to those produced in the thermal reaction of the Cu(II)-containing **5**. The light-driven O_2 reactivity of the Co(II) complexes also results in the formation of a triketone intermediate which leads either to oxidative C-C cleavage reactivity or benzoyl migration resulting in benzil formation. Notably, the latter migration chemistry is enhanced when the more highly Lewis acidic Co(III) is formed in the reaction mixture.



Scheme 2 Synthesis of Co(II) chlorodiketonate complexes **8-10**.

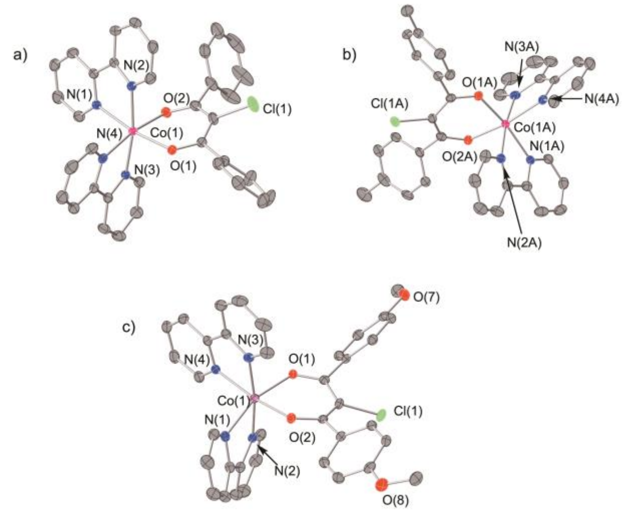


Fig 1 Thermal ellipsoid (50%) representations of the cationic portions of a) **8**, b) **9**, and c) **10**. Only one of two independent cations in the asymmetric unit of **9** is shown. Hydrogen atoms are omitted for clarity.

Results

Synthesis and Characterization. The Co(II) complexes **8-10** were prepared by mixing 2,2'bipyridine (2 eq) with $Co(ClO_4)_2\cdot6H_2O$ (1 eq) in CH_3CN followed by combining of this solution with an Et_2O solution of the lithium salt of a 2-chloro-1,3-diphenyl-1,3-propanedione (Scheme 2) formed in situ. Crude orange solids obtained from these mixtures were recrystallized (**8**, **10**: CH_3CN with Et_2O diffusion; **9**: CH_3CN/CH_2Cl_2 (5:1) with Et_2O diffusion) to give crystalline solids in 53-57% yield. Each complex was characterized by X-ray crystallography, elemental analysis, IR, ESI-MS, ^1H NMR, and UV-vis spectroscopy.

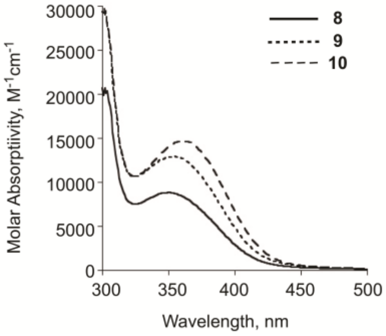
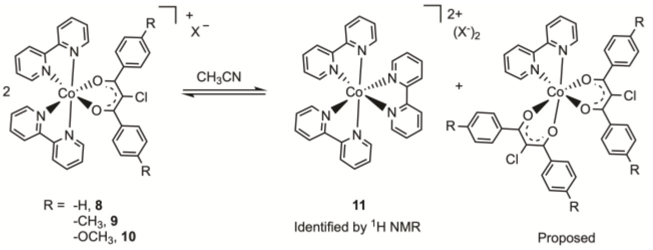


Fig 2 Absorption spectral features of **8-10** in acetonitrile.

Compound **8** crystallizes with one equivalent of Et_2O in the lattice, crystalline **9** contains 0.5 eq. Et_2O and 0.5 eq. CH_3CN, and **10** contains no solvent in the lattice. Representations of the cationic portions of **8**-**10** are shown in Fig 1. Details of the data collection and refinement are provided in Table S1. Selected bond distances and angles are given in Tables S2 and S3. Compound **9** crystallizes with two similar molecules (labelled A and B) in the asymmetric unit. The Co(II) center in **8**-**10** exhibits a pseudo-octahedral geometry with Co-N distances of 2.10-2.15 Å and Co-O distances of 2.02-2.06 Å. These distances are elongated relative to those of previously reported bis-bipyridine or phenanthroline Co(III) diketonate complexes (Co(III)-O, 1.88-1.89 Å, Co(III)-N, 1.93-1.96 Å).[9]

Each complex gives satisfactory CHN combustion results. The solid-state IR spectra **8**-**10** (Fig S1-S3) contain features at approximately 1094 and 623 cm^{-1} consistent with the presence of the perchlorate counterion. ESI-MS spectra of CH_3CN solutions of **8**-**10** (Fig S4-S6) show the presence of the expected molecular ions with appropriate isotope patterns. UV-vis spectra of **8**-**10** contain a $\pi \rightarrow \pi^*$ diketonate transition at 350-360 nm (Fig 2). The $\pi \rightarrow \pi^*$ transitions of **8**-**10** move to higher energy with increasing electron density, which is consistent with stabilization of the HOMO or destabilization of the LUMO. Differences in the molar absorptivity values for the $\pi \rightarrow \pi^*$ transitions for **8**-**10** are similar to those found for Ni(II) chlorodiketonate complexes (R = H (**8**) < R = $-CH_3$ (**9**) < R = $-OCH_3$ (**10**)).[6a] Magnetic moment measurements performed via the Evans method[10] yielded μ_{eff} = 4.6-4.8 μ_B consistent with a high-spin Co(II) in each complex. ^1H NMR data collected for **8**-**10** under paramagnetic conditions display signals for the diketonate aryl protons in the region of 5-25 ppm (Fig S7-S9), with the signal for the *ortho* protons of the diketonate aryl rings being the most downfield-shifted for each diketonate ligand. We note that the ^1H NMR spectrum for each of the analytically pure complexes **8**-**10** in CD_3CN includes signals consistent with the presence of a small amount of $[(bpy)_3Co](ClO_4)_2$ (**11**, Fig S10), which was confirmed through independent synthesis, elemental analysis and ^1H NMR analysis.[11] This indicates that some ligand exchange occurs in solution. Outlined in Scheme 3 is a proposal for the ligand exchange reactivity of **8**-**10** resulting in the formation of $[(bpy)_3Co](ClO_4)_2$ (**11**). The Co(II) bis-diketonate derivatives have not been independently identified. However, other remaining unassigned signals present in the ^1H NMR spectra of **8**-**10** may be associated with these species.



Scheme 3 Proposed ligand exchange reactivity of **8-10** in CH_3CN.

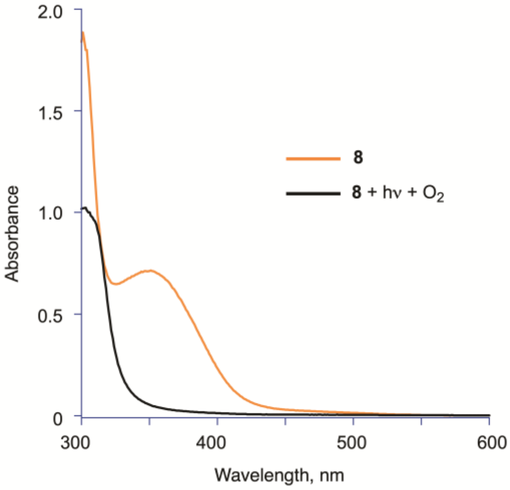


Fig 3 Absorption spectral changes upon illumination of **8** in O_2-purged CH_3CN at 350 nm.

Reactivity Studies with O_2. Orange acetonitrile solutions of **8**-**10** are generally stable with respect to O_2 for ~20 h when kept in the dark (Fig S11-S13). The *p*-OCH_3 chlorodiketonate complex **10** does show some minor degradation (Fig S13) after 20 h. Illumination of acetonitrile solutions of **8**-**10** under N_2 at 350 nm results in no reaction as determined by organic recovery studies for the chlorodiketonate ligand (Fig S14-S16). However, illumination at 350 nm under O_2 instead results in a loss in intensity of the $\pi \rightarrow \pi^*$ absorption band at ~350 nm for **8** (Fig 3). Similar spectral changes are observed for **9** and **10** (Fig S17 and S18). Using ^1H NMR to monitor the illumination reaction of **8** under O_2, loss of the Co(II) complex diketonate resonances was identified, along with the appearance of new resonances in the

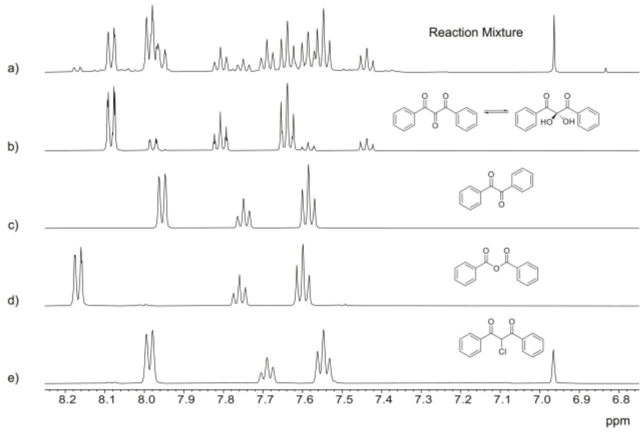
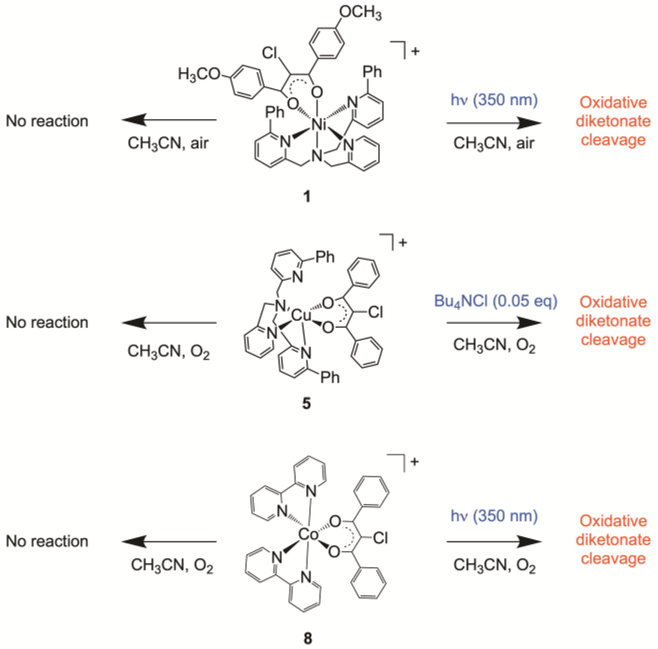


Fig 4 ^1H NMR spectra of (a) the organic products identified in the light-induced reaction of **8**. Standard samples (b-e) show that the oxidation products include 1,3-diphenylpropanetrione, benzil, and benzoic anhydride.

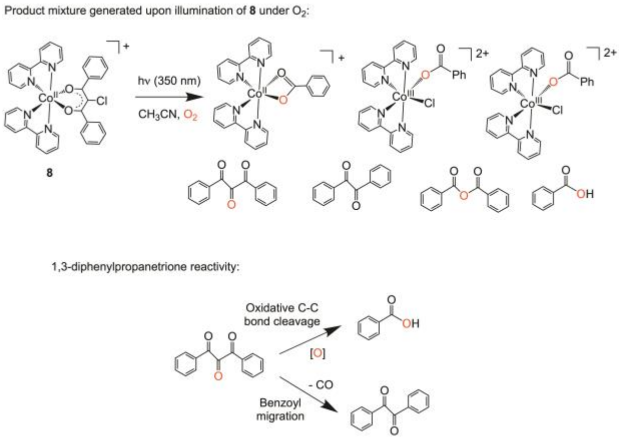
region of 7-9 ppm indicating the formation of non-coordinated aromatic products (Fig S19). We note that the signals for $[(bpy)_3Co](ClO_4)_2$ (**11**) remain unchanged in the reaction mixture. Products of the reactions of **8**-**10** were analyzed by ESI-MS and organic product extraction. For **8**, ESI-MS data shows the presence of cationic Co(II) and Co(III) species having a benzoate ligand (e.g., $[(bpy)_2Co(II)(O_2CPh)]^+$ and $[(bpy)_2Co(III)(O_2CPh)_2]^+$, Fig S20) and Co(III) chloride species such as $[(bpy)_2Co(III)Cl(O_2CPh)]^+$and $[(bpy)_2Co(III)Cl_2]^+$). Similar reaction mixtures are observed for **9** and **10** (Fig S21 and S22). Performing the light-induced reaction of **8** in the presence of $^{18}O_2$ results in >80% incorporation of one ^{18}O atom in $[(bpy)_2Co(II)(O_2CPh)]^+$ providing evidence that O_2-dependent aliphatic C-C bond cleavage has occurred $[(bpy)_2Co(^{18}OOCPh)]^+$ (Fig S23). As a control reaction to probe the importance of the diketonate chloride substituent, we generated the unsubstituted analog of **8**, $[(bpy)_2Co(PhC(O)CHC(O)Ph]ClO_4$ (**12**; Fig S24 and S25), and examined its reactivity in acetonitrile upon illumination at 350 nm for 20 h under O_2 (Fig S26 and Fig S27). Minimal change was observed in the ^1H NMR and absorprtion spectral features of **12**, indicating no reaction occurred.

The aromatic organic products derived from light-induced reactivity of the diketonate ligand in **8** include 1,3-diphenylpropanetrione, benzoic anhydride and benzil (Fig 4 and Scheme 4). Similar organic product mixtures were found for **9** and **10** (Figures S28 and S29). Isolation of the organic products from the reaction of unsubstituted diketonate complex **12** showed no reaction had taken place (Fig S30) indicating the requirement of the chloride substituent for reactivity.

The reaction quantum yield (QY) for **8** with illumination at 350 nm in acetonitrile under air is 0.0009(3) as measured using ferrioxalate actinometry. The QYs measured for the reactions of **9** and **10** under identical conditions were 0.00050(1) and 0.00124(4), respectively. For **8**-**10** and the Ni(II) chlorodiketonate series of complexes previously reported, increasing the electron density within the diketonate via a *p*-OCH_3 substituent only slightly influenced the quantum yield (e.g, **1**, 0.00038(2) vs. 0.0002(1) in $[(6\text{-}Ph_2TPA)Ni(PhC(O)C(Cl)C(O)Ph))]ClO_4)$ [6a]



Scheme 5 Triggered O_2 reactivity in divalent metal chloro-diketonate complexes.



Scheme 4 (top) Overview of reaction products identified in the light-induced reaction of **8** under O_2. (bottom) Reactions of 1,3-diphenylpropane trione leading to oxidative aliphatic C-C cleavage products.

The similarity of the organic product mixtures produced in the light-induced reactions of **8**-**10** with those found in the thermal O_2 reaction of the Cu(II) chlorodiketonate complex **5**[6b,6c] (Scheme 1(b)) is noteworthy. In the Cu(II)-mediated reaction, computational studies suggest that hypochlorite may be formed via reaction of the chlorodiketonate with O_2. This reaction also results in the formation of 1,3-diphenylpropanetrione via O-O and C-Cl bond cleavage. Hypochlorite is then proposed to act as the oxidant for aliphatic carbon-carbon bond cleavage in 1,3-diphenylpropanetrione leading to the formation of benzoic anhydride or benzoic acid. Benzil formation is proposed to occur via benzoyl migration involving 1,3-diphenylpropanetrione, which is likely facilitated by the Lewis acidic Cu(II) center. With the identified formation of 1,3-diphenylpropanetrione in the light-induced reactions of **8**-**10**, we explored reaction pathways involving this trione and a Co(II)-containing solvate complex in the presence of a possible in-situ formed oxidant (hypochlorite) to probe for aliphatic C-C bond cleavage products. Specifically, we examined the reactivity of a bpy₂-ligated Co(II) solvate complex, $[(bpy)_2Co(CH_3CN)_2](ClO_4)_2$ (**13**; Fig S31), with 1,3-diphenylpropanetrione and NaOCl in acetonitrile under various conditions. Treatment of **13** with stoichiometric amounts of 1,3-diphenylpropanetrione and hypochlorite under O_2 and stirring for 19 h at ambient temperature resulted in the formation benzil and benzoic acid (Fig S32) with significant unreacted 1,3-diphenylpropanetrione remaining. Notably, purging of an acetonitrile solution of **13** with O_2 for 8 h followed by stirring for an additional 19 h results in the solution turning dark red-brown (Fig S33; Fig S34). This solution exhibits ^1H NMR features consistent with the formation of a diamagnetic Co(III) species (Fig S35 and Fig S36). Addition of 1,3-diphenylpropanetrione and NaOCl to this solution and stirring for 19 h results in the complete consumption of the 1,3-diphenylpropanetrione with the formation of primarily benzil (Fig S37). These combined results provided evidence that 1,3-diphenylpropanetrione formed in the light induced reactions of **8**-**10** could undergo reaction with an oxidant (hypochlorite) leading to oxidative cleavage products (e.g., benzoic acid), or can undergo benzoyl migration to give benzil. The relative amounts of these products likely depends on the degree to which the Co(II) center undergoes oxidation to Co(III) in the reaction mixture, as the latter as a better Lewis acid to promote benzoyl migration. With regard to oxidation of the Co(II) center, a control reaction involving treatment of **13** with stoichiometric NaOCl in CD_3CN showed that an oxidant such as hypochlorite can directly oxidize the Co(II) center in **13** to Co(III). Changes in the ^1H NMR spectrum (Fig S38) suggest the formation of Co(III) species similar to that produced upon extended exposure of **13** to O_2.

Discussion

Synthetic systems that enable studies of divalent metal-mediated O_2-dependent aliphatic carbon-carbon bond cleavage within a diketonate ligand remain rare.[5,6,13] In this regard, studies of the oxidative cleavage of divalent metal chlorodiketonate complexes as a function of the metal ion are a novel approach toward examining the effect of metal ion on O_2 activation and aliphatic C-C cleavage.[6] As summarized in Scheme 5, at ambient temperature under air, complexes **1**, **5** and **8** are stable with respect to O_2. It should be noted that the Ni(II) and Co(II) chlorodiketonate complexes **1** and **8** are coordinatively saturated, whereas the Cu(II) complex **5** exhibits a five-coordinate metal center in the solid state. Illumination of **1** and **8** results in reactivity with O_2 leading to aliphatic C-C cleavage within the chlorodiketonate unit. The Cu(II) complex undergoes reaction with O_2 at room temperature in the presence of a catalytic amount of chloride anion.[6]

The product mixtures derived from the light-induced reactions **8**-**10** under O_2 are similar to those found in the thermal reaction of the Cu(II) chlorodiketonate complex **5** (Scheme 1). Specifically, Co(II) and Co(III) benzoate and chloride species were identified, along with 1,3-diphenylpropanetrione, benzil, benzoic anhydride and benzoic acid (Scheme 4). The level of ^{18}O incorporation is significantly higher in the benzoate products generated from **5** and **8** (>60% and 80%, respectively) versus that found in the Ni(II)-containing benzoate product **3** (36%; Scheme 1). This provides evidence for differences in the light-induced reactions pathways of Ni(II)-containing **1** versus Co(II)-containing **8**. We hypothesize that this is related to light-induced redox reactivity in the nickel-containing system leading to Ni(I) formation and free diketonate radical. Organic products resulting from radical decomposition and free diketone reactivity were identified in the Ni(II) reaction but were not identified in the reactions of **8**-**10**.[6a] We note that in the Ni(II) chlorodiketonate systems, variation in the electronic properties of the diketonate ligand impacted the organic product mixture that was generated. For example, the reactivity of **1** (Scheme 1) under O_2 was significantly higher than that found for the analog lacking the *p*-methoxy diketonate substituent. In the Co(II) series **8**-**10**, similar levels of reactivity were identified regardless of the aryl substituent present. This indicates a fundamental difference in the light-driven reaction pathways between Ni(II) and Co(II) chlorodiketonate complexes.

The similarity of the product mixtures for the reactions of **5** and **8** led us to evaluate a possible reaction pathway for the Co(II) complexes **8**-**10** that is inspired by the thermal reaction of **5**. The light-induced reactions of **8**-**10** lead to the formation of 1,3-diphenylpropanetrione derivatives, which have been identified in the reaction mixtures. We propose that an O_2-derived oxidant, potentially hypochlorite, is also formed in these reactions but could not be directly identified. To probe potential subsequent reactivity leading to aliphatic C-C bond cleavage, independent studies were performed to examine the reactivity of 1,3-diphenylpropanetrione with NaOCl in the presence of a Co(II) complex. The results of these investigations show the feasibility of these reactants to lead to the formation of benzoic acid or benzoic anhydride. Additionally, it was determined that oxidation of the Co(II) to Co(III) enhanced benzil formation from 1,3-diphenylpropanetrione. We note that we cannot currently rule out the formation of other intermediate oxidant species in the light-induced reactions of **8**-**10**. For example, the light induced formation of Cl• leading to the formation of ClO_2• could potentially provide a similar set of reaction products.

Co(II) complexes have been previously reported that promote oxidative C-C bond cleavage using O_2 as the terminal oxidant.[16] In mechanistic proposals for some of these systems, cobalt-dioxygen species or oxidants derived therefrom are proposed to be involved in C-C cleavage. For the Co(II) bipyridine-ligated systems described herein the formation of 1,3-diphenylpropanetrione appears to be a key step as this intermediate enables subsequent formation of aliphatic C-C cleavage products resulting from oxidative cleavage and benzoyl migration reactivity. Co(II) and Co(III) species in the reaction mixture likely facilitate benzoyl migration reactivity involving the triketone leading to substantial amounts of benzil formation.

Experimental

General Methods. All solvents and reagents were purchased from commercial sources and used without prior purification unless otherwise stated. Solvents were dried following previously published procedures and distilled under N_2 prior to use.[17] All synthetic procedures for Co(II) complexes were performed in a glovebox under a N_2 atmosphere unless otherwise noted. The diketone 1,3-(4′,4′-methyl)-phenylpropane-1,3-dione, chlorodiketones 2-chloro-1,3-(4′,4′-R)-phenylpropane-1,3-dione (R = -H, $-CH_3$, $-OCH_3$), and $[(bpy)_3Co](ClO_4)_2$ (**11**) were synthesized according to previously published procedures.[6a,11]

Physical Methods. ^1H NMR spectra were collected on a Brüker Advance III HD Ascend-500 spectrometer. Chemical shifts (ppm) are reported relative to the residual solvent peak in CD_2HCN (1.94 ppm, quintet). ^{1}H NMR spectra of paramagnetic Co(II) complexes were collected using the following parameters: 300 scans that consist of 8,000 data points over a spectral window of 0-120 ppm, with a 4.96 µs excitation pulse and a 30° pulse angle. FT-IR spectra were collected as KBr pellets using a Shimadzu FTIR-8400 spectrometer. Absorption spectral data was collected using a Hewlett-Packard 8453A diode array spectrometer at ambient temperature. ESI-mass spectral data was collected using a Shimadzu LCMS-2020. High resolution mass spectra were acquired at the Analytical Chemistry Instrumentation Facility at the University of California Riverside. Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ) or Atlantic Microlab, Inc. (Norcross, GA). Magnetic moments were determined using the Evans method.[10] Quantum yields were determined using ferrioxalate to measure photon flux.[18,19]

Caution! Perchlorate salts of metal complexes containing organic ligands are potentially explosive. Only small amounts of materials should be prepared (~50 mg) and these should be handled with great caution.[20]

[(bpy)$_2$Co(PhC(O)CClC(O)Ph)]ClO$_4$ (**8**). A solution of Co(ClO$_4$)$_2$·6H$_2$O (50.0 mg, 0.137 mmol) in CH$_3$CN (~3 mL) was combined with solid 2,2′-bipyridine (bpy) (42.7 mg, 0.273 mmol) at ambient temperature. The resulting mixture was stirred for 30 min. In a separate vial, 2-chloro-1,3-diphenyl-1,3-propanedione (35.3 mg, 0.137 mmol) and lithium bis(trimethylsilyl) amide (22.9 mg, 0.137 mmol) were combined in Et$_2$O (~3 mL) and stirred for 10 min to produce a pale yellow solution. The two solutions were then combined and stirred for an additional four hours. This resulted in the formation of a turbid orange solution. After removing the solvent under reduced pressure, the resulting orange precipitate was washed twice with 10 mL of Et$_2$O and dried under reduced pressure. X-ray quality crystals were grown via Et$_2$O diffusion into an CH$_3$CN solution containing a few drops of CH$_2$Cl$_2$ (53%). ESI-MS: *m/z* calc. for C$_{35}$H$_{26}$N$_4$ClO$_2$Co, 628.1 [M-ClO$_4$]$^+$; found: 628.1. Anal calcd. for C$_{35}$H$_{26}$N$_4$Cl$_2$O$_4$Co·O(CH$_3$CH$_2$)$_2$: C, 58.22; H, 4.76; N, 6.96; found: C, 58.32; H, 4.51; N, 7.19. UV-Vis λ_{max}, nm (ε, M^{-1}cm^{-1}): 350 (8800). FT-IR (KBr, cm^{-1}): 1091 (ν_{ClO_4}) , 621 (ν_{ClO_4}); μ_{eff} = 4.83 μ_B.

[(bpy)$_2$Co(CH$_3$PhC(O)CClC(O)PhCH$_3$]ClO$_4$ (**9**)**.** This complex was prepared and crystalized following the same procedure as **8** (57%). ESI-MS: *m/z* calculated for C$_{37}$H$_{30}$N$_4$ClO$_2$Co 656.1 [M-ClO$_4$]$^+$; found: 656.6; Anal calcd. for C$_{37}$H$_{30}$N$_4$Cl$_2$O$_4$Co: C, 58.59; H, 4.25; N, 7.39; found: C, 58.88; H, 4.52; N, 7.62. UV-Vis λ_{max}, nm (ε, M^{-1}cm^{-1}): 353 (11100). FT-IR (KBr, cm^{-1}): 1091 (ν_{ClO_4}) , 621 (ν_{ClO_4}); μ_{eff} = 4.67 μ_B.

[(bpy)$_2$Co(CH$_3$OPhC(O)CClC(O)PhOCH$_3$]ClO$_4$ (**10**). This complex was prepared following the same procedure as **8** (55%). ESI-MS: *m/z* calculated for C$_{37}$H$_{30}$N$_4$ClO$_4$Co 688.1 [M-ClO$_4$]$^+$; found: 688.3; Anal calcd. For C$_{37}$H$_{30}$N$_4$Cl$_2$O$_8$Co·0.15CH$_2$Cl$_2$: C, 55.55; H, 4.05; N, 6.98; found: C, 55.47; H, 3.95; N, 7.03. UV-Vis λ_{max}, nm (ε, M^{-1}cm^{-1}): 360 (13400). FT-IR (KBr, cm^{-1}): 1069 (ν_{ClO_4}), 620 (ν_{ClO_4}); μ_{eff} = 4.66 μ_B.

[(bpy)$_3$Co](ClO$_4$)$_2$ (**11**). A solution of 2,2′-bipyridine (bpy) (3 eq) in CH$_3$CN (~3 mL) was combined with solid Co(ClO$_4$)$_2$·6H$_2$O (1 eq) at ambient temperature. The reaction mixture was stirred for 4 h and then brought to dryness under vacuum. The remaining solid was dissolved in CH$_3$CN (1 mL) and this solution was added to excess Et$_2$O (~18 mL). Storing this mixture at room temperature for 24 h resulted in the deposition of a precipitate. The solvent was decanted from this precipitate via pipet. A second precipitation procedure was performed from CH$_3$CN/Et$_2$O and the solid isolated was dried under vacuum. Anal calcd. for C$_{37}$H$_{30}$N$_4$Cl$_2$O$_8$Co·H$_2$O: C, 48.41; H, 3.52; N, 11.29; found: C, 48.15; H, 3.45; N, 11.24. A ^{1}H NMR spectrum of **11** in CD$_3$CN matched the signals reported for [(bpy)$_3$Co](PF$_6$)$_2$.[11]

[(bpy)$_2$Co(PhC(O)CHC(O)Ph)]ClO$_4$ (12). The complex was prepared and isolated following the same procedure as **8** (30%). ESI-MS: *m/z* calc. for C$_{35}$H$_{27}$N$_4$O$_2$Co, 594.1461 [M-ClO$_4$]$^+$; found: 594.1493; UV-Vis λ_{max}, nm (ε, M^{-1}cm^{-1}): 351 (14230).

[(bpy)$_2$Co(CH$_3$CN)$_2$](ClO$_4$)$_2$ (**13**). In dry CH$_3$CN (3 mL) under a N$_2$ atmosphere, [Co(H$_2$O)$_6$](ClO$_4$)$_2$ (50 mg, 1.4 × 10^{-4} mol) was combined with 2,2′-bipyridine (43 mg, 2.7 × 10^{-4} mol) and the resulting mixture was stirred for 2 hours at ambient temperature. The solvent was then removed under reduced pressure providing an orange precipitate. This precipitate was dissolved in a minimal amount of CH$_3$CN and was recrystallized by slow diffusion of Et$_2$O. The resulting orange crystals were of sufficient quality for single crystal X-ray crystallography.

Reactivity of *in situ* generated [(bpy)$_2$Co(CH$_3$CN)$_2$](ClO$_4$)$_2$ (13) with 1,3-diphenylpropanetrione and NaOCl. Under N$_2$, [Co(H$_2$O)$_6$](ClO$_4$)$_2$ (20 mg, 5.5 × 10^{-5} mol) and bpy (17 mg, 1.1 × 10^{-4} mol) were combined in dry acetonitrile (15 mL) and stirred for 2 hours at ambient temperature. The solution was removed the glovebox and combined with 1,3-diphenylpropanetrione (13 mg, 5.5 × 10^{-5} mol) and NaOCl (3.3 mg, 4.4 x 10^{-5} mol). Oxygen was then bubbled through the solution for two minutes. The resulting solution was stirred for 19 hours and then an organic extraction was performed. A second solution was prepared similarly but was oxygenated for 8 h prior to the addition of 1,3-diphenylpropanetrione and NaOCl. This longer oxygenation produced a red/black solution suggesting oxidation of the Co(II) center.

X-ray crystallography. X-ray diffraction data for **8**-**10** were collected at the University of Montana at 100 K on a Bruker D8 Venture using MoKα radiation (λ = 0.71073 Å). Data for each complex was corrected for absorption using the SADABS[21] area detector correction program. Using Olex2[22], the structures were solved using the SHELXT[23] program with direct methods and refined with the SHELXL[24] refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from difference Fourier maps, but their final positions were placed in geometrically calculated positions and were refined using a riding model. Isotropic thermal parameters of the placed hydrogen atoms were fixed to 1.2 times the *U* value of the atoms to which they are attached (1.5 times for the methyl groups). Calculations and refinement of structures were carried out using APEX3[25], SHELXTL[26], and OLEX2[22] software.

The checkCIF for **9** suggested a center of symmetry element however this is just a pseudo element as the center of symmetry is close but not perfect. To further evaluate this matter, the data were solved in the space group *Pnma*. This resulting model exhibits poor structural parameters when compared to structures in Cambridge Structural Database using the Cambridge Crystallographic Data Centre program Mogul7[27] and Mercury8.[28] Therefore, we have elected to present the structure in the *Pna2(1)* setting.

A single crystal of **13** was mounted on glass fiber loop using paratone oil. Data collection was performed using a Rigaku XtaLAB Mini II Diffractometer with MoKα radiation (λ = 0.71073 Å) at 100 K. An absorption correction was done using a Gaussian grid with a 0.5 mm 1D horizontal Gaussian beam correction for the graphite monochromator. The structure was solved using Olex2[22] with SHELXT[23] using intrinsic phasing method and refined using the SHELXL[24] program with the least square method. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in geometrically calculated positions and further refined using a riding model. Isotropic parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are attached (1.5 times for the methyl groups).

Photoillumination studies. Solutions of **8-10** and **12** in dry CH_3CN under N_2 (15 mL, 2.0 mM) were prepared in 30 mL Pyrex test tubes sealed with rubber septa and tape. An absorption spectrum was collected for each sample by removing a 100 µL aliquot and adding it to 2700 µL of CH_3CN (7.1×10^{-2} mM). For O_2 reactivity studies, the solution was purged with O_2 for two minutes before illuminating for twenty hours at 350 nm. Following illumination, another absorption spectrum was collected with that sample being then used for ESI-MS. The remaining reaction solution was concentrated under vacuum. A ^1H NMR of the remaining residue was collected in CD_3CN. The ^1H NMR sample was then added back to the reaction vessel and the solvent was then removed under vacuum. The crude product was dissolved in 1.5 M HCl (15 mL) and stirred for ten minutes before CH_2Cl_2 (15 mL) was added and stirred for an additional ninety minutes. The solution was transferred to a separation funnel and the organic compounds were collected in the CH_2Cl_2 layer following three washes of 1.5 M HCl (15 mL). The CH_2Cl_2 fraction was dried over Na_2SO_4, filtered, concentrated under vacuum, and dried on vacuum line for two hours before a ^1H NMR was collected. The ^1H NMR solution was then added back to the reaction vessel and dried for 24 hours before the residue was analyzed using mass spectrometry.

Conclusions

The results presented herein demonstrate that bipyridine-supported Co(II) chlorodiketonate complexes exhibit light-induced oxidative aliphatic C-C bond resulting in products similar to the thermal reaction pathway found for structurally similar Cu(II) complexes. Both involve formation of a 1,3-diphenylpropanetrione intermediate that is susceptible to oxidative cleavage reactivity or benzoyl migration to give benzil.

Author Contributions

SNA and LMB formulated the project. SNA and JGDE performed the experimental studies. SNA and LMB prepared the manuscript.

Conflicts of interest

There are no conflicts to declare.

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