Lanthanide photocatalysts for organic synthesis and small-molecule activation

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Divalent lanthanide (Ln) compounds, of which the best known is SmI_2, are excellent reducing agents with unique reactivity profiles.[1] SmI_2 is typically deployed in up to 10-fold excess, often in combination with toxic additives. Reactions catalytic in Ln(II) reagents that retain the reactivity and selectivity of the stoichiometric transformations have been pursued without a significant breakthrough for decades.[2] I will present our results on the photochemical generation of the active Ln(II) species from a stable Ln(III) precursor (Figure 1) to enable Ln(II)-catalyzed reduction reactions. C–halogen, C═C, C═X (X = O, N), P═O, and N═N reductions, as well as C–C, C–X (X = N, S, P), and N–N couplings were possible with yields and selectivities comparable to or better than those afforded by the stoichiometric parent transformations.[3] Reactions could be carried out at room temperature in aqueous solvent mixtures and with mild sacrificial reductants. Reaction outcomes could be altered by changing the ligand or the lanthanide or through the addition of environmentally benign additives.[4] The activation of several small molecules (CO_2, (bi)carbonates, CO, N_2) using lanthanide photocatalysts will be presented, and the proposed reaction mechanisms will be discussed.[5]

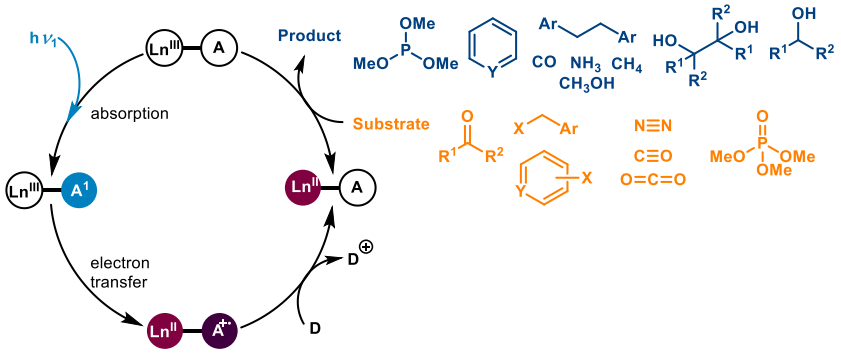

Figure 1. Catalytic cycle with selected substrates and products.

References

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