화학과 대학원 세미나

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Transition Metals in Radical Chemistry: From Coordination- to Photo-chemistry for Catalysis

The first part of the talk will discuss the development of a selective and efficient route for C−H amination utilizing transition metal nitrenoid complexes. Drawing inspiration from Cytochrome P450, a weak-field dipyrrin ligand was adopted to furnish cobalt imido complexes in atypical open-shell electronic configurations, enhancing their propensity for homolytic C–H bond cleavage. A comprehensive kinetic analysis demonstrated that the cobalt imide synthesized following this approach is indeed competent for catalytic C–H amination. In an attempt to improve the efficacy of C–H amination, the steric profile of the ancillary ligand was further modified to generate a bent and significantly basic cobalt imide, which enabled the catalytic amination of strong primary C–H bonds. Additionally, through tuning the molecular oxidation state, we were able to isolate unusual organoazide adducts and demonstrate their viability as nitrene group transfer reagents along with their *in crystallo* conversion to the high-valent cobalt nitrenoid complexes.

The chemistry of a singly-reduced iridium chromophore will be discussed in the second part of the talk. One-electron reduced photosensitizers have been invoked as key intermediates for photoredox catalysis including multi-photon excitation and electrophotocatalytic processes. To the best of our knowledge, however, such a mono-reduced photocatalyst has not been isolated across any class of photoredox catalysts. Towards this end, a family of mono-reduced heteroleptic iridium chromophores was crystallographically and spectroscopically characterized to reveal a ligand-centered reduction as their ground states. These studies demonstrate the first characterization of thus far elusive reduced iridium chromophores, providing opportunities to revisit a commonly invoked mechanism for photoredox catalysis.

References

1 "C–H Amination Mediated by Cobalt Organoazide Adducts and the Corresponding Cobalt Nitrenoid Intermediates", Baek, Y.; Das, A.; Zheng, S-L.; Reibenspies, J. H.; Powers, D. C.; Betley, T. A. *J. Am. Chem. Soc.* **2020,** *142*, 11232.

2 "Direct Manipulation of Metal Imido Geometry: Key Principles to Enhance C–H Amination Efficacy", Baek, Y.; Hennessy, E. T.; Betley, T. A. *J. Am. Chem. Soc.* **2019,** *141*, 16944.

3 "Catalytic C–H Amination Mediated by Dipyrrin Cobalt Imidos", Baek, Y.; Betley, T. A. *J. Am. Chem. Soc.* **2019,** *141*, 7797.

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