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

F. Glaser$^1$, C. B. Larsen$^1$, O. S. Wenger$^1$*

$^1$ Department of Chemistry, University of Basel, St. Johans-Ring 19, CH-4056 Basel, Switzerland
email: felix.glaser@unibas.ch

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).

![Catalytic cycle for the light-driven base-promoted homolytic aromatic substitution reaction catalysed by [Mo((tBu)CNAr$_3$NC(tBu)$_3$)].](image)

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