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# Transient Absorption Spectroscopy Offers Mechanistic Insights for an Iridium/Nickel-Catalyzed C–O Coupling

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**ABSTRACT:** We report mechanistic insights into an iridium/nickel photocatalytic C–O cross-coupling reaction from timeresolved spectroscopic studies. Using transient absorption spectroscopy, energy transfer from an iridium photocatalyst to a catalytically relevant Ni(II)(aryl) acetate acceptor was observed. Concentration-dependent lifetime measurements suggest the mechanism of the subsequent reductive elimination is a unimolecular process occurring on the long-lived excited state of the Ni(II) complex. We envision that our study of the productive energy-transfer-mediated pathway would encourage the development of new excited-state reactivities in the field of metallaphotocatalysis that are enabled by light harvesting.

aking lessons from natural photosynthesis to separate the roles of light absorption and reactivity,<sup>1</sup> the merger of transition metal catalysis and photocatalysis (termed metallaphotocatalysis) has helped realize a wide range of elusive chemical transformations in organic chemistry over the past 5 years.<sup>2,3</sup> In general, "one-photon"-initiated mechanisms, photoinduced electronic energy transfer (EnT)<sup>4,5</sup> and electron transfer (ET),<sup>6</sup> are acknowledged to account for the enhanced reactivities of metal complexes.<sup>2</sup> The EnT pathway offers access to excited states via photosensitization from photoexcited chromophores, while the ET pathway takes advantage of the enhanced redox activity of photoexcited chromophores to access highly reactive oxidation states of metal complexes. The ET pathway requires a thermodynamic redox potential match, while in the EnT scenario, one optimizes either spectral or molecular orbital overlap, depending on the detailed mechanism being Förster or Dexter type.<sup>7</sup> For a given reaction, an unambiguous mechanistic description is required, as different mechanisms may lead to sharply different optimization strategies.

In the context of nickel-catalyzed cross-coupling, metallaphotocatalytic strategies have been successful in further promoting challenging bond formations under mild conditions. Such advances have been attributed to the efficient photoactivation of reductive elimination steps to forge C–C,  $^{8-11}$  C–O,  $^{12,13}$  and C–N<sup>14</sup> bonds by either oxidation  $^{8-11,14,15}$  or excitation<sup>11,16</sup> of Ni(II) intermediates (Figure 1). Oxidationinduced reductive elimination mediated by photoinduced ET has been implicated in a recent mechanistic study by Nocera and co-workers.<sup>17</sup> They showed that a Ni(III) state can be accessed via sequential ET events involving both iridium photoinduced ET and nickel oxidative addition. The mechanistic understanding of EnT-mediated reductive elimination, however, remains relatively underexplored.<sup>4,5,18-20</sup> One such attempt is reported in an iridium/nickel-catalyzed esterification of aryl halides with carboxylic acids (Figure 1), by MacMillan and co-workers.<sup>13</sup> Preliminary mechanistic studies showed that the catalytic reaction yield is correlated





Triplet-Triplet Energy Transfer vs Photoinduced electron/hole transfer

**Figure 1.** Mechanistic overview of photocatalytic C–O cross-coupling.

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**Figure 2.** (A) Extinction spectra of 1 and 2 in DMF. Inset: absorption spectra of a mixture of 96  $\mu$ M 1 and 192  $\mu$ M 2 versus linear summed individual spectra (for mixtures of other ratios, see Figures S20–S22). All measured in a 2 mm J. Young optical glass cuvette. (B) Stern–Volmer plot of quenching from 2 (measured by time-correlated single-photon counting (TCSPC), Figure S23) and *tert*-butyl-isopropyl amine (measured by steady-state fluorometer, Figure S24).

with the triplet energy of iridium photocatalysts. In conjunction with the unfavorable thermodynamics for photoinduced ET between iridium photocatalysts and nickel intermediates, a triplet-triplet EnT mechanism was favored, yielding a photoexcited Ni(II) that begets reductive elimination.

We subsequently realized it is difficult to reject the ET pathway solely based on thermodynamics, considering the fact that the oxidation potential of the nickel intermediate is interpreted from an irreversible cyclic voltammogram which tends to underestimate its reducing power (Figure S10).<sup>3,21,22</sup> Here, we report mechanistic insights for the elementary C–O reductive elimination step gained from time-resolved spectroscopic studies. These studies include the dynamics of the iridium/nickel photoactivation and the following reductive elimination step. We find that the reductive elimination can be driven by excited-state reactivities via a diffusion-controlled EnT process from an exogenous photocatalyst.

To identify the primary quencher, we conducted steady-state and time-resolved Stern-Volmer quenching experiments on photocatalyst tris(2-phenylpyridinato)iridium(III)  $(Ir(ppy)_3)$ 1. For the choice of quenchers, we targeted a stable Ni(II)(Ar)acetate complex 2 (4,4'-dimethoxy-2,2'-bipyridyl)-2,6-bis-(trifluoromethyl)phenylnickel(II) acetate (Figure 2A) with catalytically relevant ligands as a model system for studying the elementary C-O bond formation step of interest.<sup>13,15</sup> Quenching of photoexcited 1 by 2 can result in either oxidation to Ni(III) via ET or excitation of the nickel complex via EnT to provide sufficient thermodynamic driving force for the key reductive elimination step. tert-Butyl-isopropyl amine base (hereon referred to as amine) exploited in the reaction was also examined due to its potential to serve as a holetransfer relay between photoexcited 1 and 2, indirectly accomplishing the oxidation of 2. It was found that 2 predominantly quenches photoexcited 1 compared to amine (Figures 2B, S23, and S24). We note that the static quenching rate constant of nickel complex 2 could not be ascertained because the strong absorption band of 400 nm resulted in a strong inner filter effect (Figure 2A).<sup>25</sup> At the concentration allowing for a measurable quenching rate for nickel 2, the solution becomes optically dark and no longer eligible for

emission measurements (for derivations see Supporting Information (SI), p S46).

We next questioned the nature of the quenching interaction between 2 and photoexcited 1. Either photoinduced ET or EnT can take place. ET leads to the formation of new redox species (cationic Ir(IV)/anionic Ni(I) or anionic Ir(II)/ cationic Ni(III)). EnT gives rise to photoexcited 2 and ground-state Ir(III) photocatalyst 1. Time-resolved transient absorption measurements were performed to detect these products of different pathways, fleetingly present in solution. In a mixture of 1 and 2, photoexciting at 400 nm results in simultaneous formation of photoexcited Ir and Ni species owing to their overlapping absorption in the visible region (Figure 2A). Within the excited-state lifetime of 2 ( $\tau$  = 4.22(0.05) ns), transient spectra of the mixture can be reproduced by a linear combination of individual species (Figures S45 and S46). Moreover, the fact that ground-state complexation is minimal, as suggested by steady-state absorption and NMR measurements (Figures 2A inset, S2-S8, S20-S22), indicates that neither excited-state intermolecular interaction nor ultrafast static quenching operates between 1 and 2. Instead, quenching should occur in a purely diffusion-controlled fashion between photoexcited 1 and ground-state 2, which will become observable beyond the nanosecond time scale. Moving toward a later time delay when photoexcited 2 has decayed, the majority of transient signals of the mixture of 1 and 2 as well as 1, 2, and amine (see SI for discussion, p S41) in the visible range of 350-600 nm resemble those of photoexcited 1 (Figure S47), featuring diagnostic peaks of ground-state bleaching (GSB) at 410 nm and excited-state absorption (ESA) at 520 nm. Excited-state population dynamics of 1 can be extracted from the decay rates in these regions, which are found to be synchronized (Figure 3B,D and Table 1, rows 2-5), implying that the population of iridium species only flows from Ir(III) 1 excited state to its ground state on the microsecond time scale. The quenching rate of nickel acetate 2 can also be extracted from tabulated decay data of mixtures with different concentrations of 2 via Stern–Volmer analysis, yielding a rate constant of 1.7(0.1)  $\times$  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which is consistent with the value from TCSPC (Figure 2B).



**Figure 3.** (A) Temporal evolution of photoinduced dynamics of a mixture of 96  $\mu$ M **1** and 192  $\mu$ M **2** in DMF,  $\lambda_{exc} = 400$  nm (500 nJ/ pulse), 2 mm J. Young optical glass cuvette. (B) Single-wavelength traces of the corresponding mixture in (A) at 410 nm ( $\tau = 0.93(0.02)$   $\mu$ s) and 520 nm ( $\tau = 1.00(0.01)$   $\mu$ s). (C) Temporal evolution of photoinduced dynamics of a mixture of 96  $\mu$ M **1**, 192  $\mu$ M **2**, and 3.8 mM *tert*-butyl-isopropyl amine in DMF,  $\lambda_{exc} = 400$  nm (500 nJ/ pulse), 2 mm optical glass J. Young cuvette. (D) Single-wavelength traces of the corresponding mixture in (C) at 410 nm ( $\tau = 0.94(0.04)$   $\mu$ s) and 520 nm ( $\tau = 1.03(0.01)$   $\mu$ s).

Table 1. Decay Rate (Error) of GSB and ESA Signals of Photoexcited 1 at Different Wavelengths in the Mixture ( $\lambda_{exc}$ = 400 nm, 500 nJ/pulse)

0 1.41(0.04) 1.47(0.01) 1.45(0.01) 1.46(0.01	us)
	)
34   1.36(0.04)   1.41(0.02)   1.45(0.02)   1.43(0.03)	)
68 1.31(0.02) 1.33(0.02) 1.31(0.01) 1.27(0.02)	.)
192 0.93(0.02) 1.01(0.01) 1.00(0.01) 1.02(0.02)	.)
$192^b  0.94(0.04)  1.05(0.01)  1.03(0.01)  1.00(0.02)$	.)

<sup>*a*</sup>Mixture contains only 96  $\mu$ M **1** and **2** of varying concentration in DMF. <sup>*b*</sup>Mixture contains 96  $\mu$ M **1**, 192  $\mu$ M **2**, and 3.8 mM *tert*-butyl-isopropyl amine in DMF.

EnT can de-excite the Ir(III) excited state and regenerate ground-state Ir(III) 1, concomitantly producing a kinetically invisible photoexcited Ni(II) 2 accounting for the correlated decays and the lack of new signals. Spectroscopic invisibility of photoexcited 2 is supported by a sequential model<sup>26</sup> in which the contribution of its transient signal is estimated to be only 0.4% (for derivations see SI, p S47). Reversing the inverted kinetics by increasing the concentration of acceptor, as shown by Glorius and co-workers,<sup>19</sup> is not practical in our study due to the absorptive nature of nickel acetate 2 (for derivations see SI, pp S47–S48). Additionally, begetting the same population dynamics as EnT, ET with fast recombination where back ET happens faster than the forward photoinduced ET is not a product-forming channel, since excitation energy is wasted via thermal relaxation (for discussion see SI, p S42). Therefore, EnT is favored to be the productive pathway that provides the

necessary driving force for reductive elimination (see SI, p S62, for discussion of FRET and Dexter possibilities).

Having gained insight into the photoactivation mechanism between iridium and nickel, we sought to understand the subsequent reductive elimination step from photoexcited Ni(II) **2**—specifically, whether it is a direct excitation-induced process or an oxidation-induced process mediated by photoexcitation of nickel (Figure 4A). The second pathway is proposed based on Doyle and co-workers' recent study on a similar Ni(II)(Ar) halide complex, where it was demonstrated that a photoexcited Ni(II) complex is capable of oxidizing, after diffusion, another Ni(II) complex in its ground state to give the Ni(III) and Ni(I) pair.<sup>27</sup> This suggests that excitation of nickel could simply act as a checkpoint along the way to Ni(III) in facilitating reductive elimination.

To test this bimolecular redox hypothesis, we performed a concentration-dependent transient absorption measurement on Ni(II) **2**. If the disproportionation pathway operates, the observed excited-state lifetime of **2** is expected to decrease as ground-state Ni(II) concentration increases. No clear concentration dependence was observed for the excited-state lifetime of **2** (Figure 4B), suggesting the photoinduced disproportionation pathway is not significant. TD-DFT calculations showed that initial photoexcitation at 400 nm of **2** is predominantly metal-to-ligand charge transfer (MLCT) in nature<sup>16</sup> (Figure S59).

Along the lines of the work by Doyle and co-workers,<sup>27</sup> we assign our long-lived excited state of nickel 2 to be a spinflipped triplet state because of the striking similarities in excited-state lifetimes between nickel acetate and nickel halide complexes in their study. Therefore, we conclude that it is the long-lived triplet excited state of 2 that directly undergoes reductive elimination to form the final product. Stoichiometric study also shows that direct photoexcitation at 450 nm of 2



**Figure 4.** (A) Schemes of excitation-induced pathway and oxidationinduced pathway between excited-state and ground-state molecules of 2 that eventually leads to product formation. (B) Single-wavelength traces at 405 nm of transient absorption spectra of 2 in DMF,  $\lambda_{exc}$  = 400 nm (1000 nJ/pulse), 2 mm J. Young optical glass cuvette,  $\tau_{280nm}$  = 3.78(0.07) ns,  $\tau_{400nm}$  = 4.12(0.13) ns,  $\tau_{500nm}$  = 4.00(0.08) ns.



EnT enabled product formation

Oxidation enabled product formation

**Figure 5.** Proposed productive channels for C–O cross-coupling reaction. Solid arrows are the steps that have been consolidated in this study. Dotted arrows indicate plausible elementary steps currently under investigation.

leads to appreciable product formation,<sup>13</sup> demonstrating the viability of the EnT pathway. The proposed EnT pathway here differs intrinsically from a recent study by Miyake and co-workers on a photocatalyst/nickel photocatalytic C–N cross-coupling reaction, where the reactivity was proposed to be promoted by Ni(I)/Ni(III) species generated via intra-molecular ET within the excited state of the nickel acceptor.<sup>18</sup>

So far, we have presented an excitation-induced reductive elimination channel of nickel catalysis initiated by diffusioncontrolled EnT from exogenous photocatalysts. This, however, may not be the sole functional pathway for the catalytic reaction (see SI, p S45, for discussion for possible mechanisms of reaction with NiBr<sub>2</sub> precursor), considering that reductive elimination from 2 can also be facilitated by oxidation using a mild single-electron oxidant (ferrocenium tetrafluoroborate,  $E_{1/2}$ [Fe<sup>III</sup>/Fe<sup>II</sup>] = 0.49 V vs SCE, Table S1). We suspect that the oxidation channel may come into play when the coupling substrate changes. As a result, the electronic structure of the formed Ni(II) acetate intermediate may vary based on the observation that highest occupied orbitals (Figure S56) are metal-, aryl-, or carbonyl-centered, as demonstrated by DFT calculation. Therefore, the photoactivation between photoexcited iridium photocatalyst and nickel intermediate can be altered from EnT to ET that leads to the formation of Ni(III), begetting oxidation-induced reductive elimination.

In conclusion, we have demonstrated evidence supporting two catalytically relevant product-forming channels for an iridium/nickel photocatalytic C–O cross-coupling reaction (Figure 5), especially the diffusion-controlled EnT channel<sup>7,28,29</sup> to produce a photoexcited organometallic complex that subsequently undergoes reductive elimination. More importantly, the enhanced reactivity is directly bound to the electronic excited state. We envision that this effective strategy of accessing excited states via solution-based diffusioncontrolled EnT consolidated in our study will motivate the development of new excited-state reactivities in the field of EnT-mediated photochemistry.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b12835.

Stoichiometric experimental procedures, spectroscopy data, analysis, derivations, and further discussions, including Figures S1–S59 and Tables S1–S6 (PDF)

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#### Notes

The authors declare no competing financial interest.

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