

# Time-Resolved UV-IR Experiments that Suggest Photoactivated Fe-Cu Dinuclear Catalyst

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## ABSTRACT

Heterodinuclear complexes with a direct metal-metal bond offer the possibility of unique mechanisms and intermediates. The  $\text{Cp}(\text{CO})_2\text{Fe-Cu}(\text{IPr})$  ( $\text{IPr} = \text{N,N-bis(2,6-diisopropylphenyl)imidazol-2-ylidene}$ ) heterodinuclear complex **1** is known to photochemically catalyze arene borylation. To examine possible initial steps of photo-initiated catalysis, we synthesized a triethylsilyl-substituted Fe-Cu catalyst that provided cyclohexane solubility to conduct time-resolved UV-IR studies. Time-resolved vibrational spectroscopic measurements suggest that photolysis of **1** stimulates CO dissociation without Fe-Cu metal-metal bond cleavage. This suggests that arene borylation catalysis may begin with a photochemical step rather than a relatively endothermic cleavage of the Fe-Cu bond. A new possible catalytic cycle is proposed.

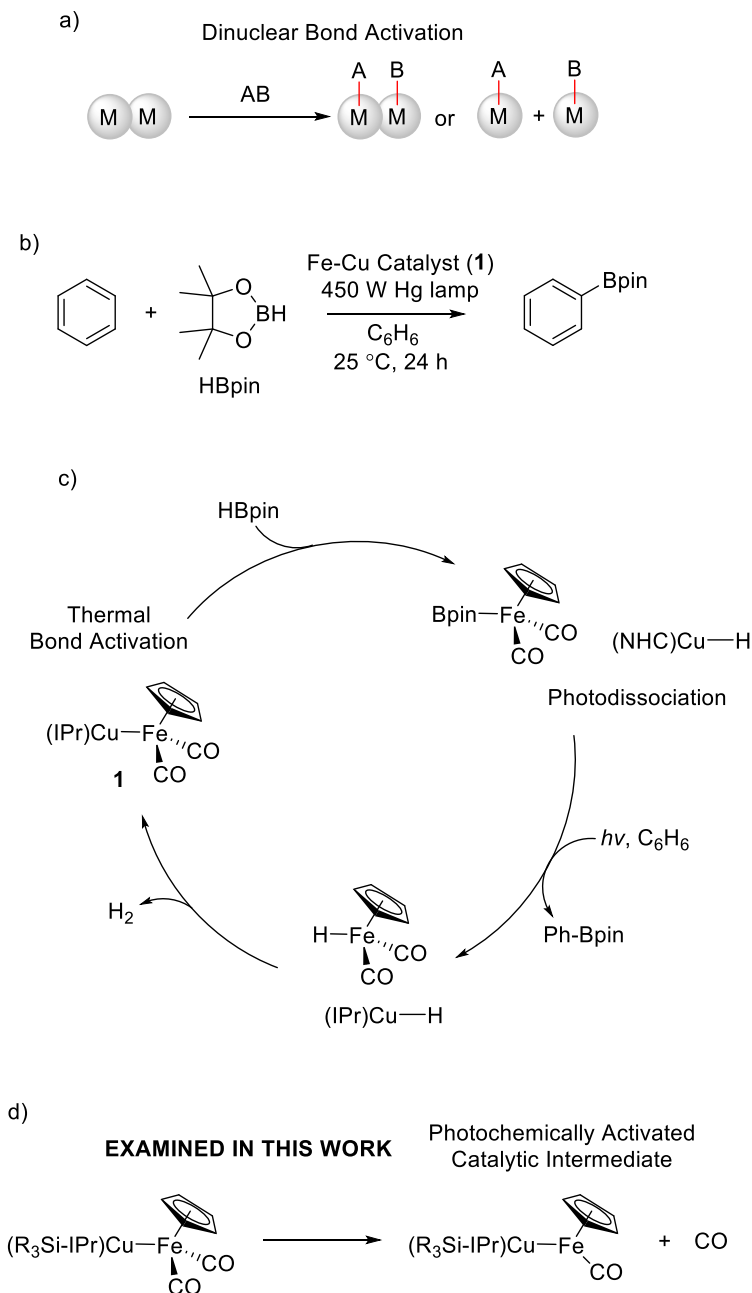
## INTRODUCTION

Compared to catalysts with a single metal and ligand framework, transition-metal heterodinuclear catalysts with a direct metal-metal bond offer the potential of unique mechanisms and intermediates, oxidation states, reactivity, and selectivity, especially for bond activation reactions (Scheme 1a).<sup>1</sup> This divergent reactivity results from the ability of substrates to be activated across two metals and for organometallic mechanisms to occur over both metals (e.g. dinuclear oxidative addition). While heterodinuclear-mediated and catalyzed reactions were reported for classic transformations, such as alkene and ketone hydrogenation,<sup>2</sup>  $\alpha$ -olefin hydroformylation,<sup>3</sup> ethylene polymerization,<sup>4</sup> and olefin metathesis,<sup>5</sup> recently there has been a large effort to exploit dinuclear catalyst for very challenging transformations.<sup>6,7,8,9,10</sup> However, a major limitation to the further design and use of heterodinuclear catalysts is the identification of catalytic mechanisms. In many heterodinuclear-catalyzed reactions the mechanism responsible for unique reactivity and/or selectivity is unknown.

Mankad recently reported the photochemical catalytic arene borylation using the  $\text{Cp}(\text{CO})_2\text{Fe-Cu}(\text{IPr})$  heterodinuclear complex **1** (Scheme 1b; (IPr = N,N-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)).<sup>11</sup> In this reaction with yields up to 70%, the C-H bond of arenes, and the B-H bond of HBpin are activated and coupled, which for benzene results in phenylboronic acid pinacol ester (PhBpin). Based on earlier work from Hartwig,<sup>12</sup> the original mechanistic proposal involved thermal HBpin bond activation to generate the pair of mononuclear species (IPr)Cu-H and  $\text{Cp}(\text{CO})_2\text{Fe-BPin}$  (Scheme 1c). Then, photo-promoted CO ejection leads to the mononuclear, coordinately unsaturated  $\text{Cp}(\text{CO})\text{Fe-BPin}$  intermediate that reacts with benzene to produce PhBpin. A ligand crossover experiment was performed as evidence of thermal/dark reactions for ligand exchange with complex **1**. For example, mixing (IPr)CuFeCp\*(CO)<sub>2</sub> with

(IMes)CuFeCp(CO)<sub>2</sub> (IMes = N,N'-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) results in (IPr)CuFeCp(CO)<sub>2</sub> and (IMes)CuFeCp\*(CO)<sub>2</sub>. However, this thermal crossover reaction required 48 hours to reach equilibrium and based on density functional theory (DFT) calculations Keith and Mankad proposed a direct bimolecular reaction that is likely unconnected to borylation catalysis.<sup>13</sup>

The initial steps of this catalytic process are intriguing for several reasons. The thermal B-H bond activation across the Fe-Cu bond leading to (IPr)Cu-H and Cp(CO)<sub>2</sub>Fe-BPin mononuclear species requires a  $\Delta H$  value of >25 kcal/mol. This suggests that there would be an extremely low concentration of the Cp(CO)<sub>2</sub>Fe-BPin intermediate available for photoactivation and the quantum yield of these types of metal carbonyl complexes are relatively low. Alternatively, it could be possible that catalyst **1** undergoes CO photodissociation to initiate catalysis. However, this catalyst has a single Fe-Cu metal-metal bond that could fragment upon irradiation rather than CO dissociation. CO photodissociation from **1** would give the monocarbonyl intermediate (IPr)CuFeCp(CO), which could then undergo dinuclear B-H activation and subsequent arene borylation.



**Scheme 1.** a) Schematic view of bond activation reactions across a metal-metal bond of a heterodinuclear complex. b) Mankad's Fe-Cu photochemical heterodinuclear-catalyzed benzene borylation reaction. c) Previously proposed catalytic cycle involving dinuclear thermal (dark) B-H bond activation, mononuclear CO photodissociation, and reformation of the Fe-Cu catalyst **1**. d) Alternative first catalytic step involving photodissociation of CO from **1** to generate a coordinatively unsaturated heterodinuclear intermediate. IPr = IPr = N,N-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).

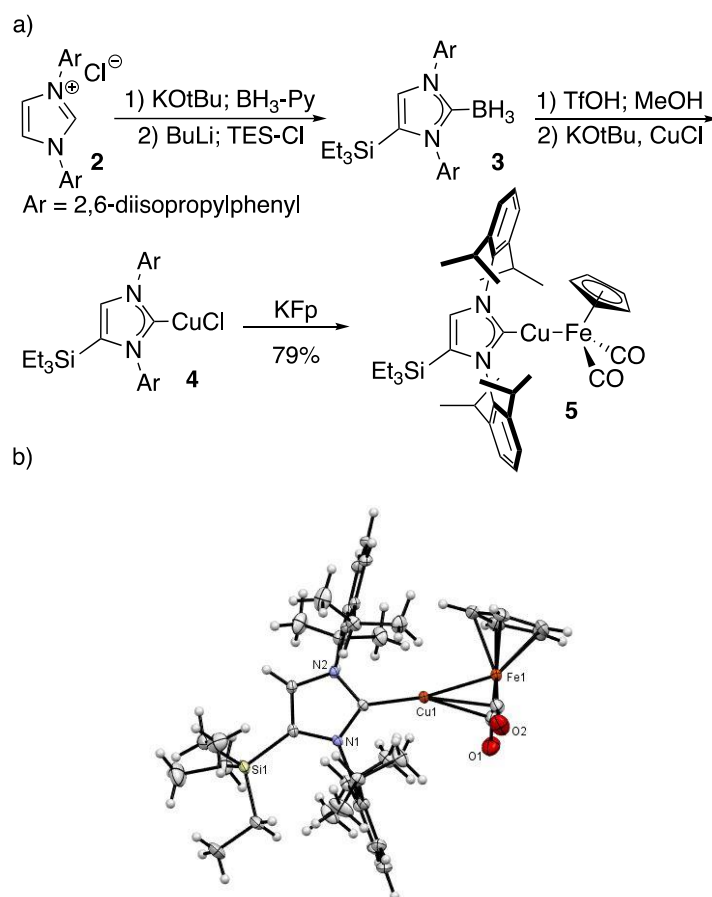
One approach to examine the feasibility of heterodinuclear CO photodissociation to initiate catalysis is to use time-resolved vibrational spectroscopy to directly detect a the monocarbonyl (IPr)CuFeCp(CO) intermediate.<sup>14</sup> In this work we report the synthesis and X-ray characterization of a triethylsilyl-substituted Fe-Cu catalyst that provided cyclohexane solubility to conduct time-resolved UV/IR studies. We also present time-resolved vibrational spectroscopic measurements that show that photolysis of the catalysis with UV light suggests that CO photodissociation from the **1** is plausible without metal-metal bond cleavage (Scheme 1d). Overall, this provides the ability to propose a catalytic cycle for photocatalytic arene borylation.

## RESULTS AND DISCUSSION

To identify the initial photo-generated intermediates, microsecond step-scan FTIR measurements of the CO vibrational spectrum was performed using catalyst **1**. However, initial UV/IR experiments in benzene solvent showed overlap of the Fe-CO modes with vibrational modes in the solvent. Alkane solvents have no absorbances in the metal-CO region of the spectrum, but the dinuclear catalyst **1** is not soluble in the alkane at high enough concentrations to allow measurement of the vibrational spectrum. To address this limitation, we synthesized a silyl-substituted version of the Fe-Cu complex (**5**, Scheme 2) that provided significant solubility in cyclohexane, and the silyl-appended catalyst is competent for borylation.<sup>11</sup>

The synthesis of complex **5** began with protection of commercially available imidazolium ligand **2** with borane at the 2-position. Next, deprotonation of the imidazole with *n*-butyl lithium followed by quenching with chlorotriethylsilane provided silylated imidazole **3**. The borane group was then removed by treatment with triflic acid and methanol and the corresponding imidazolium

salt was exposed to sodium tert-butoxide and CuCl to provide the desired copper(I) carbene complex **4**. To finish the synthesis, complex **4** was treated with anionic potassium cyclopentadienyldicarbonylferrate (KFp) to provide the final heterobimetallic complex **5** in 79% yield. X-ray quality single crystals of complex **2** were grown via vapor deposition with hexanes and toluene and the X-ray crystal structure is shown in Scheme 2b. Importantly, while the addition of the triethylsilane imparted solubility in cyclohexane, it did not significantly impact the bonding of the Fe-Cu complex. For example, the Fe–Cu distance in **5** is 2.349 Å, which is nearly identical to **1** (2.346 Å).<sup>15</sup>



**Scheme 2.** a) Synthetic scheme for the triethylsilyl-substituted Fe-Cu complex **5**. b) X-ray structure of **5**.

With a cyclohexane soluble version of the Fe-Cu catalyst synthesized, we proceeded with UV-IR and time-resolved FTIR experiments. Alkane solutions are typically viewed as weakly coordinating solvents, but can induce caging effects.<sup>16</sup> Spectroscopic measurements were performed using a modified Bruker IFS-66 FTIR spectrometer in step scan mode. The detector was a small area MCT with a rise time of 10 ns, and an optical filter which limited the signal to the region from 1400-2150  $\text{cm}^{-1}$ . The internal 14-bit digitizer was used, yielding spectra every 5 microseconds, with a resolution of 4  $\text{cm}^{-1}$ . UV light for excitation was from a Continuum YAG, with frequency tripling optics which yielded 9 ns pulses at 355 nm, and pulse energies were kept less than 5 mJ to minimize sample degradation, and thermal effects. This wavelength was selected because complex **5** has a broad absorption band in the UV from 300-400 nm (see supporting information), and so the 355 nm laser light will excite the complex to the same excited electronic state as the mercury lamp used by Mankad. Samples were 3 mM in concentration and were purged with nitrogen gas to keep them air and water free.

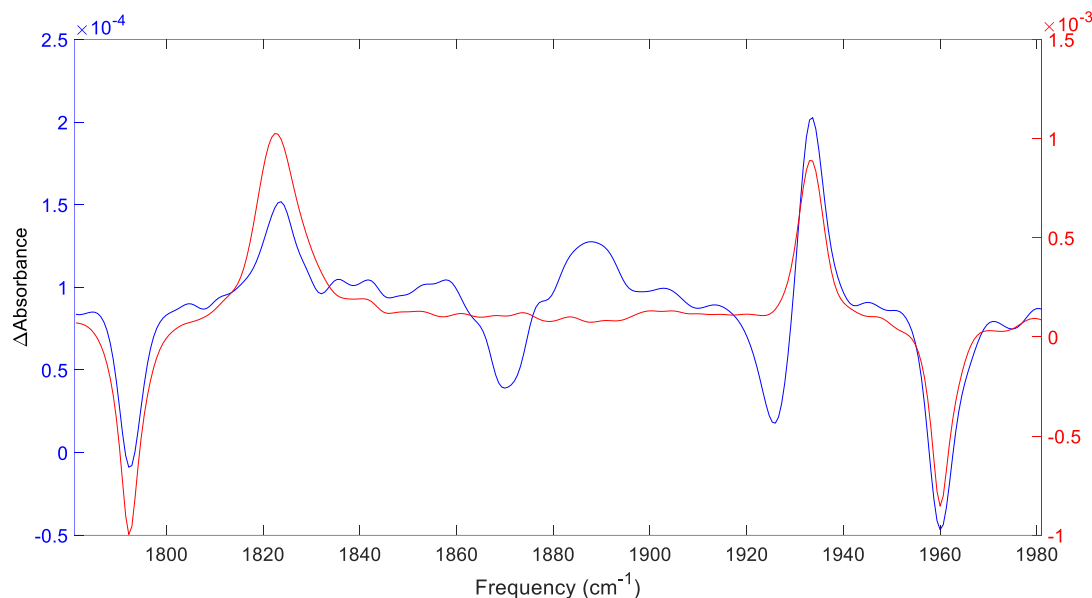
The blue plot in Figure 1 shows an initial FTIR spectrum after UV excitation for a solution containing complex **5**. The two Fe-CO stretches for the initial dicarbonyl dinuclear complex at 1869 and 1925  $\text{cm}^{-1}$ , show a decrease in absorbance after excitation. In addition to the disappearance of these peaks we found a new positive peak indicative of a monocarbonyl Fe-CO stretch that occurs at 1888  $\text{cm}^{-1}$ . Importantly, the disappearance of the two peaks and formation of a new peak indeed suggests CO photodissociation from **5** to generate a coordinatively unsaturated  $(\text{Et}_3\text{Si-IPr})\text{CuFeCp}(\text{CO})$  intermediate, rather than breaking of the Fe-Cu bond, which would have shown two new CO absorbances. Consistent with these measurements, M06-L<sup>17</sup>/6-31G\*\*[LANL2DZ] (chosen because of the first-row transition metals) DFT calculations in cyclohexane solvent gave antisymmetric and symmetric CO stretches for **5** at 1857 and 1907  $\text{cm}^{-1}$ .



<sup>1</sup> (scaled using a 0.952 factor).<sup>18</sup> The (Et<sub>3</sub>Si-IPr)CuFeCp(CO) structure gave a stretch at 1818 cm<sup>-1</sup>. In all structures the CO stretching values are slightly red shifted.

Unfortunately, complex **5** showed a very low quantum yield for CO photodissociation that could be due internal conversion to the electronic ground state, and non-radiative cooling. This somewhat complicated the IR spectrum because trace amounts of a highly photoactive Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> (**6**) led to significant absorbances in the IR spectra at 1792, 1822, 1933, and 1960 cm<sup>-1</sup>. To confirm these peaks are due to **6**, the overlaid red plot in Figure 1 shows an IR spectrum of a solution containing only **6** after UV excitation. The overlap between the red and the blue spectra is very close and shows that none of the peaks between 1865 and 1925 cm<sup>-1</sup> arise from **6**. DFT calculations of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> gave stretches at 1803 and 1940 cm<sup>-1</sup>, which is consistent with red and blue shift of absorbances away from the absorbances for complex **5**.

Importantly, the presence of **6** can be detected prior to UV light photolysis, which indicates that while the NMR is relatively absent of unwanted side products a minor amount of **6** could not be removed. Indeed, it is well known that metal-metal bond fragmentation is well known to be competitive with CO photodissociation.<sup>14</sup> For example, for (CO)<sub>5</sub>M-M(CO)<sub>5</sub> type species that there can be competition between metal-metal bond homolysis, dissociation of CO, and nondissociative relaxation,<sup>19</sup> and these routes are generally heavily influenced by excitation wavelength.<sup>20</sup> While we cannot completely rule out that a minor amount of Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> is formed under UV light exposure due to Fe-Cu metal fragmentation,<sup>21</sup> this is less likely since this compound is present prior to photolysis. Additionally, we do not see new CpFe(CO)<sub>2</sub> absorbances in time-resolved studies (see below).

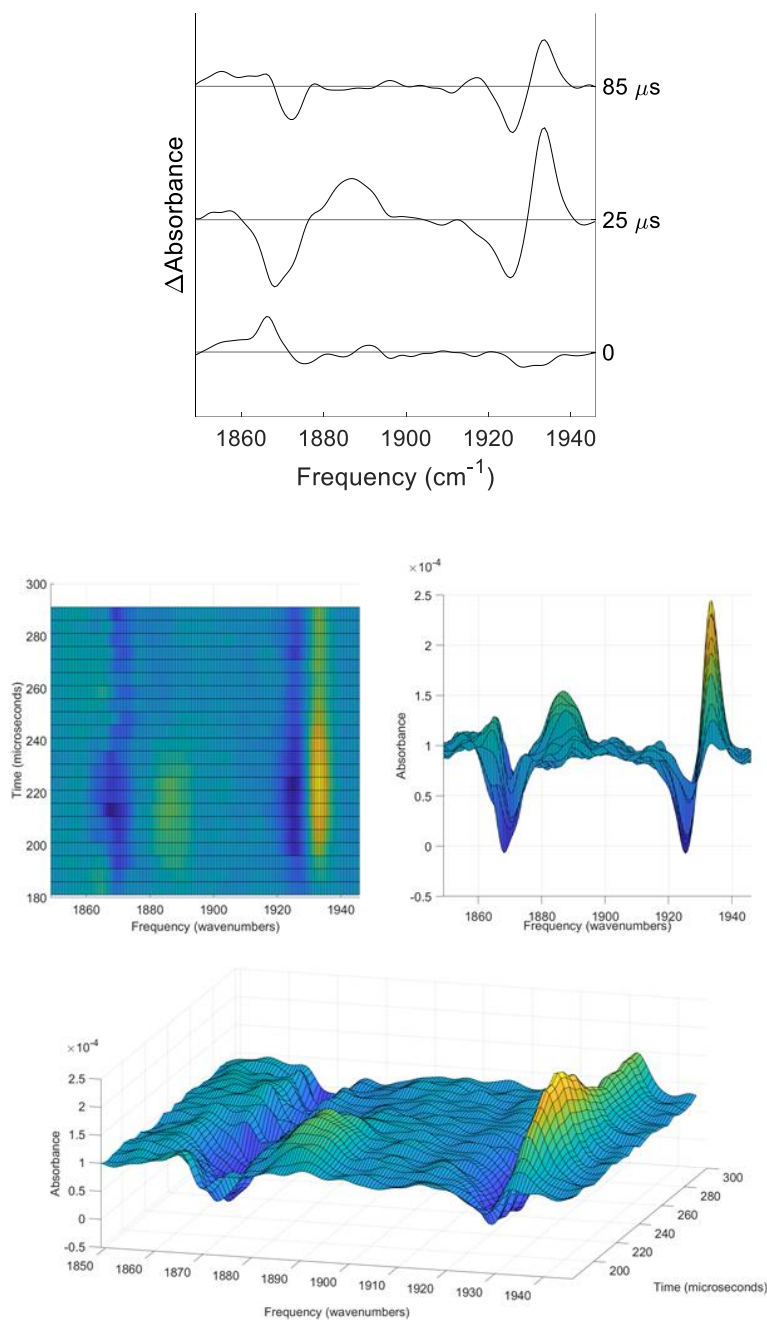


**Figure 1.** Plot of IR frequency versus absorbance. Blue: Change in IR absorbance of complex **5** after UV pulses at 355 nm. Red: Change in IR absorbance of  $\text{Cp}_2\text{Fe}_2(\text{CO})_4$  after UV pulses at 355 nm.

Our assignment of a dicarbonyl to monocarbonyl change upon exposure to UV light is consistent with many previous reports for mononuclear or homodinuclear complexes. For example, as a comparison to our measured values,  $(\text{acac})\text{Rh}(\text{CO})_2$  in cyclohexane showed dicarbonyl stretches at 2082 and 2013  $\text{cm}^{-1}$  and then the monocarbonyl showed a single stretch at 1996  $\text{cm}^{-1}$ .<sup>22</sup> For this  $(\text{acac})\text{Rh}(\text{CO})_2$  complex, the transient bleaches at the CO stretch frequencies were recovered at about 40 ps time. Also related, Lees showed that  $\text{CpRh}(\text{CO})_2$  in decalin with 313 and 458 nm light that the monocarbonyl can be trapped with triphenylphosphine.<sup>23</sup> For this complex the bleaching of dicarbonyl CO bands occurred at 2046 and 1982  $\text{cm}^{-1}$  with concurrent new monocarbonyl peak at 1954  $\text{cm}^{-1}$  for the phosphine bound structure. Harris also examined several dicarbonyl Cp-metal complexes. For example, triplet  $\text{CpCo}(\text{CO})_2$  in a heptane shows a monocarbonyl at 1990  $\text{cm}^{-1}$  and remains for about 660 ps.<sup>24,25</sup> While a tricarbonyl, but related to borylation reactions, Hartwig, Webster, and Harris reported nanosecond and microsecond IR for

$\text{Cp}^*\text{W}(\text{CO})_3(\text{Bpin})$ . In pentane, UV-IR analysis showed bleaches at 1899, 1914, and  $2000\text{ cm}^{-1}$ .<sup>26</sup> These peaks changed on the 30-200 ps time scale. In addition to these bleaches there was also peaks from W-BPin fragmentation with very fast recombination and the growth of a  $\text{Cp}^*\text{W}(\text{CO})_3(\text{pentane})$  complex, which can be seen on the nanosecond and microsecond time scales.

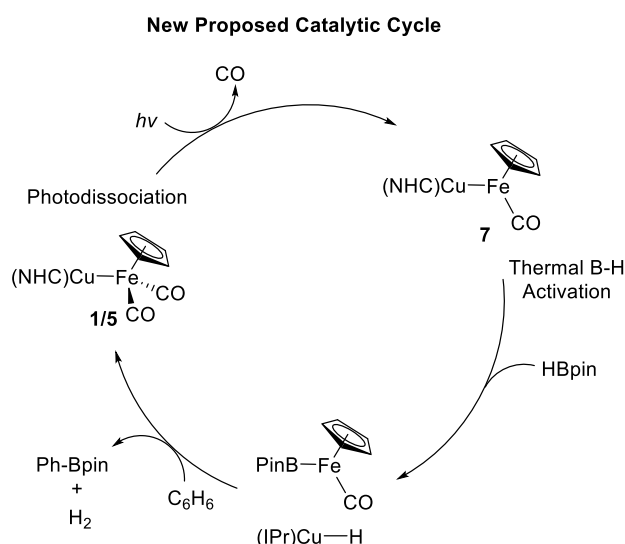
We next examined time-resolved changes in the IR spectrum of **5**. Figure 2 shows snapshots of the evolution of the absorbance peaks over 85  $\mu\text{s}$ . At 25  $\mu\text{s}$  after UV excitation the two negative peaks at 1868 and  $1925\text{ cm}^{-1}$  have fully formed. However, the two negative peaks are not long lasting. These peaks slowly decrease over time, likely due to CO recombination. At 85  $\mu\text{s}$  while these two negative peaks are still clearly visible, they are substantially decreasing. The positive peak at  $1885\text{ cm}^{-1}$  is completely gone by 85  $\mu\text{s}$ . This indicates that when **5** is not in the presence of the reaction partners, such as HBPIn and benzene, the activated catalyst likely only remains in the active form for a short time. However, under catalytic conditions ( $\text{Et}_3\text{Si-IPrCuFeCp}(\text{CO})$ ) likely persists for substantially longer time through coordination with reaction substrates.



**Figure 2.** Top: Change in absorbance spectrum of **5** before UV laser excitation, 25  $\mu\text{s}$  after excitation, and 85  $\mu\text{s}$  after excitation. Bottom: Several multidimensional plots of change in absorbance after laser exposure.

With the static and time-resolved IR information, it is now possible to propose an alternative catalytic cycle. Scheme 3 shows that UV-induced CO dissociation results in conversion

of heterodinuclear **5** (or **1**) to the corresponding dinuclear monocarbonyl intermediate **7**. After **7** is formed, while not directly tied to the current UV-IR studies, it is likely that this complex **7** is thermally reactive towards HBpin and can undergo B-H addition across the Fe-Cu metal-metal bond to generate (NHC)Cu-H and Cp(CO)Fe-BPin. The remainder of the catalytic cycle is similar to Mankad and Keith's proposal where the Fe-BPin complex can react with benzene to generate the Ph-Bpin and reformation of the dinuclear complex generates H<sub>2</sub>.



**Scheme 3.** Revised catalytic cycle based on UV-IR examination of heterodinuclear complex **5**.

## CONCLUSIONS

In this work we examined the possibility of photocatalysis being initialized through UV-induced CO photodissociation from an Fe-Cu dinuclear catalyst. To accomplish this, we synthesized a new silylated, alkane-soluble Fe-Cu complex. Static and time-resolved IR after UV laser excitation showed that the Fe-Cu metal-metal bond remains intact and that CO dissociation occurs. This suggests that catalysis begins with a CO photodissociation rather than thermal B-H bond activation as previously proposed. While the lifetime of intermediate **7** is likely on the  $\mu$ s

time scale or less, this is still long enough to undergo subsequent thermal reactions. However, from this work it was clear that this dinuclear complex has a very low quantum yield of photodissociation of CO. Therefore, further in-depth studies will be required to directly detect dinuclear and mononuclear intermediates for reaction between the photoactivated (Et<sub>3</sub>Si-IPr)CuFeCp(CO) intermediate and HBPIn and benzene. This work does not provide direct comparison of possible rates for reaction between the dinuclear photogenerated monocarbonyl with substrates versus thermal generated mononuclear complexes and photoactivation.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details and procedures. The Supporting Information is available free of charge on the ACS Publications website.

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### Author Contributions

‡These authors contributed equally. K.J.C. assisted in synthesis, performed UV/IR studies, and computed vibrational frequencies. J.T.D. performed UV/IR studies. D-H.K. initiated synthesis and UV/IR studies. E.E.M. and M.R.T. completed synthesis. D.J.M. direct synthesis work, interpreted data, and edited the manuscript. M.C.A. directed UV/IR studies, interpreted data, and edited the

manuscript. D.H.E conceived of the project, directed research, interpreted data, and wrote and edited the manuscript.

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