

How Does Iridium(III) Photocatalyst Regulate Nickel(II) Catalyst in Metallaphotoredox-Catalyzed C-S Cross-Coupling? Theoretical and **Experimental Insights**

Hang Ren,^{†,},^{\nabla} Guang-Fu Li,^{†,},^{\nabla} Bo Zhu,[†] Xiao-Dong Lv,[†] Li-Shuang Yao,[‡] Xin-Long Wang,[†] Zhong-Min Su,^{*,†,§,},[†] and Wei Guan^{*,†,‡}

[†]Faculty of Chemistry, National & Local United Engineering Lab for Power Battery, Key Laboratory of Polyoxometalate Science of Ministry of Education, Northeast Normal University, Changchun 130024, People's Republic of China

[‡]State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China

[§]School of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun 130022, People's Republic of China

^{II} Jilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry, Changchun 130022, People's Republic of China

Supporting Information

ABSTRACT: Photoredox-mediated iridium/nickel dual catalysis has successfully triggered a series of traditionally challenging carbon-heteroatom cross-coupling reactions. However, detailed mechanisms, such as the catalytic cycles for dual catalysts and the role of base additive, remain controversy in these reactions. In this study, a highly chemoselective C-S cross-coupling of thiols with heteroaryl iodides has been investigated by density functional theory (DFT) calculations and emission quenching experiments. Interestingly, the oxidation state modulation mechanism merging oxidative quenching $(Ir^{III} - *Ir^{III} - Ir^{IV} - Ir^{III})$ and nickel catalytic cycles (Ni^{II}-Ni^I-Ni^{II}-Ni^{II}) is favorable. It is



consisted of four major steps: pyridine mediated proton-coupled electron transfer, oxidative addition of heteroaryl iodides with Ni(I)-halide complex, reductive elimination, and single-electron transfer. In contrast, the radical mechanism initiated by reductive quenching of *Ir^{III} with thiols is impractical, because oxidative addition or σ -bond metathesis from Ni(II)-thiolate intermediate is highly energy-demanding. This study will hopefully benefit the future understanding of such photoredoxmediated dual catalytic systems.

KEYWORDS: C-S cross-coupling, photoredox catalysis, iridium, nickel, density functional calculations

INTRODUCTION

The carbon-heteroatom (C-X) bond-forming reaction is of particular interest in the field of modern organic chemistry, because the introduction of heteroatoms is essential to the functionalization of organic compounds.¹ Especially, the C-S bond is of utmost importance in biological, pharmaceutical, and industrial applications.² Undoubtedly, it is urgent to develop the C-S bond-based synthesis to fulfill the increasing demand of future pharmaceutical applications. Although several fascinating catalytic achievements have been made for C-N and C-O bond constructions, the efficient and selective formation of C-S bond remains relatively rare.³ A general approach for building C-S bond involves the transition metalcatalyzed cross-coupling of organic halides with thiols or disulfides. An accepted consensus of the catalytic cycle is the double electron transmetalation mechanism, which consists of

three elementary steps: (i) oxidative addition, (ii) transmetalation, and (iii) C–S reductive elimination.^{1b} Regrettably, although the approach is sometimes effective, the activity of the transition-metal catalysts may be suppressed by either the high energy-demanding double electron transmetalation process or the strong coordination of thiolates to catalysts. In this regard, reaction conditions are often dependent on high catalyst loading, specially designed ligands, high temperature, excess of strong base, etc.⁴ To a great extent, limitations of the further development of this approach are inextricably linked to the reactions that are rooted in the two-electron pattern.⁵ Therefore, it is urgent to explore a new synthetic strategy for

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achieving highly selective cross-coupling reactions to construct the C–S bond.

Inspired by the organo-singly occupied molecular orbital (SOMO) catalysis,⁶ chemists strive to use a single-electron transfer (SET)-mediated route to conduct the cross-coupling cycle. With the increasing awareness of sustainable development in synthetic chemistry, photoredox catalysis is turned to be an ideal enabling technology.⁷ Upon irradiation with visible light, photocatalysts (such as ruthenium and iridium polypyridyl complexes) are converted to their excited states, which can serve as strong 1e-oxidant and 1e-reductant simultaneously. Thereby, they can be induced to activate organic substrates or adjust the oxidation state of transitionmetal catalysts via unique SET pathways under environmentally friendly conditions. The active intermediates can then engage in organo-catalytic cycles.⁸ One intriguing utilization can be traced back to 2008 with the covers of $[Ru(bpy)_3]Cl_2$ photocatalyzed the asymmetric alkylation of aldehydes, [2 + 2]enone cycloadditions and reductive dehalogenation reactions by the MacMillan Yoon, and Stephenson groups, respectively.⁹ This strategy was marked as a milestone to construct C-Cbond using photocatalysis involving SET processes.^{83,9} Notably, with the characteristic of abundant, inexpensive, and several available oxidation states, nickel complex acts as an ideal transition-metal catalyst.¹⁰ In this regard, photoredox/ nickel dual catalysis, which is the combination of photocatalysis and nickel catalysis, has become a novel and powerful synthetic strategy for building various C-C and challenging C-X (C-O, C-N, C-P, and C-S) bonds via unique SET pathways. Notably, such a dual catalysis can enable synthetic transformations to proceed in a more mild and selective manner than the individual catalysts, hence expand the scope of the C-X formation modes.¹¹

More recently, Johannes and co-workers successfully constructed C–S bonds by the cross-coupling of 4-methoxybenzyl thiol (**RSH**) and 4-iodotoluene (**ArI**) with $Ir^{III}[dF(CF_3)ppy]_2(dtbbpy)PF_6/Ni^{II}(bpy)Cl_2$ (Ir^{III}/Ni^{II}) metallaphotoredox approach, as shown in Scheme 1.¹² It is notable

Scheme 1. C-S Cross-Coupling of 4-Methoxybenzyl Thiol and 4-Iodotoluene by Ir^{III}/Ni^{II} Metallaphotoredox Catalysis



that the desired product (**P**) can be obtained in excellent yield in the presence of pyridine (**Py**) under room temperature while completely none forms in the absence of **Py**. A tentative radical mechanism including a photoredox-mediated iridium reductive quenching cycle ($Ir^{III} - *Ir^{III} - Ir^{II} - Ir^{III})$ was proposed to provide fundamental information into the dual catalytic platform. Besides the questionable mechanism, however, some other important details remain obscure. For example,

- (i) How does the Py promote the reaction?
- (ii) What is the nature of the dual catalysts?
- (iii) What is the origin of the high chemo-selectivity of C–S cross-coupling?

In fact, it is quite difficult to identify the precise mechanism experimentally, because of the rather short lifetime of relevant reactive intermediates. By contrast, computational modeling of the reaction mechanism has been more broadly applied.¹³ At present, there have been some progress on theoretical mechanistic studies of Ir^{III}/Ni^{II} metallaphotoredox catalyzed C-X cross-coupling reactions. For instance, Ma and coworkers investigated the mechanism of C-N cross-coupling by Ir^{III}/Ni^{II} metallaphotoredox catalysis. Their calculation results suggest the radical mechanism merging iridium reductive quenching and nickel catalytic cycles appears more feasible than the triplet-triplet energy transfer mechanism.¹⁴ In contrast, Guan and co-workers illustrated that Ir^{III}/Ni^{II} metallaphotoredox catalyzed C-O cross-coupling occurs through oxidation state modulation mechanism¹⁵ merging oxidative quenching and nickel catalytic cycles.¹⁶ In addition, Chen and co-workers took the vinylation reaction as an example to investigate photophysical properties of Ir^{III} polypyridyl complexes and their photoredox-mediated excited-state SET paths in detail.¹⁷ In view of the above studies, we questioned which type of mechanism would be more suitable for C-S bond formation. On this account, two probable mechanisms have been put forward with understandings of the present reaction. As shown in Scheme 2a, a radical mechanism is comprised of photoredox-mediated iridium reductive quenching (Ir^{III}-*Ir^{III}-Ir^{III}-Ir^{III}) and nickel catalytic cycles (Ni^{II}-Ni^I-Ni^{II}-Ni^{IV}-Ni^{II} or Ni^{II}-Ni^{II}-Ni^{II}-Ni^{II}). Specifically, in the reductive quenching photoredox cycle, Ir(III) photocatalyst (a) initially absorbs a photon to produce an excited state *Ir(III) (b). Then, b is reductively quenched by RSH to generate a radical cation RSH^{•+} and Ir(II) species (c). Py selectively abstracts a proton from the sulfydryl group of RSH^{•+} to deliver S-centered radical (RS[•]). In parallel, single-electron reduction of Ni(II) catalyst (d) by c generates Ni(I) halide complex (e) and the ground state photocatalyst Ir(III). Then, RS[•] would be rapidly captured by e to afford Ni(II) thiolate species f. The following oxidative addition of ArI to Ni(II) center and reductive elimination yield the C-S coupling product and catalyst **d** (Ni^{II}-Ni^I-Ni^{II}-Ni^{II}). Besides, starting from f, a σ -bond metathesis between Ni–I and S-C(aryl) bonds might occur to yield P and regenerate d (Ni^{II}-Ni^{II}-Ni^{II}). An alternative mechanistic pathway, an oxidation state modulation mechanism consisting of oxidative quenching $(Ir^{III} - *Ir^{III} - Ir^{IV} - Ir^{III})$ and nickel catalytic cycles $(Ni^{II} - Ni^{I} - Ni^{II} - Ni^{II} - Ni^{II} - Ni^{II} - Ni^{II} - Ni^{II} - Ni^{II})$ is given in Scheme 2b. First, upon irradiation of the Ir(III) to *Ir(III), Ni(II) catalyst will be reduced to e complex by the oxidative quenching $*Ir^{III} \rightarrow Ir^{IV}$. Then, the successive coordination of **RSH** and **Py** provides a Ni(I) thiolate intermediate (i) through proton transfer step. The subsequent oxidative addition and reductive elimination steps lead to the formation of the desired C–S bond. Alternatively, a σ -bond metathesis between Ni–I and S-C(aryl) bonds might also occur from i. Finally, singleelectron oxidation of Ni(I) halide (k) by Ir(IV) regenerates a and **d** simultaneously.

To this end, to provide a deeper insight into the mechanism of the C–S cross-coupling by Ir^{III}/Ni^{II} metallaphotoredox catalysis, we have comparatively investigated two types of

Scheme 2. Two Mechanisms of the C–S Cross-Coupling Reaction by Ir^{III}/Ni^{II} Metallaphotoredox Catalysis: (a) Radical Mechanism and (b) Oxidation-State Modulation Mechanism



RESULTS AND DISCUSSION

probable mechanisms mentioned above. Both DFT calculations and emission quenching experiments indicate that the oxidation state modulation mechanism merging oxidative quenching (Ir^{III} — $*Ir^{III}$ — Ir^{IV} — Ir^{III}) and nickel catalytic (Ni^{II} — Ni^{II}) cycles is more favorable. Furthermore, the pyridine-mediated stepwise proton-coupled electron transfer (PCET) step takes on a non-negligible role in the C–S cross-coupling. We hope such knowledge would benefit a better understanding of the present reaction mechanism and future development of versatile C–X bond construction reactions by such Ir/Ni—metallaphotoredox catalysis.

COMPUTATIONAL DETAILS AND MODELS

In the present calculations, the C–S cross-coupling of RSH and ArI with the existence of Py catalyzed by Ir^{III}/Ni^{II} dual catalyst was selected as the model reaction, as shown in Scheme 1.

DFT calculations were performed using the Gaussian 09 program.¹⁸ The (U)M06 method¹⁹ was used for unrestricted geometry optimizations in the gas phase. The LANL2DZ was employed for Ni, I, and Ir atoms with effective core potentials (ECPs) for its core electrons.²⁰ The 6-31++G(d,p) level was used for H atoms in the sulfydryl and methylene groups, and the 6-31G(d) level was applied for all of the other atoms. The excited state of *Ir(III) was obtained by geometry optimization of the triplet state of Ir(III). Frequency analyses were calculated at the same theoretical level to ensure whether it is a saddle point or minimum at 298.15 K and 1 atm. Intrinsic reaction coordinate (IRC)²¹ calculations were performed to confirm that the transition states indeed connect the right reactants and products. The single-point energies of all stationary points were performed at the SMD²²(CH₃CN)/ (U)M06/[6-311++G(d,p)/SDD²³(Ni, I, and Ir)] level. In addition, considering the change in standard states from gas phase to aqueous solution, the translational entropy was corrected with the method developed by Whitesides et al.²⁴ In order to evaluate the reliability of the computational method, the photophysical properties of Ir(III) photocatalyst and redox potentials of relevant complexes were calculated (see Figures S1 and S2, Scheme S1, and Tables S1-S3 in the Supporting Information). The 3D molecular structures were generated using the CYL view program.²⁵

Radical Mechanism. Effort was first put into examining the energy demands of the radical mechanism. Above all, a radical coupling partner is generated through a pyridinemediated stepwise PCET step, as shown in Figure 1. In the



Figure 1. Energy profile $(\Delta G^{\circ}_{298,15})$ of **Py**-assisted proton coupled electron transfer process (bond length given in Angstroms). Hydrogen atoms are omitted for the sake of clarity.

reductive quenching photocatalytic cycle, the photoredox catalyst Ir(III) absorbs visible light to reach its excited state *Ir(III). *Ir(III) can then facilitate the oxidation of RSH to deliver RSH^{•+} and reduced Ir(II) species with Gibbs free energy change (ΔG°) of 3.6 kcal/mol (Figure S3 in the Supporting Information). This SET process is feasible according to the redox potential evaluations (see Scheme S1 in the Supporting Information). Based on Marcus electron transfer theory,²⁶ furthermore, the activation barrier of this SET step was calculated to be 9.3 kcal/mol.²⁷ Subsequently, the approach of Py toward RSH^{•+} results in the formation of complex 1 ($\Delta G^{\circ} = -0.3$ kcal/mol), where H atom of the sulfydryl group binds with the N atom of Py through nearlinear N···H-S hydrogen-bonding interaction. Next, a proton transfer (PT) step occurs via an almost barrier-free transition state TS1 to generate the radical coupling partner RS[•]. The Gibbs activation energy ($\Delta G^{\circ \ddagger}$) and ΔG° of this PT step is

only 1.1 kcal/mol and -12.5 kcal/mol, respectively. In **TS1**, the S–H bond is slightly elongated to 1.44 Å from 1.41 Å in **1**, while the N–H bond is shortened to 1.62 Å from 1.76 Å in **1**. This indicates the breaking of S–H bond and that the formation of the N–H bond is in process. Furthermore, the spin density of S atom changes from 0.27 in **1** to 0.88 in **RS**[•] throughout the PT step. An alternative hydrogen atom transfer (HAT) from **RSH** to **Py**^{•+} may provide **RS**[•]; however, the oxidation of **Py** by ***Ir(III)** via SET to afford **Py**^{•+} and **Ir(II)** with an energy barrier of 27.9 kcal/mol. The high energy demand of the SET step and the mismatched redox potential results exclude such HAT mechanisms. Accordingly, **RS**[•] is expected to proceed via the stepwise PCET step and can be rapidly intercepted into a nickel catalytic cycle.

Hereafter, we will discuss the triplet nickel catalytic cycle, because the singlet surface lies higher than the triplet (see Figure S4 in the Supporting Information). As shown in Figure 2, the single electron reduction of Ni(II) by Ir(II) delivers a



Figure 2. Energy profiles $(\Delta G^{\circ}_{298.15})$ of $Ni^{II}-Ni^{II}-Ni^{II}-Ni^{IV}-Ni^{II}$ and $Ni^{II}-Ni^{II}-Ni^{II}-Ni^{II}$ cycles.

Ni(I) intermediate 2 and regenerates the photoredox catalyst Ir(III) with a small $\Delta G^{\circ \dagger}$ value of 6.0 kcal/mol and a ΔG° value of -3.2 kcal/mol. Also, this SET step is supported by the matched redox potential (see Scheme S1 in the Supporting Information). Subsequently, 2 captures RS[•] to generate a stable Ni(II)-thiolate species 3, where the Ni-Cl bond is almost perpendicular to the bpy ligand plane with a large energy downhill of 39.6 kcal/mol. Starting from 3, the directly oxidative addition of the Ar-I bond can occur via the concerned three-membered-ring (Ni-C3-I) transition state TS2. In TS2, the C3–I distance (2.58 Å) is longer than that in ArI (2.13 Å), indicating that the cleavage of the C3–I bond is in progress. As a result, an octahedral Ni(IV) complex 4 can be obtained with completely broken C3–I bond ($d_{C3-I} = 2.93$ Å). The $\Delta G^{\circ \ddagger}$ and ΔG° values of the process are 41.3 and 38.7 kcal/mol, relative to 3, respectively. Then, through the transition state TS3, where the distance of C3-S bond distance is shortened to 2.62 Å from 3.03 Å in 4, the reductive elimination occurs with a high energy barrier of 42.2 kcal/mol to afford Ni(II) complex 5. In 5, the C3-S bond is completely formed (1.79 Å). At last, the C–S cross-coupling product (P)

will be extruded to complete the catalytic cycle and regenerate Ni(II) catalyst. As another possibility for the radical mechanism, however, the oxidative addition that occurs prior to RS^{\bullet} addition is more unfavorable than the present one, because the energy barrier is 54.3 kcal/mol, with respect to 3 (see Figure S5 in the Supporting Information).

Considering the high-valent Ni(IV) intermediate is kinetically and thermodynamically inaccessible, the viability of the σ -bond metathesis mechanism was evaluated. In **TS5**, a fourcentered C3–I–Ni–S ring is formed, where the C3–I, Ni–I and C3–S distances change to 2.53, 2.78, and 2.46 Å, respectively, indicating the C3–I bond cleavage and the C3–S bond formation occur simultaneously. The $\Delta G^{\circ \ddagger}$ and ΔG° values of the process are 34.1 and –19.8 kcal/mol, relative to 3, respectively. Although the σ -bond metathesis effectively decreases the activation barrier of the radical mechanism, the high energy barrier cannot still be overcome by the experimental conditions.

Oxidation-State Modulation Mechanism. Alternatively, we must turn our attention to the oxidation-state modulation mechanism. As shown in Figure 3, photoexcited *Ir(III) is oxidatively quenched by Ni(II) via SET process to generate the ground-state Ir(IV) and Ni(I) species 2, which is exergonic by -3.8 kcal/mol. This SET step is very facile, because of the matched redox potential (Scheme S1) and a low energy barrier of 3.1 kcal/mol. Furthermore, a rapid and sensitive luminescence turn-off response was observed upon addition of Ni(II) in the Ir(III) solution (Figure 4). The emission quenching was clearly seen upon addition of 2 mM Ni(II), and almost completely quenched emission (~98%) was observed when the concentration of Ni(II) reached 30 mM. Stern-Volmer (S-V) plot (Figure 4a, inset) gives a curve bending upward, indicating that the emission quenching of *Ir(III) becomes more efficient with the increase of Ni(II) concentration. Also, the excited state lifetimes in the presence of quencher Ni(II) (2 mM) (111 ns) are obviously shorter than that of without addition of Ni(II) (146 ns). Combining the nonlinear S-V curve and the change in excited-state lifetime, the dynamic and static quenching processes may coexist in the quenching process.²⁸ The quenching rate constant is evaluated to be $\sim 5.55 \times 10^9$ M⁻¹ s⁻¹. In addition, no overlap was observed between the emission spectrum of Ir(III) and UV-absorption spectrum of Ni(II) indicates the absence of energy transfer between Ir(III) and Ni(II) (see Figure S6 in the Supporting Information). The above results reveal that the emission quenching of *Ir(III) can be attributed to the SET process from the excited state Ir(III) complex to the ground-state Ni(II) complex.

After the oxidative quenching $*Ir(III) \rightarrow Ir(IV)$, the consecutive coordination of RSH and Py forms the nickel(I) intermediate 9 with a ΔG° value of -6.5 kcal/mol. Subsequently, a PT occurs via a four-centered (Ni-S-H-N) transition state TS6 to afford a nickel(I) thiolate intermediate 10 with a small $\Delta G^{\circ \dagger}$ value of 6.1 kcal/mol. The Ni-Cl and S-H distances are elongated to 5.64 and 2.09 Å in 10 from 2.31 and 1.37 Å in 9, respectively. The chloride anion (Cl⁻) spontaneously dissociates from nickel(I) center to counter the pyridinium cation [HPy]⁺. Thereafter, [HPy]⁺Cl⁻ ion pair acts as a solvent molecule to interact with the rest of the nickel moiety, because the dissociation of the [HPy]⁺Cl⁻ from 10 requires a ΔG° value of 13.5 kcal/mol. Here, successive SET and PT were defined as the stepwise proton-coupled electron transfer (PCET). Note that a strong pre-



Figure 3. Energy profiles $(\Delta G_{298.15}^{\circ})$ of the Ni^{II}-Ni^{II}-Ni^{II}-Ni^{II}-Ni^{II} and Ni^{II}-Ni^I-Ni^{II}-Ni^{II} cycles.



Figure 4. (a) Steady-state emission quenching of *Ir(III) $(10 \,\mu\text{M})$ with addition of different concentration Ni(II) complex in the CH₃CN solution (inset shows Stern–Volmer analysis of the results). (b) Corresponding photographs of *Ir(III) $(10 \,\mu\text{M})$ with addition of different concentration of Ni(II) complex (6–30 mM) in the CH₃CN solution under sunlight (top) and UV lamp irradiation (bottom), respectively.

equilibrium hydrogen-bonding interaction between N atom of Py and H(-S) atom of RSH in the PT step causes high chemoselectivity of C-S versus C-C cross-coupling (see Figure S7 in the Supporting Information).¹⁶

Prior to the following oxidative addition of the C–I bond of **ArI** to the Ni(I) center, the C=C double bond of **ArI** first coordinates with the Ni(I) center of **10** in a η^2 -side-on manner to provide a four-coordinate nickel(I) intermediate **11** with a ΔG° value of -6.1 kcal/mol. Subsequently, the C3–I bond is cleaved via the transition state **TS7** to afford a nickel(III) aryl thiolate intermediate **12** with a moderate $\Delta G^{\circ \ddagger}$ value of 19.4 kcal/mol. Then, C–S reductive elimination occurs through the transition state **TS8** to form the four-coordinate Ni(I) intermediate **13**. This reductive elimination from nickel(III) complex needs a very small $\Delta G^{\circ \ddagger}$ value of 3.2 kcal/mol,

relative to 11. In contrast, an alternative σ -bond metathesis from 11 was also evaluated to require much larger $\Delta G^{\circ \dagger}$ value of 31.3 kcal/mol, as shown in Figure 3 (blue line). Finally, the SET process between 13 and Ir(IV) complexes can release the desired product P and regenerate Ni(II) and Ir(III) to restart the catalytic cycle. According to the above results, the ratedetermining step of Ni^{II}–Ni^I–Ni^{II}–Ni^{II} cycle is an oxidative addition, with a $\Delta G^{\circ \dagger}$ value of 19.4 kcal/mol, which can be overcome under room temperature. Overall, the Ir^{III}/Ni^{II} cooperative catalysis is reflected not only in thermodynamics but also in kinetics. Kinetically, Ir(III) photoredox-mediated excited-state SET process triggers the single electron reduction of Ni(II) to the active Ni(I) species with a very low energy barrier (3.1 kcal/mol). Thermodynamically, photocatalytic cycle (Ir^{III}–*Ir^{III}–Ir^{IV}–Ir^{III}) contributes

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an extra huge driving force (27.3 kcal/mol) for the entire catalytic reaction.

Note that the difference of oxidative addition steps between the radical mechanism and the oxidation state modulation mechanism is originated from the oxidation states of nickel center. Generally, the oxidation process of high-oxidation-state metal is more disadvantageous. In this regard, the former involving Ni^{II} \rightarrow Ni^{IV} transformation is obviously less favorable than the latter involving Ni^I \rightarrow Ni^{III} transformation. In addition, we also employed the activation strain model to analyze their energy-barrier differences (Figure S8 in the Supporting Information).²⁹ It can be suggested that the oxidative addition of **ArI** to high-oxidation-state Ni^{II} center results in considerably larger distortion between the Ni catalyst and the substrate, which accordingly leads to the larger bond activation barrier.

CONCLUSIONS

An oxidation state modulation mechanism, which consists of Ir^{III}-*Ir^{III}-Ir^{IV}-Ir^{III} oxidative quenching and Ni^{II}-Ni^{II}-Ni^{III}-Ni^I-Ni^{II} catalytic cycles, has been proposed and proved to be the most viable for photoredox-mediated iridium(III)/nickel-(II) dual-catalyzed C-S cross-coupling of thiols with heteroaryl iodides. The catalytic cycle starts with a thermodynamically and kinetically favorable single electron transfer process, where photoexcited *Ir(III) is oxidatively quenched by Ni(II) to generate the ground-state Ir(IV) and Ni(I)(bpy)Cl complex. This active nickel(I) species successively interacts with 4-methoxybenzyl thiol and pyridine to form a nickel(I) thiolate intermediate through proton transfer step. A subsequent two-electron oxidative addition and reductive elimination process constructs the C-S bond. Then, the second exergonic single electron transfer process between nickel(I) iodide and Ir(IV) complexes can regenerate Ni(II) and Ir(III) to restart the catalytic cycle. Importantly, the pyridine-mediated stepwise proton-coupled electron transfer process successfully accelerates the reaction. The oxidative addition is the rate-determining step, with an energy barrier of 19.4 kcal/mol. Furthermore, the proposed oxidative quenching cycle has been demonstrated to be favorable through the redox potential evaluations, the activation barriers of single electron transfer, and the emission quenching experiments. We hope the mechanistic insights could benefit deep understanding of iridium/nickel cooperative catalysis and the future development of new C-X cross-coupling reactions.

ASSOCIATED CONTENT

Supporting Information

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Computational details, experimental information, and Cartesian coordinates of optimized structures (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: zmsu@nenu.edu.cn (Z.-M. Su).

*E-mail: guanw580@nenu.edu.cn (W. Guan).

ORCID 💿

Xin-Long Wang: 0000-0002-5758-6351 Zhong-Min Su: 0000-0002-3342-1966 Wei Guan: 0000-0001-7000-0274

Author Contributions

 $^{\nabla}$ These authors contributed equally.

Notes

The authors declare no competing financial interest.

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