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Reaction Mechanisms

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Photoinduced Group Transposition via Iridium-Nitrenoid Leading to Amidative Inner-Sphere Aryl Migration

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Abstract: We herein report a fundamental mechanistic investigation into photochemical metal-nitrenoid generation and inner-sphere transposition reactivity using organometallic photoprecursors. By designing Cp*Ir-(hydroxamate)(Ar) complexes, we induced photo-initiated ligand activation, allowing us to explore the amidative σ (Ir–aryl) migration reactivity. A combination of experimental mechanistic studies, femtosecond transient absorption spectroscopy, and density functional theory (DFT) calculations revealed that the metal-to-ligand charge transfer enables the σ (N–O) cleavage, followed by Ir-acylnitrenoid generation. The final innersphere σ (Ir–aryl) group migration results in a net amidative group transposition.

Introduction

Recent advances in photoredox catalysis have allowed the generation of highly reactive intermediates to achieve challenging transformations.^[1-3] In this regard, exploring photochemical reactivity in transition metal complexes has gained prominence, enabling precise control of reaction pathways (Scheme 1a). For example, the metal-to-ligand charge transfer (MLCT) process has proven useful in furnishing reactive open-shell intermediates via outer-sphere electron or energy transfer.^[4–7] Moreover, recent studies have revealed that photoexcitation of transition metal complexes can facilitate inner-sphere photoactivation of organometallic intermediates^[8–10] to induce metal-bound

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Angew. Chem. Int. Ed. 2024, 63, e202408123 (1 of 9)



(c) This work: Photoinduced group transposition of Cp*Ir(Ar)(hydroxamate)



Scheme 1. Photoinduced amidative group transposition via a nitrenoid pathway.

substrate activation,^[11] controlled metal-ligand cleavage,^[12-15] and cross-coupling^[16-20] reactivity. In particular, photoinduced Ni-catalyzed cross-coupling reactions have been triumphed by Doyle, MacMillan, and co-workers,^[21,22] where subsequent studies unveiled the pivotal role of homolytic Ni-carbon bond cleavage, which is otherwise difficult to achieve under thermal conditions.^[23-29] Outer-sphere group transfer processes can also be effectively leveraged through light absorption. For instance, Miller and colleagues demonstrated photochemical ethane formation from a [Cp*Ir(bpy)(Me)]⁺ complex via Ir-methyl bond homolysis.^[30] Also, Miller and Wenger independently explored photo-triggered hydrogen evolution,^[31-33] or hydrogen atom transfer^[34] using cationic [Cp*Ir(LL)(H)]⁺ type complexes. Similarly, Chirik, Scholes, and co-workers provided mechanistic insights into visible light-promoted hydrogenation using neutral [Cp*Ir(LX)(H)] type complexes.^[35,36]

Given the growing interest in the photochemistry of organometallic complexes, developing new types of photoprecursors becomes essential to gain deeper insights into the mechanistic understanding of reaction design. In this context, exploring metal-nitrenoid formation through photochemical approaches is especially noteworthy^[37] considering its versatility in the C-N bond formation.[38-42] In fact, Powers and co-workers elegantly demonstrated photoinduced stoichiometric amino group transfer reactivity using dirhodium^[43] or manganese^[44] ligated N-halosulfonamido complexes. Such photochemical approaches are not only efficient for generating metal-nitrenoid species, but they are also beneficial for the structural characterization of transient metal-nitrenoid intermediates via photocrystallographic analysis as detailed by Powers,^[45-47] Schneider,^[48,49] Betley,^[50] and Albrecht,^[51] mostly using metal-azide complexes. Our group also recently captured a mechanistic snapshot of a metal-acylnitrenoid transfer using light-harvesting rhodiumdioxazolone complexes.^[52]

Among various photolabile reactive amino group precursors, hydroxylamine derivatives have been considered versatile in accessing synthetically valuable N-centered radicals or nitrenes via intermolecular outer-sphere redox events with excited-state photocatalysts.^[53-60] To our best knowledge, photoactivation of metal-bound hydroxylamine precursors via an inner-sphere charge transfer pathway has been, in contrast, unexplored even though photoactivation of these complexes is envisaged to be highly versatile for enabling the C–N bond formation (Scheme 1b).^[61-64] However, securing a preparative route for thermally stable but photoactive organometallic precursors is challenging to achieve this goal.^[65,66]

In this context, we were curious about utilizing metalhydroxamates as a systematic blueprint to investigate our mechanistic study on photoinduced metal-nitrenoid transfer. The key to synthetically accessing metal-hydroxamates turned out to be using chelating bidentate hydroxamates, which could increase the thermal stability of the targeted metal complexes and, as a result, endow their photoabsorption properties. In this study, we reveal our design of photo-responsive half-sandwich $Cp*Ir(k^2-N,N)(Ar)$ complexes with a bidentate hydroxamate ligand to explore the Ir-acylnitrenoid generation in situ and subsequent innersphere transfer (Scheme 1c). Our combined experimental and computational mechanistic studies have unveiled that designed Cp*Ir(hydroxamate)(Ar) complexes undergo visible-light-induced ligand activation via $\sigma(N-O)$ cleavage, followed by Ir-acylnitrenoid formation, and then intramolecular σ (Ir–aryl) migration to ultimately leading to a net "group transposition". Femtosecond transient absorption data from the designed Cp*Ir(hydroxamate)(Ar) complex and its control analog, in which N-O dissociation is intentionally blocked, also supports this conclusion.

Results and Discussion

Synthesis and Photochemical Properties of Iridium-Hydroxamate Complexes

In pursuit of our objective to investigate the photoinduced formation of metal-acylnitrenoids, we elaborated on synthesizing thermally accessible but photoactive precursors. The treatment of bidentate hydroxamate а *N*-(acetyloxy)picolinamide (L1) with $[Cp*IrCl_2]_2$ in the presence of a stoichiometric amount of NEt₃ gave a Cp*Ir-(L1)Cl complex Ir1a almost quantitatively. Further ligand exchange of Ir1a with AgOTFA proceeded smoothly to access Ir2a. Then, transmetalation was meticulously achieved to furnish Cp*Ir(L1)(Ar) complex Ir3a, with aryl boronate in the presence of *n*-tetrabutylammonium fluoride (TBAF) and Cu(OAc)₂ in THF (59% in two steps, Figure 1a). The structure of Ir3a was unambiguously characterized by single-crystal X-ray diffraction (SCXRD) analysis. The observed Ir–C(Ar) bond length of 2.063(4) Å is in a similar range with analogous metal-C(Ar) bond lengths of Ir (2.050(2) Å), Rh (2.0349(19) Å), and Ru-C(Ar) (2.071 (2) Å) bond lengths.^[67-70] Also, the Ir-N(amido) and N-O bond lengths are 2.061(3) Å and 1.428(5) Å, respectively.

Having successfully synthesized the targeted half-sandwich Cp*Ir(hydroxamate)(Ar) complex Ir3a, we next explored its photochemical properties. From UV-Vis absorption measurement of Ir3a in acetonitrile (250 µM) at room temperature, two distinct absorption peaks were observed in the UV-A to visible light region (361 nm and 422 nm), resulting in the bright yellow coloration in both solid-state and its solution (Figure 1b, black line). The photoluminescence spectrum of Ir3a recorded at 258.15 K showed a broad emission band at 600-800 nm region, suggesting a chargetransfer character^[71] of the lowest-lying triplet excited state with a singlet-triplet energy gap of ~51 kcal/mol (Figure 1b, red line). Additionally, when emission was measured at 77 K in 2-methyl tetrahydrofuran glass, an emission band was observed at $\lambda_{em} = 607$ nm with 1.28 µs lifetime, yet, this peak was diminished at room temperature (see the Supporting Information for the detailed results). The lack of photoluminescence at room temperature is ascribed to the excited state reactivity and potential non-radiative decay processes (see below).

Significantly, the measured absorption maxima were tentatively assigned as the MLCT band, using time-dependent density functional theory (TDDFT) calculations. It unveiled that the two lowest-energy electronic absorption features correspond to transitions occurring at 431 nm (HOMO to LUMO) and 381 nm (HOMO-1 to LUMO). The frontier orbital analysis suggested that the HOMO and HOMO-1 predominantly comprise Ir(*d*) orbitals and partial amide π character, whereas the LUMO mainly exhibits the π^* character of the pyridinyl fragment. Hence, TDDFT results support our assignment of the two absorption bands as MLCT characters (Figure 1c). Indeed, our assignment on the charge transfer event is in agreement with the photoluminescence features of analogous cationic and neutral Cp*Ir type complexes.^[30,35,36,71]



Figure 1. Synthesis and photochemical properties of a Cp*Ir(Hydroxamate)(Ar) complex Ir3a. (a) Synthesis of Ir3a. Isolated yields. SCXRD: singlecrystal X-ray diffraction. In the crystal structure, hydrogen atoms are omitted for clarity. (b) UV–Vis spectrum of Ir3a in acetonitrile (250 μM, RT, black) and photoluminescence of Ir3a in acetonitrile (258.15 K, red). (c) TDDFT-simulated electronic transitions and molecular orbital plots of Ir3a. Gaussian 16, SMD(acetonitrile)-B3LYP-D3/6-31G**.

Photoinduced Group Transposition Reactivity of Cp*Ir(hydroxamate)(Ar) Complexes

After characterizing the photochemical features of the Cp*Ir(hydroxamate)(Ar) complex Ir3a, we next investigated its photochemical reactivity (Scheme 2a). When irradiating Ir3a with a 450 nm light source^[72] in CH₃CN (0.02 M) for 30 min, to our surprise, we observed a complete conversion of Ir3a, forming a new iridium species Ir4a (87% in NMR yield). Crystal structure obtained from the photolysis mixture revealed that the original aryl moiety is migrated to the N atom of the iridium ligated amido group, where the acetate of the hydroxamate ligand is relocated to the Ircenter to form Ir4a, which is an outcome of a net functional group metathesis. In stark contrast, while no conversion occurred at room temperature, heating Ir3a in acetonitrile at 80°C in the dark for 16 h yielded only 8% of **Ir4a**, with the majority of Ir3a remaining intact, thus suggesting that the photochemical approach is indeed critical in this amidative group transposition.

The present reaction system, however, was rather sensitive to the choice of solvent, as the reaction in methanol led to the predominant formation of Ir-amido complex Ir5 (88 % yield), with only 10 % of Ir4a. Other solvents such as acetone, THF, EtOAc, CH_2Cl_2 , and benzene were ineffective in furnishing the desired complex Ir4a, yet produced Ir5 as major (see the Supporting Information for the detailed results). The structure of Ir5 was also unambiguously characterized through SCXRD analysis, and its formation was ascribed to the cleavage of the N–O bond with concomitant hydrogen atom transfer (see below).

Angew. Chem. Int. Ed. **2024**, 63, e202408123 (3 of 9)

Next, substituent effects of various Ir-Ar complexes on the unprecedented group transposition were explored (Scheme 2b). After preparing a series of Cp*Ir-(hydroxamate)(Ar) derivatives with different aryl groups (Ir3a-e), we examined their photochemical amidative group transposition reactivity. Interestingly, absorption maxima of Ir3b-e were similar to that of Ir3a at 360 nm and 420 nm (see the Supporting Information for detailed results). Notably, when operating a larger-scale reaction using Ir3a, the product yield remained still high (82%). With para-(arvl)substituents such as Cl (Ir3b), H (Ir3c), and Me (Ir3d), we still observed high efficiency of the group transposition, resulting in the formation of the respective product complexes Ir4b-d (70-90%). In the case of methoxy substitution (Ir3e), however, the yield was moderate, furnishing Ir4e in 54%. Importantly, the structures of all reactant and product complexes were unambiguously characterized through SCXRD analyses.

The group transposition reaction proceeded smoothly with a methyl-substituted pyridine (**Ir3f**), affording the corresponding product complex **Ir4f** (78%). Additionally, changing the acetate group to pivalate (**Ir3g** and **Ir3h**) resulted in the formation of C–N coupled products **Ir4g** (64%) and **Ir4h** (78%), yet required diluted conditions for higher efficiency.

Experimental Mechanistic Study

After exploring the photoinduced group transposition reactivity of various Ir-Ar complexes, we next tried to under-





Scheme 2. Photochemical group transposition of Cp*Ir(hydroxamate)(Ar) complexes. [a] Ir3a (0.01 mmol) in solvent (0.02 M) was irradiated with 450 nm LED for 30 min under Ar atmosphere at room temperature. [b] Ir3a (0.01 mmol) in CH₃CN (0.02 M) was heated to 80 °C for 30 min under Ar atmosphere in the dark. [c] Ir3 (0.05 mmol) in CH₃CN (0.02 M) was irradiated with 450 nm LED for 30 min under Ar atmosphere at room temperature. Isolated yields. [d] Run for 3 h. [e] Run in 0.01 M. [f] Run in 0.005 M. In SCXRD, hydrogen atoms are omitted for clarity.

stand the fundamental inner-working aspects of this intriguing transformation. In the initial stage, we hypothesized that photoinduced N–O bond dissociation would take place. One puzzling issue here is to rationalize the character of the key N–O bond cleavage, as either net homolytic or heterolytic cleavage would be operative,^[44,73] thus resulting in an Irnitrene radical intermediate^[74–76] or Ir-nitrenoid, respectively.

To elucidate the key intermediate responsible for the amidative group transposition, we conducted various diagnostic mechanistic probe experiments. As shown in Scheme 3a, a Cp*Ir(hydroxamate)(Ar) complex **Ir3i** that contains a 2-methyl-2-phenylpropionate group furnished α -methyl styrene upon irradiation, which is attributed to be formed via N–O homolysis, radical decarboxylation, followed by hydrogen atom transfer.^[77] Also, trapping experiments using TEMPO or γ -terpinene^[78] further support the formation of radical intermediates upon photolysis (see the Supporting Information for detailed results). Noteworthy is that an open-shell species observed from an electron paramagnetic resonance (EPR) experiment is indicative of the radical formation under our standard group transposition conditions (see the Supporting Information for detailed.

On the other hand, when employing 1.5 equiv. of Ph_3P under the standard photolysis conditions of **Ir3a**, we successfully isolated an iminophosphorane complex **Ir6** in 84 % yield (Scheme 3b). The structure of **Ir6** was unambiguously characterized through SCXRD analysis, revealing the P–N bond length of 1.623(8) Å, consistent with previously reported structures of Ru-acyliminophosphorane complexes.^[79–81] The formation of this iminophosphorane strongly indicates the involvement of singlet metal-nitrenoid intermediate, reported by others as compelling evidence of the intermediacy of metal-nitrenes,^[82–86] yet, at this stage, we cannot entirely rule out the possibility whether other electronic configurations of Ir-nitrenoids such as Ir-nitrene radicals are also involved in this process (see below).

Having investigated the initial N–O photodissociation step, which may undergo homolytic or heterolytic bond cleavage, we next scrutinized the Ir–Ar group migration by designing a crossover experiment (Scheme 3c). When a mixture of **Ir3b** and **Ir3f**, each bearing different substituent groups at the aryl and the pyridine moiety, was irradiated, only conserved products **Ir4b** (44%) and **Ir4f** (42%) were observed, and no crossover product **Ir4a** was found. The crossover experiment suggests that the photoinduced Ir–Ar migration most likely occurs via an intramolecular C–N bond formation mechanism.

The reaction quantum yield of the photoinduced group transposition of **Ir3a** to **Ir4a** was measured using photo NMR actinometry ($\phi = 0.32$, Scheme 3d).^[87] When the photochemical reaction progress of **Ir3a** was monitored using photo NMR spectroscopy with 445 nm fiber optics,^[88,89] the product complex **Ir4a** was gradually generated upon consumption of starting material under irradiation. When





Scheme 3. Mechanistic probe experiments. [a] Yields are determined by ¹H NMR analysis of the crude reaction mixture in the presence of an internal standard. [b] Isolated yield. BAr^F₄ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

the light was turned off, no reactivity was observed, thus suggesting that our reaction system is photo-responsive.

Femtosecond Transient Absorption Measurements

After initial experimental investigations on the photoinduced group transposition of Cp*Ir(hydroxamate)(Ar) complexes, we were curious about the photophysical mechanisms of the target complex. As aforementioned, the excited state of Cp*Ir(hydroxamate)(Ar) complexes can potentially undergo excited state reactivity, leading to the group transposition outcome, yet potential non-radiative decay pathways still exist. Hence, to obtain insights into the photophysical mechanism, we conducted a series of femtosecond transient absorption spectroscopic (TAS) analyses using two iridium complexes: (i) the reactant complex Ir3a that undergoes the desired photoinduced group transposition reaction and (ii) an analogous complex Ir3j, with an N-Bn functionality instead of the original N-O bond. While the latter shows qualitatively similar absorption features to Ir3a, treating Ir3j to the standard photoinduced group transposition reaction conditions did not induce any aryl group migration reactivity, and all starting complexes remained intact (see the Supporting Information for detailed results). Therefore, by subjecting Ir3a and Ir3j to the TAS study, we expected to distinguish the features originating from the photoinduced group transposition process with non-radiative decay processes.

When **Ir3a** was subjected to the TA experiment (up to 2000 ps, $\lambda_{ex} = 400$ nm), we observed a fast rise time component ($\tau_1 = 0.31 \pm 0.03$ ps) at 575 nm, a decay profile at the 450–700 nm region, and a rise and decay profile at around 370 nm. The latter two profiles are well described by two time constants ($\tau_2 = 31 \pm 2$ ps and $\tau_3 = 456 \pm 5$ ps), which were obtained via the global analysis of the data (Figure 2a and 2b).

With analogous Ir–Ar complex **Ir3j**, when the sample was subjected to the TAS experiment at the same timescale (2 ns, $\lambda_{ex} = 400$ nm), we could only observe a decay profile at all regions (350–700 nm) after the pump. We conducted global fitting using a bi-exponential function on the decay profiles monitored at several different wavelengths (see Figure S32). As a result, we obtained two time constants of 40 and 901 ps (Figures 2c and 2d), which could be tentatively attributed to the vibrational relaxation from the hot triplet excited state and the non-radiative decay of the triplet excited state **Ir3j**, respectively.

Based on the observations from TAS, we assigned that the longest time constant observed from **Ir3a** (τ_3 =456 ps) might be related to the non-radiative decay of triplet excited state **Ir3a**. Of note, longer-lived components (>1 ns) might have originated from the product complex **Ir4a**. While the fast ground state recovery could be interpreted to deviate from the relatively high measured reaction quantum yield 521377.3, 2024, 36, Downloaded from https://onlinelibary.wiley.com/doi/10.1002/anie.202408123 by Korea Advanced Institute Of, Wiley Online Library on [2708/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License



Figure 2. Transient absorption data for Ir3a and Ir3j in acetonitrile, pumping at 400 nm (ΔOD = change in optical density). (a) Contour plot for TA spectra of Ir3a and (b) global kinetic analysis for various wavelengths. (c) Contour plot for TA spectra of Ir3j and (d) global kinetic analysis for various wavelengths.

(32 %, Scheme 3d), we attribute this to the different setups for TAS and reaction quantum yield measurement.^[90] Hence, we tentatively assigned the shorter time constants (τ_1 =0.31 ps and τ_2 =31 ps) as the timescale for the initial photoinduced N–O bond cleavage and the following Ir–Ar migration events, respectively.

Computational Study

Based on the collected mechanistic insights from combined experimental and newly performed femtosecond transient absorption spectroscopic studies, a mechanistic proposal is summarized in Figure 3a. Once excited, the Ir3a would undergo fast intersystem crossing to reach its triplet state ³Ir3a. Then, the N–O bond homolysis would lead to furnishing a radical pair (²IrA and acyloxy radical), which may undergo a redox event to form a polar pair of Ir-nitrenoid species ¹IrA and acetate. Alternatively, we cannot entirely rule out the possibility of a direct N-O bond heterolysis at this stage. Then, an intramolecular aryl migratory C-N bond formation and the final Ir-O recombination would form the desired product Ir4a, where either ¹IrA or ²IrA might be responsible at this phase. In addition to the photoinduced group transposition mediated by Ir-nitrenoid intermediates, we also evaluated the thermodynamic feasibility of potential photoinitiated chain propagation pathways to regenerate reactive intermediates, yet, these pathways are thermodynamically less likely to take place (see the Supporting Information for the detailed descriptions).

To further understand the mechanism of the current photoinduced group transposition reaction, we next conducted DFT calculations using **Ir3a** as the model system (Figure 3b). Once excited into its triplet state, the subsequent N–O bond cleavage barrier is 6.5 kcal/mol (³**Ir3a**-**TS**), generating a radical pair of ²**IrA** and acetyloxy radical (–15.1 kcal/mol). Furnished ²**IrA** intermediate may undergo electron transfer with acetyloxy radical to furnish a singlet Ir-nitrenoid intermediate ¹**IrA** and acetate anion. Notably, this redox process has a substantial thermodynamic driving force of 17.3 kcal/mol. On the contrary, while the triplet ³**Ir3a** can mediate photoinduced direct C–N bond coupling presumably via metal oxidation,^[90,91] this pathway involves a higher barrier of 25.8 kcal/mol (See the Supporting Information for the detailed results).

As the next step of the proposed mechanism, we compared the barriers of the Ir–Ar group migration pathway from Ir-nitrene radical ²IrA and one-electron oxidized Ir-nitrenoid ¹IrA. The Ir–Ar migration barrier from Ir-nitrene radical intermediate ²IrA is 23.9 kcal/mol to form ²IrB. Also, the P–N bond formation barrier in the presence of external triphenylphosphine is 23.1 kcal/mol, which is almost similar to the intramolecular C–N bond formation pathway (see the Supporting Information for the detailed results). From ¹IrA, the aryl migratory C–N coupling barrier traversing a transition state ¹IrA-TS is much lower with 13.1 kcal/mol, furnishing the desired product complex ¹IrB.

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Figure 3. (a) Proposed reaction mechanism. (b) Gibbs energy profiles of photoinduced group transposition reaction of Ir3a. Gaussian 16, SMD(acetonitrile)-B3LYP-D3/6-311 + G**|SDD(Ir)//B3LYP-D3/6-31G**|LANL2DZ(Ir).

Of particular note, the barrier for the triphenylphosphine trapping is only 9.6 kcal/mol, which is in agreement with the experimental observation on the exclusive formation of iminophosphorane complex **Ir6** (see above, see the Supporting Information for the detailed results). At the present stage, the lower P–N bond formation barrier of ¹**IrA** compared to ²**IrA** intermediate is attributed to the more electrophilic nature of ¹**IrA** than ²**IrA**. Therefore, we suggest ¹**IrA** intermediate as the key intermediate for the C–N bond formation, yet, we cannot entirely rule out the possibility that ²**IrA** is involved during this process.

Finally, to unveil the nature of this $\sigma(\text{Ir}-\text{Ar})$ group migration process from the singlet nitrenoid intermediate ¹IrA, an intrinsic bond orbital (IBO) analysis^[91,92] was conducted on the IRC trajectories of ¹IrA-TS (Figure 4). During the C–N bond formation, the initial $\sigma(\text{Ir}-\text{C})$ bond migrates to the $\sigma(\text{N}-\text{C})$ bond (presented in red lobes), and the $\pi(\text{Ir}-\text{N})$ bond becomes the $\text{Ir}(d_{xy})$ orbital (shown in blue lobes). The net outcome of this inner-sphere type aryl transfer reaction could be ascribed as the Ir–C migration to an electrophilic Ir-acylnitrenoid intermediate.^[93–98]



Figure 4. IBO analysis on C–N bond formation via ¹IrA-TS. IBO exponent2 based on B3LYP-D3/def2-TZVP.

Conclusion

In conclusion, this fundamental study revealed the first example of a photochemical approach to facilitate group transposition of a new type of Cp*Ir(hydroxamate)(Ar) complexes. We elucidated the mechanistic pathways governing this metathesis reactivity through various control experiments, femtosecond transient absorption measurements, and DFT calculations, leading us to propose the following elementary steps: photoexcitation, N–O bond cleavage to

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furnish electrophilic Ir-acylnitrenoid, and aryl migratory C–N/Ir–O bond formation. This study enhances our understanding of fundamental aspects of the photochemical behaviors of metal complexes and their chemical reactivity to lead to unprecedented inner-sphere group transposition. Ongoing research in our group aims to characterize photochemically generated metal-nitrenoids and explore their potential catalytic utility.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Angew. Chem. Int. Ed. 2024, 63, e202408123 (8 of 9)

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