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Light-Driven Base-Promoted Homolytic Aromatic Substitution Reactions Catalyzed by a Mo^0 Complex

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Photoredox chemistry has been established as a versatile method in organic synthesis during recent years.[1] Milder conditions, new synthetic pathways and more sustainable chemical transformations combined with a broad functional group tolerance are the main advantages of these processes in many cases.[2,3]

We have previously demonstrated that a homoleptic Mo^0 complex bearing chelating diisocyanide ligands can be used as a strong photoreductant able to perform net redox-neutral transformations beyond the capability of the popular *fac*-$[Ir(ppy)_3]$ catalyst.[4,5] In this study, we report a net redox-neutral base-promoted homolytic aromatic substitution (BHAS) reaction catalysed by this same Mo^0 catalyst that cannot be performed with *fac*-$[Ir(ppy)_3]$, and have systematically investigated different substrates with altered geometric and electronic properties to gain deeper mechanistic insight (**Figure 1**).

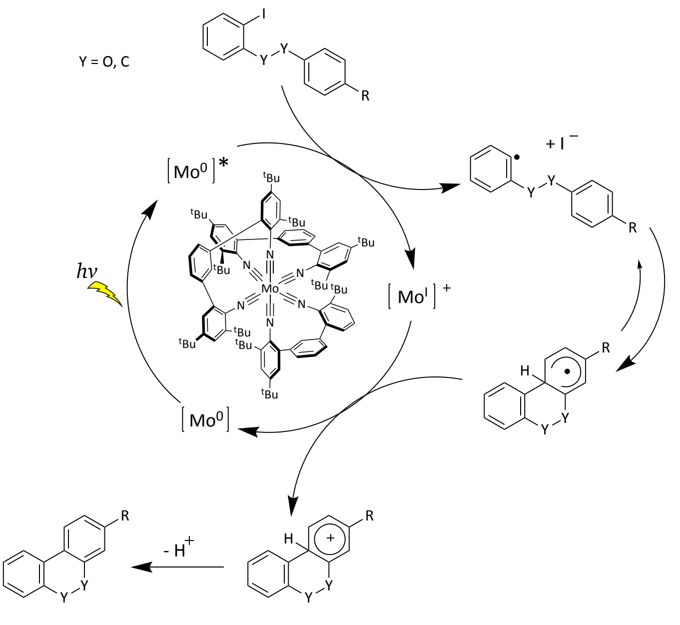

Figure 1. Catalytic cycle for the light-driven base-promoted homolytic aromatic substitution reaction catalysed by $[Mo((^tBu)CNAr_3NC(^tBu))_3]$.

[1] M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898-6926.
[2] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322-5363.
[3] N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075-10166.
[4] L. A. Büldt, X. Guo, A. Prescimone, O. S. Wenger, *Angew. Chem., Int. Ed.* **2016**, *55*, 11247-11250.
[5] L. A. Büldt, O. S. Wenger, *Angew. Chem., Int. Ed.* **2017**, *56*, 5676-5682.