Photoinduced Ligand-to-Metal Charge Transfer of Cobaltocene: Radical Release and Catalytic Cyclotrimerization

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ABSTRACT. Irradiation of cobalt metallocenes at the ligand-to-metal charge transfer energies results in labilization of the cyclopentadienyl-cobalt bond and radical release. The cyclopentadienyl radical is detected by EPR spectroscopy using a spin trap and can also be chemically trapped using hydrogen-atom-donating reagents. This reaction presents a new photochemical method of generating new cobalt complexes or of forming cyclopentadienylcobalt(I) species that are active for catalytic [2+2+2] cyclotrimerization reactions. More importantly, these results also show that cobaltocene should not be considered as a photostable redox reagent under many conditions, including those relevant for photovoltaics or photocatalysis.

INTRODUCTION

The well-behaved and reversible electron transfer from late transition metal metallocenes like ferrocene (Fc) and cobaltocene ($CoCp_2$) and their derivatives have made them widely used as chemical redox agents and as references in electrochemical measurements.[1] These complexes have also been used in conjunction with optically-active molecules and materials in photocatalysis and photochemical applications, playing the role of redox mediators, as reducing agents for catalyst precursors, or as optically-active redox buffers for doping in semiconductor materials or in carbon nanotube-based devices.[2-6] Of particular interest has been the increasing use of cobaltocene or other metallocenes as dopants in photovoltaic devices.[6-10] In these applications, the metallocene-containing components are often irradiated at high intensities for prolonged periods of time (in one example, 100 mW/cm^2 for >1 h).[6] Although the metallocenes are expected to play a role as an innocent electron-transfer agent, it is clear that these compounds may be able to participate in photochemical reactions under these conditions.[11] An improved understanding of the photochemistry of these compounds is therefore important for their continued use in these systems.

In previous studies of metallocene photochemistry, ferrocenes have been demonstrated to be photostable under many conditions.[11-12] However, early metal metallocenes like zirconocene and titanocene derivatives[11, 13] and cyclopentadienyl compounds of main group elements (e.g. Hg, Sn)[14] have been shown to undergo photoinduced radical chemistry. Specifically, photoexcitation to a ligand-to-metal charge transfer (LMCT) state weakens the cyclopentadiene-metal interaction and can release the cyclopentadienyl radical, $Cp\cdot$. This photoinduced reactivity has been harnessed for photoinitiated polymerization reactions.[15] Similar transformations have not been reported for late transition metal metallocenes, however. For example, while $CoCp_2$ has been reported to undergo photodecomposition when irradiated at high energies ($\lambda_{exc} = 254$ nm), the mechanism of this process has not been reported and the products have not been characterized beyond identification as polymeric species.[16-17]

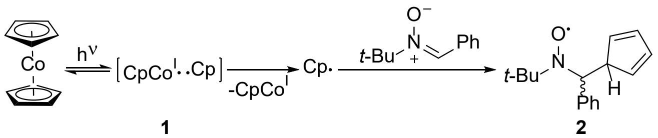
Here, we show that photoexcitation of $CoCp_2$ at certain energies releases a cyclopentadienyl radical that can be identified by spin trapping. The wavelength dependence of this process was measured, permitting identification of the LMCT band relevant to radical release. The resulting $[CpCo^I]$ synthons can be trapped by other ligand donors and are also active for cyclotrimerization catalysis.

RESULTS AND DISCUSSION

Photoinduced cyclopentadienyl radical release. $CoCp_2$ has been previously observed to undergo photodecomposition with high energy irradiation.[11, 16-17] In our initial experiments, however, no bleaching of the $CoCp_2$ absorption bands was observed for a THF solution of $CoCp_2$ when irradiated with blue light (λ_{exc} = 405 nm, 7.1 mW/cm^2) over 8 h. Some bleaching (ca. 20%) was observed when irradiated with UV light (λ_{exc} = 365 nm, 61 mW/cm^2) over 16 h (Fig. S1). This behavior is different from that of zirconocenes, which have been reported to undergo bleaching of their LMCT absorption features within minutes upon photoexcitation.[15]

Spin traps like *N*-tert-butyl-α-phenylnitrone (PBN) have been previously used to identify the cyclopentadienyl radical (Cp·) released upon photolysis of main group cyclopentadienyl compounds (e.g. Cp_2Hg, Cp_2Sn), via the formation of a nitroxyl radical adduct.[18] Scheme 1 shows the proposed reaction. Upon photoexcitation, the caged radical pair **1** is formed. This species can recombine to regenerate $CoCp_2$ or can undergo radical cage escape to form $[CpCo^I]$ and Cp·. The cyclopentadienyl radical then adds to the PBN spin trap to form the resulting cyclopentadienyl-PBN nitroxyl radical adduct (**2**).

Scheme 1. Spin Trapping of Photodissociated Cyclopentadienyl Radical



1 **2**

Figure 1 shows the EPR spectrum of a benzene solution of $CoCp_2$ and PBN after irradiation (λ_{exc} = 405 nm, 7.1 mW/cm^2) for 5 h at room temperature. This spectrum shows the characteristic six-line feature of a nitroxyl radical with *a*(N) = 14.4 G and *a*(H) = 2.2 G as the primary component, although smaller features corresponding to other unidentified paramagnetic species are observed.[19] These parameters are consistent with a previously published report of **2**.[18] Photoexcitation for longer periods of time increased the intensity of this feature. These results confirm the transient formation of Cp· from photoexcitation of $CoCp_2$.

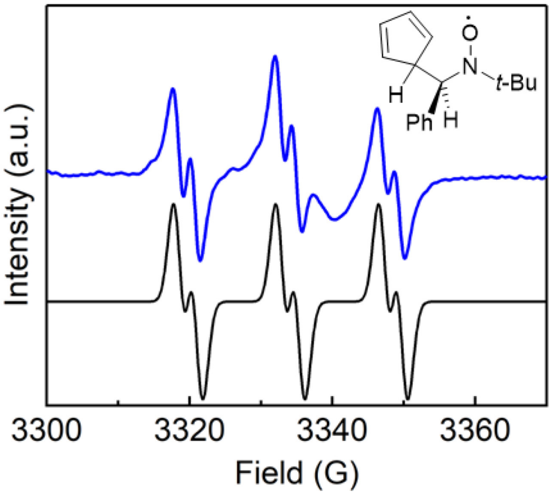


Figure 1. EPR spectrum of cyclopentadienyl-PBN adduct (**2**) formed by photoexcitation of a benzene mixture of $CoCp_2$ and PBN for 5 h (blue). Simulation of EPR spectrum with *a*(N) = 14.4 G and *a*(H) = 2.2 G (black).

The low quantum yields of this reaction are low, consistent with high rates of recombination of **1** to regenerate $CoCp_2$ rather than release Cp·. Additionally, in the absence of a spin trap or other quenching reagent, ^{1}H NMR spectroscopy of irradiated $CoCp_2$ solutions does not show either hydrogen-atom abstraction from solvent or the formation of Cp· or its coupled product, bicyclopentadienyl. This is consistent with rapid recombination of **1** to regenerate $CoCp_2$; in this scenario, the addition of excess PBN or other reactive chemical quenchers is required for **1** to undergo further radical transformations. Similarly efficient recombination has been previously reported for the photolytic cleavage of titanocene derivatives,[13] and analogous mechanisms have been proposed for LMCT photoredox reactions mediated by Co(III) alkyl complexes.[20]

Figure 2 compares the yields of **2** measured by EPR spin quantification when toluene solutions of $CoCp_2$ and PBN (5 equiv) were irradiated at different wavelengths for 6 h while maintaining the same photon flux. Irradiation of toluene solutions of $CoCp_2$ and PBN with blue light (λ_{exc} = 365 and 405 nm) formed the most **2** (27% and 23% conversion, respectively), while longer wavelengths of irradiation (λ_{exc} = 440 and 530 nm) formed only trace amount of **2**. Interestingly, irradiation of the samples with UV light (λ_{exc} = 310 nm) also formed minimal **2**, as measured by EPR spectroscopy.

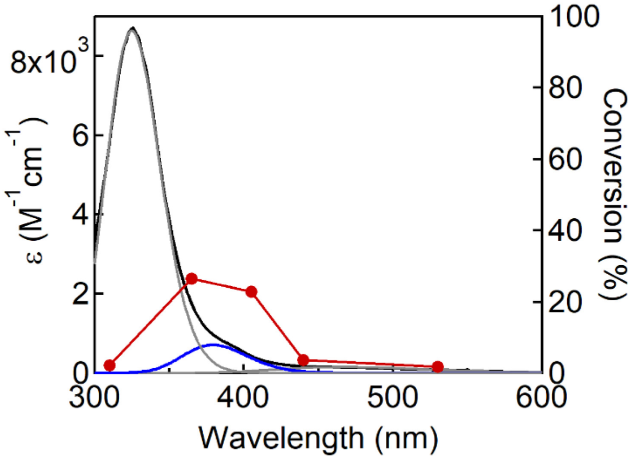


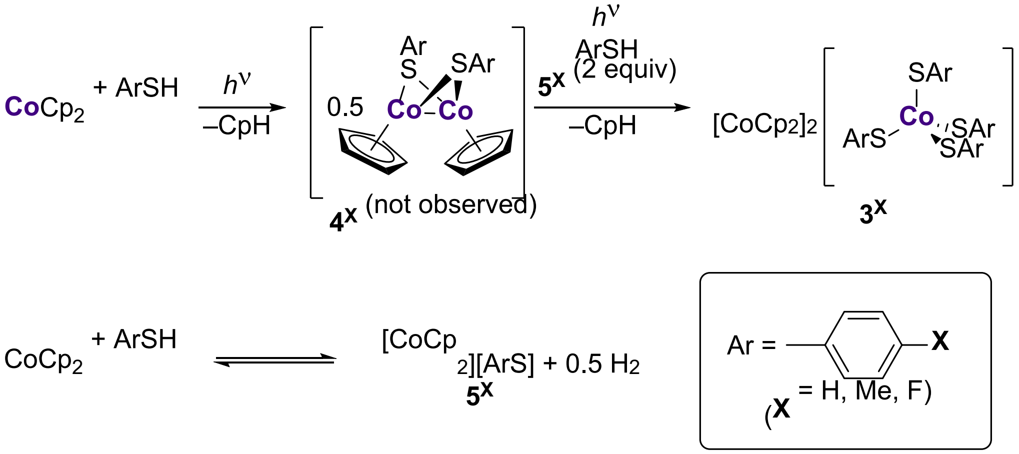
Figure 2. Comparison of the absorption spectrum of $CoCp_2$ (THF solution, black) and the wavelength-dependent yield of **2** (red) upon irradiation of a toluene mixture of $CoCp_2$ and PBN at the same photon flux (4.41 × 10^{16} s^{-1} cm^{-2}) for 6 h, determined by EPR spin

quantification. Bands corresponding to different LMCT transitions are shown in gray and blue ($^2E_{1g} \rightarrow {}^2E_{1u}$).

Figure 2 also compares the absorption spectrum of a THF solution of $CoCp_2$ to the wavelength-dependent yields of **2** described above. The absorption spectrum of cobaltocene has been previously assigned.[21-22] From the observed wavelength dependence, the onset of formation of **1** (and subsequent release of Cp·) is proposed to occur via the lowest energy LMCT transition ($e_{1u} \rightarrow e_{1g}$, $^2E_{1g} \rightarrow {}^2E_{1u}$), as this band has been previously assigned at 27,030 cm^{-1} (370 nm).[21-22] Our results also indicate that photoexcitation at the d-d transitions ($^2E_{1g} \rightarrow {}^2A_{2g}$, $^2E_{2g}$, $^2A_{1g}$, or $^2E_{1g}$, which occur from 15,150–21,190 cm^{-1} (470–660 nm) or at the higher energy LMCT bands (at 325 nm and 280 nm)[21] do not form **2**, despite the higher molar absorptivity coefficients of the latter transitions. While photoexcitation of d-d transitions should not be expected to release Cp·, the low yield measured for **2** formation at higher energies was unexpected. These higher energy UV photons may result in further reactions of radical species, possibly forming other EPR-silent byproducts. Additionally, PBN also absorbs UV photons (Fig. S4), which may decrease $CoCp_2$ photoexcitation and slow down product formation.

Photochemical thiophenol addition to cobaltocene. We attempted to chemically trap the resulting radical products using thiophenols as H-atom donors. Irradiation of a 1:1 mixture of $CoCp_2$ and $4\text{-}FC_6H_4SH$ in C_6D_6 at room temperature formed a dark green precipitate, $\mathbf{3^F}$ (Scheme 2). Similar green products $\mathbf{3^H}$ and $\mathbf{3^{Me}}$ were formed upon irradiation of mixtures of $CoCp_2$ and PhSH or $4\text{-}MeC_6H_4SH$, respectively. The ^1H NMR spectra of DMSO-d_6 or CD_3CN solutions of $\mathbf{3^X}$ (X = H, Me, F) show paramagnetically shifted and broadened resonances that are consistent with those of the previously reported $[Co(SAr)_4]^{2-}$ anion (Figs. S7, S8).[23] The absorption spectra of these complexes also match that of the previously reported salt $[Et_4N]_2[Co(SPh)_4]$ prepared from the addition of PhSH to $Co(NO_3)_2·6H_2O$ with excess base (Fig. S6).[24] When a 4:3 thiophenol:cobaltocene stoichiometry is used, the reaction is complete within 20 h by ^{1}H NMR spectroscopy and **3^{H}** is isolated in 83% yield. Figure 3 shows the single crystal X-ray diffraction structure of crystals grown by vapor diffusion of diethyl ether into a DMF solution of **3^{F}**, confirming its assignment as $[CoCp_2]_2[Co(SAr^F)_4]$, in which the dianionic tetra(4-fluorobenzenethiolato)cobaltate ion is charge-balanced by two cobaltocenium cations. In this structure, the Co^{II} center is distorted tetrahedral, with Co–SAr bond lengths of 2.281(8)–2.319(8) Å, similar to the previously published structures of related tetra(benzenethiolato)cobaltate anions that have been studied for their magnetic properties.[24-25]

Scheme 2. Formation of $[CoCp_2]_2[Co(SAr)_4]$ (3^{X})



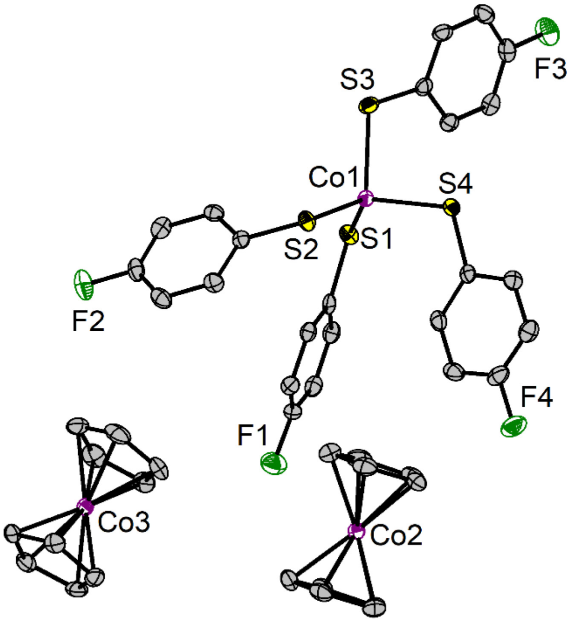
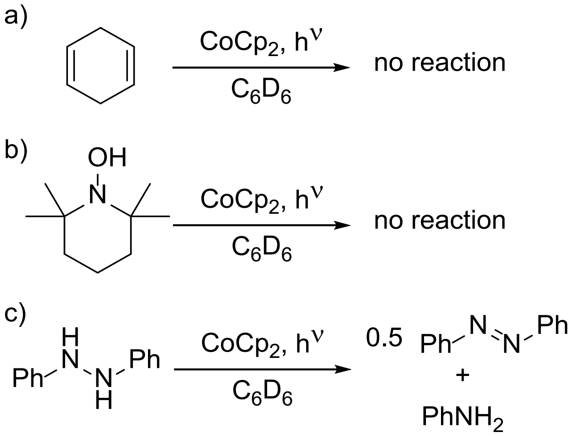


Figure 3. Solid-state structure of $\mathbf{3^F}$ as 50% thermal ellipsoids. Hydrogen atoms and a second molecule in the asymmetric unit are omitted for clarity.

In the above experiments, cyclopentadiene was observed in the ^{1}H NMR spectra (Fig. S5), and likely forms by H-atom transfer from ArSH to the Cp· radical formed from photoexcitation. However, the yield of cyclopentadiene is relatively low compared to $CoCp_2$ consumption, indicating competing Cp· reaction pathways other than H-atom abstraction. The expected byproduct of H-atom transfer would be the previously reported dimeric thiolate-bridged $[CpCoSAr]_2$ complex (Scheme 2, $\mathbf{4^X}$).[26-28] This species was not observed by ^{1}H NMR spectroscopy, perhaps indicating that the second photoinduced H-atom transfer step to form a second equivalent of cyclopentadiene and $[Co(SAr)_2]$ is fast. From there, addition of $[CoCp_2][SAr]$ (Scheme 2, $\mathbf{5^X}$, formed from the reduction of ArSH to release H_2) to $[Co(SAr)_2]$ would yield $\mathbf{3^X}$. While H_2 is not observed by ^{1}H NMR spectroscopy in these experiments due to the low concentrations used, we were able to prepare compound $\mathbf{3^H}$ by irradiation of a mixture of $CoCp_2$ and PhSSPh. In this latter reaction, PhSSPh could be reduced by $CoCp_2$ to form $[CoCp_2][SPh]$, and the reaction could proceed as described above with the release of the corresponding phenyl cyclopentadienyl thioether rather than cyclopentadiene. In short, these experiments demonstrate that the photoexcitation of $CoCp_2$ in the presence of chemical quenchers can facilitate both H-atom transfer to Cp· and trap the dissociated cobalt-containing fragment.

Reactions with other hydrogen atom donors. Next, the photoinduced reaction between $CoCp_2$ and other H-atom donors was studied to understand the low yield of cyclopentadiene formation during irradiation of $CoCp_2$ with thiophenols. We first tested the H-atom donor reagents 1,4-cyclohexadiene and 9,10-dihydroanthracene, as the bond dissociation free energies (BDFEs) of the X–H bonds in these compounds are lower than that of thiophenol (67.8 vs. 80.2 kcal/mol for 1,4-cyclohexadiene in the gas phase and thiophenol in C_6H_6, respectively).[29] However, irradiation of C_6D_6 solutions of $CoCp_2$ and 1,4-cyclohexadiene or 9,10-dihydroanthracene (λ_{exc} = 365 nm, 16 h) results in no conversion to cyclopentadiene or the expected aromatic products (benzene or anthracene, respectively, Scheme 3a), as measured by ^{1}H NMR spectroscopy (Figs. S9, S10). Irradiation of solutions of $CoCp_2$ with H-atom donors with weak O–H bonds (TEMPO-H and 2,4,6-tri-tert-butylphenol, BDFEs of 63.8 and 75.5 kcal/mol, respectively, in C_6H_6)[29] also resulted in no conversion to cyclopentadiene (Scheme 3b, Figs. S11, S12). These reactions demonstrate that the X–H BDFE of the H-atom donor does not dictate radical capture from **1**.

Scheme 3. Irradiation of $CoCp_2$ and (a) Cyclohexadiene or (b) TEMPO-H Does Not Form Cyclopentadiene from H-Atom Transfer; (c) Photoinduced Cobalt-Mediated Diphenylhdyrazine Disproportionation



We hypothesized that the higher reactivity between thiophenols and photoexcited $CoCp_2$ compared to the above H-atom donors was promoted by coordination of the Lewis basic sulfur of thiophenol to the photodissociated [$CpCo^I$] fragment, preventing radical recombination. In comparison to thiophenol, the H-atom donors discussed above might be expected to coordinate less strongly due to weaker donation or greater steric hindrance. To test this hypothesis, a C_6D_6 solution of $CoCp_2$ and 1,4-cyclohexadiene was irradiated in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) added as a chelating ligand for the cobalt-containing fragment (λ_{exc} = 365 nm, 16 h). Although no cyclopentadiene was observed by ^1H NMR spectroscopy, a new singlet resonance at 4.63 ppm is observed that is consistent with reported ^1H NMR spectrum of CpCo(dppe) (Fig. S13).[30] The ^{31}P NMR spectrum of the mixture showed the formation of several new resonances (δ 90, 28, –15, and –40 ppm). While these new phosphine-containing products have not yet been assigned or isolated, they demonstrate dppe is indeed participating in the reaction and likely interacting with the $CpCo^I$ fragment. Irradiation of a mixture of $CoCp_2$ and dppe without 1,4-cyclohexadiene does not form any new ^{31}P NMR signals, again indicating that all three components of the reaction are necessary.

1,2-Diphenylhydrazine was chosen as another H-atom donor that might be able to coordinate to cobalt. A C_6D_6 solution of $CoCp_2$ and excess 1,2-diphenylhydrazine was irradiated over 16 h at room temperature (λ_{exc} = 405 nm, 7.1 mW/cm^2). ^{1}H NMR spectroscopy of this mixture showed consumption of $CoCp_2$ accompanied by disproportionation of 1,2-diphenylhydrazine to yield a 1:2 mixture of azobenzene and aniline in 32% conversion (Scheme 3c, Fig. S15). Only minor conversion (ca. 5%) to azobenzene and aniline was observed for a similar reaction mixture that was heated in the dark (60° C for 16 h). Similarly, irradiation of 1,2-diphenylhydrazine in the absence of $CoCp_2$ yields only small amounts of azobenzene (ca. 11%), but no aniline. However, the addition of $CpCo(CO)_2$ to 1,2-diphenylhydrazine forms azobenzene and aniline both thermally and under photoexcitation (21% and 27% yield after 14 h, respectively). Irradiation of $Cp^*{}_2Co$ and 1,2-diphenylhydrazine also results in 1,2-diphenylhydrazine disproportionation (31%, Fig. S16. These results indicate that $CpCo^I$ moieties are capable of mediating diphenylhydrazine disproportionation, and support the proposal that irradiation of $CoCp_2$ releases Cp· and the reactive $CpCo^I$ fragment that then interacts with 1,2-diphenylhydrazine. The yield of 1,2-diphenylhydrazine disproportionation shows a similar wavelength dependence as that of spin trapping (Figs. S17, S18), and some minimal solvent dependence (Table S1).

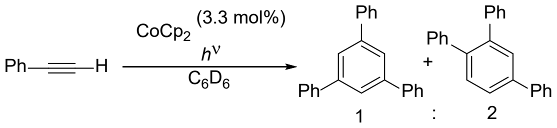
Although H-atoms are transferred within and from the 1,2-diphenylhydrazine and 5,10-dihydrophenazine substrates, neither cyclopentadiene nor its dimerized Diels-Alder product, dicyclopentadiene, are observed in the ^{1}H NMR spectra of these reactions. However, an insoluble precipitate formed during the course of the reaction. While Co^0 metal might be expected as a byproduct, powder X-ray diffraction (PXRD) of the material shows only broad signals, indicating a material of low crystallinity (Fig. S20). Elemental analysis of the precipitate by inductively coupled plasma optical emission spectroscopy (ICP-OES) indicated the presence of cobalt. The FTIR spectrum of this precipitate also displays C–C stretching bands (1350–1600 cm^{-1}), indicating an organic component arising from cyclopentadienyl- or diphenylhydrazine-derived products

(KBr pellet, Fig. S21). This material may be consistent with previously observed unidentified polymeric products formed upon photodecomposition of $CoCp_2$ at higher energies.[17] We cannot rule out that this cobalt-containing product is responsible for mediating diphenylhydrazine disproportionation, as cobalt phosphide nanocrystals have been previously been demonstrated to reversibly store hydrogen.[31]

Catalytic [2+2+2] Trimerization. $CpCo^I$ fragments are known to be catalytically active for [2+2+2] cyclotrimerization reactions and other similar transformations of π-systems, typically using $CpCoL_2$ complexes as precatalysts (L = CO, phosphines, alkenes).[32-34] In the precatalyst activation steps, dissociation of the ancillary L-type ligand can be challenging, often requiring photoinitiation, and many efforts have targeted the formation of precatalysts with ligands that more readily dissociate. From our above results, we hypothesized that the photoinduced LMCT and dissociation of Cp· could enable the use of $CoCp_2$ and an H-atom donor as a precatalyst mixture that could then be activated with light for catalytic cyclotrimerization, eliminating the need for thermal L-type ligand dissociation/substitution. There have been similar recent reports of photoinitiated or photocontrolled transition-metal-catalyzed cyclotrimerization reactions.[35-36]

A C_6D_6 solution of phenylacetylene with a catalytic amount of $CoCp_2$ (3.3 mol%) was irradiated for 24 h (λ_{exc} = 365 nm, 78 mW/cm^2). Integration of the ^{1}H NMR spectrum of this resulting mixture showed 43% consumption of PhCCH, as well as the expected regioisomers of [2+2+2] cyclotrimerization, 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene, in a 1:2 ratio (Scheme 4). In comparison, the same cyclotrimerization of PhCCH catalyzed by $CpCo(CO)_2$ (3.3 mol%) under photoinitated thermal conditions (90 °C, 24 h) was reported to achieve 80% PhCCH conversion.[37] Other related cyclopentadienylcobalt(I) precatalysts similarly require photoactivation, high temperatures, or microwave conditions for cyclotrimerizations.[34]

Scheme 4. Photoinitiated Phenylacetylene Trimerization



Typical cyclotrimerization reactions using $CpCoL_2$ precatalysts proceed first by dissociation of the L ligand (CO, phosphines, etc.) followed by coordination of the alkyne substrate. The resulting dialkyne complex then undergoes oxidative cyclization to form the metallocyclopentadiene intermediate that further reacts.[38-39] We expected that photodissociation of Cp· should release a $[CpCo^I]$ fragment that can then be trapped by two equivalents of PhCCH to form the dialkyne complex $CpCo(\eta^2\text{-}PhCCH)_2$. However, irradiation of $CoCp_2$ solutions in the presence of other L-type ligands such as PPh_3 or 1,5-cyclooctadiene (COD) did not form the expected $CpCoL_2$ complexes. This unexpected result may be due to further photodecomposition of the subsequent $CpCoL_2$ complexes, which also absorb strongly. In support of this hypothesis, irradiation of a THF solution of $CpCo(CO)_2$ (λ_{exc} = 365 nm, 63 mW/cm^2) resulted in decomposition of the complex at room temperature, as measured by bleaching of the absorption features ($t_{1/2}$ ~ 4 h, Fig. S22).

We considered the alternative explanation that the catalytic cyclotrimerization is promoted by reduced Co(0) nanoparticles or other heterogeneous materials formed upon photodecomposition of $CoCp_2$. To test this possibility, a benzene solution of $CoCp_2$ was first irradiated in the absence of alkyne to generate the hypothetical Co^0 nanoparticles (λ_{exc} = 365 nm, 78 mW/cm^2, 12 h). Subsequent addition of phenylacetylene to this mixture followed by heating for 24 h at 60 °C showed only 4% consumption of phenylacetylene by ^{1}H NMR spectroscopy. While we cannot rule out the formation of another photogenerated molecular Co complex as the catalytically active species, these results indicate that photoexcitation of $CoCp_2$ in the presence of phenylacetylene promotes this reaction. Lastly, photoexcitation of a mixture of $CoCp_2$ with the bulkier substrate diphenylacetylene formed no cyclotrimerized product, again consistent with a more sterically-hindered [CpCo^I] catalytic species.

CONCLUSIONS

We have shown that irradiation of cobaltocene and related derivatives at select wavelengths and under certain conditions can result in release of cyclopentadienyl radicals and in the formation of new cobalt complexes. The latter species are active for further transformations, including catalytic cyclotrimerization. Ultimately, while the example transformations discussed above may not be synthetically useful compared to existing thermal procedures, they highlight the photoinstability of $CoCp_2$ and demonstrate that reactive species can be formed under excitation that may participate in a variety of transformations, particularly when ligand donors are present that can coordinate to cobalt. In the context of photocatalytic or photovoltaic applications, cobaltocene cannot, unlike ferrocenes, be considered completely photostable. This observation necessitates caution in their use as redox mediators in such systems, or in other fundamental photo/electrochemical studies, as discussed above. In situations at very negative potentials where ferrocenes cannot be used in place of cobaltocene, it is clear from our studies that proper wavelength selection will be critical to avoid formation of unwanted products or reactive species.

EXPERIMENTAL SECTION

General Considerations. Unless indicated otherwise, reactions were carried out in oven-dried glassware in a MBraun glovebox under a nitrogen atmosphere. Anhydrous diethyl ether, tetrahydrofuran (THF), and acetonitrile were purified using a J.C. Meyer solvent system. Anhydrous *N*,*N*-dimethylformamide (DMF) was stored over 3 Å molecular sieves. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories and purified as follows: DMSO-d_6 was dried over molecular sieves and distilled under vacuum twice. C_6D_6 was dried over sodium/benzophenone ketyl radical and vacuum transferred before use. CD_3CN was dried over CaH_2 and vacuum transferred before use. ^1H NMR spectra were recorded on a Bruker 400 MHz instrument, a Bruker 500 MHz instrument, or a Varian 600 MHz instrument, with shifts reported relative to the residual solvent peak (2.50 ppm for DMSO-d_6, 7.16 ppm for C_6D_6, 1.96 ppm for CD_3CN). EPR spectra were recorded at room temperature as solution samples in 4 mm quartz tubes using a Bruker EMX instrument with a frequency of 9.36 GHz. EPR spectra were simulated using EasySpin[19] (5.2.35) in Matlab (R2021b). Electronic absorption spectra were measured on solution samples in 1-cm sealable quartz cuvettes using an Agilent Cary 60 instrument. PXRD data were collected on samples drop-cast on a glass slide, using a Bruker AXS D8 Advance diffractometer. Single crystal X-ray diffraction data were collected using a Bruker APEX-II CCD diffractometer. FTIR spectra were collected on samples in KBr pellet using a Thermo Nicolet 380 spectromter. Inductively coupled plasma optical emission spectroscopy (ICP-OES) data were collected on a Perkin Elmer Avio 200 in axial view. Trace metal grade concentrated HNO_3 (Alfa Aesar, 0.5 mL) was added to a plastic vial containing the precipitate, and the mixture was allowed to digest for 16 h. The mixture was then passed through a 0.22 µm glass fiber syringe filter and diluted to 10 mL with HNO_3 (5 %) prior to analysis.

Photoexcitation Experiments. Single color surface mount StarBoard LEDs were purchased from DigiKey (405 and 530 nm) and Mouser Electronics (310, 365, and 445 nm). Each LED was attached to an aluminum heat sink (Newark, SA-LED-113E) using Thermalcote Thermal Grease (Newark). The optical power was measured with a Standa power meter.

The LED assembly was placed at the bottom of a ring stand and was connected to the power supply. The sealed sample was placed 2 inches above the LED. A flow of air was passed to cool the assembly. The position of the LED and sample was kept constant between experiments.

Spin Trapping. In the glovebox, an EPR tube was charged with a solution of $CoCp_2$ (0.03 μmol) and *N*-tert-butyl-α-phenylnitrone (PBN, 0.15 μmol, 5 equiv) in benzene (0.3 mL). The sample was irradiated for 5 h (λ_{exc} = 405 nm, 7.1 mW/cm^2) before EPR measurement. Spin quantification experiments were calculated using a calibration curve using toluene solutions of TEMPO radical (0–2 μM).

[$CoCp_2$]$_2$[Co(SAr)$_4$]. As a representative reaction, in the glovebox, an NMR tube was charged with a solution of $CoCp_2$ (0.006 g, 0.030 mmol, 3 equiv) and 4-methylbenzenethiol (0.005 g, 0.040 mmol, 4 equiv) in CD_3CN (0.5 mL). The sample was irradiated for 20 h at room temperature (λ_{exc} = 365 nm, 78 mW/cm^2) until complete conversion of $CoCp_2$ was observed by ^{1}H NMR spectroscopy. Diethyl ether was layered over the resulting emerald green solution, forming **2^{Me}** as X-ray quality dark green crystals. ^{1}H NMR (CD_3CN, 400 MHz): δ 26.9 (12 H, Me), 17.3 (8 H), 5.53 (20 H, Cp), –33.4 (8 H) ppm. These spectral data are consistent with those of a previously reported complex with tetraethylammonium counterions.[23]

Disproportionation of 1,2-Diphenylhydrazine. In the glovebox, an NMR tube was charged with a solution of $CoCp_2$ (0.016 mmol) and 1,2-diphenylhydrazine (0.031 g, 0.160 mmol, 10 equiv) in C_6D_6 (0.4 mL). The sample was irradiated for 16 h at the indicated excitation wavelength before the ^{1}H NMR measurement.

Catalytic [2+2+2] Cyclotrimerization of Phenylacetylene. In the glovebox, an NMR tube was charged with a solution of $CoCp_2$ (0.016 mmol) and phenylacetylene (51 μL, 0.480 mmol, 30 equiv) in C_6D_6 (0.4 mL). The sample was irradiated for 16 h (λ_{exc} = 365 nm, 78 mW/cm^2) before the ^{1}H NMR spectrum was measured. Conversion was quantified by integration of the phenylacetylene protons against the resonances corresponding to the products (1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene).

ASSOCIATED CONTENT

Supporting Information. Additional EPR, NMR, electronic absorption spectra, and crystallographic details (PDF).

Accession Codes

CCDC 2215316 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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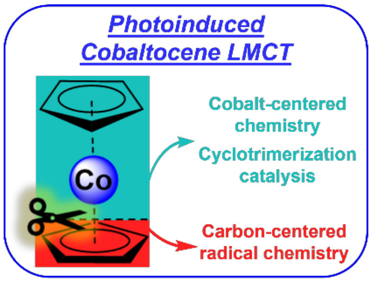

Irradiation of cobaltocene forms cyclopentadienyl radical via ligand-to-metal-charge transfer, enabling the use of cyclopentadienylcobalt(I) fragments for catalysis or further derivatization.