

PRF#: 57861-DN13

Title: Photodehydrogenative Coupling of Aromatic Hydrocarbons with a Manganese Catalyst

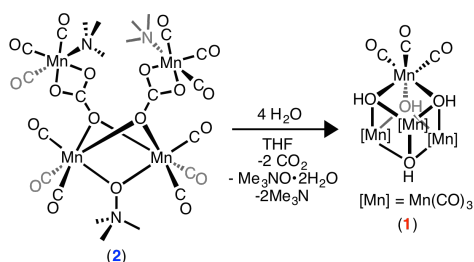
PI: David Lacy, University at Buffalo

PROGRESS REPORT NARRATIVE

Summary

Two papers related to aim 1 and aim 2 of the project were published in *Inorganic Chemistry* during the summer of 2017 prior to the start date of the grant. Efforts to complete aim 3 (catalysis) led us to publish two *Dalton Transaction* papers in 2018. Personnel supported included two graduate students who are the first authors on the two *Dalton Transaction* papers. Additionally, a postdoc was briefly supported with funds from the grant; a manuscript detailing this work has been submitted and is currently under revision and details additional mechanistic insight related to aim 2 of the project. Finally, an undergraduate was supported over the summer for work related to aim 3. The papers that are the result of PRF funding and the support provided therein have been critical to the advancement of my career, primarily by providing the first reports and external support from the Lacy research group and serving as indication of a successful beginning of my independent career.

Scientific Details Related to the Project

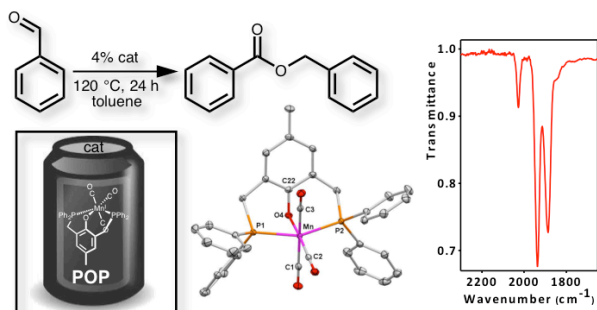


Our initial efforts were guided by our finding that irradiation of a manganese tetramer $[\text{Mn}(\text{CO})_3(\mu_3\text{-OH})_4]$ caused photodehydrogenative coupling of benzene and toluene. Before the start date of the grant, we published two reports that detailed the atom precise synthetic methodology of this tetramer and completed a mass-balanced study of its photochemical decomposition. The details in these two papers essentially were the first two aims of our grant application. These two projects were completed by graduate student prior to Sept 1st 2017.

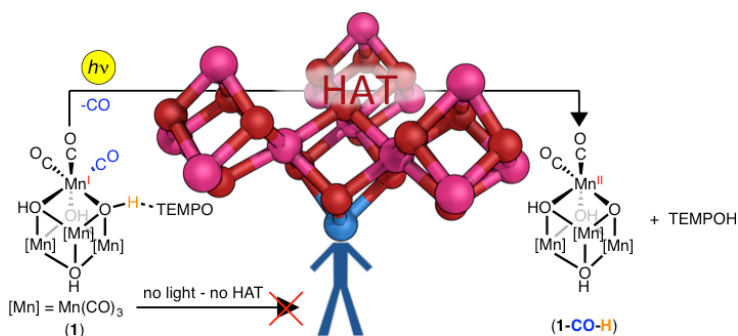
Another graduate student and an undergraduate in my laboratory aided the second paper that detailed the decomposition of the tetramer. Collectively, these reports are critical to my career because they served as my first two independent papers. They also highlighted several of the Lacy research group capabilities that include mechanistic work, EPR spectroscopy, NMR and FTIR spectroscopy, photochemical expertise, and abilities in synthesis.

Subsequent efforts to develop our findings toward catalysis (aim 3) required us to follow alternative paths, as the tetramer compound was too unstable and could only carry out single turnover reactions. Inspired by some of David Milstein's work using Mn-pincer complexes in dehydrogenative coupling reactions, we began a new (but related) thrust of using phenolic pincer and bidentate ligands with manganese to carry out a variety of transformations.

We chose the phenolic/phosphine ligand platform because they are easily tuned and are well suited for metal centers that are not prone to undergo oxidative addition, like Mn(I). Hence, we carried out the first coordination chemistry study of Mn(I) phenolic pincer ligands and disclosed some preliminary catalytic activity of these complexes. These findings were recently published in *Dalton Transactions* in a paper titled "*Bisphosphine phenol and phenolate complexes of Mn(I): Manganese(I) catalyzed Tishchenko reaction*". A particular important finding of this report is that Mn(I) phenolate complexes catalyze the Tishchenko reaction, which is a green atom-efficient method of preparing esters from aldehydes. We are currently actively pursuing the improvement of these catalysts by various ligand design changes. The limitations of this reaction actually enabled us to discover a plausible mechanism and therein opened avenues for several other types of catalytic transformations. Our publication of this paper is critical to my career in that we are trying to break into a field of catalysis and needed to demonstrate our abilities in this area.



Despite our failures in turning the tetramer chemistry into catalytic applications, we are still interested in gaining additional insights into the mechanism of its decomposition. The chemistry of its decomposition hinted

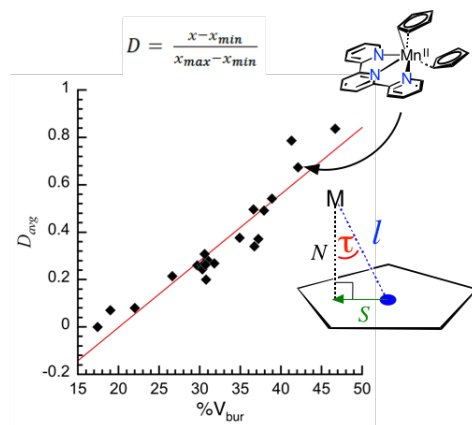


that the O–H bonds in the tetramer, which are quite strong, are significantly weakened when irradiated. This reminded us of a new type of chemical reactivity that takes advantage of X–H bond weakening and is beginning to emerge as a synthetically useful tool to reduce unsaturated molecules. We have completed an investigation that demonstrates O–H bonds in the tetramer are indeed significantly weakened when irradiated and can transfer H-atoms to

substrates like TEMPO. This finding is leading us into other areas of catalysis with new Mn-pincer type catalysts that take advantage of O–H bond weakening. Although we have yet to find a hit, we are actively pursuing these strategies. The potential big impact here is for us to find a completely new strategy to couple substrates with O–H bonds (water, alcohols) to unsaturated molecules like alkenes and alkynes. Traditional methods often use mercury. Recently gold and cobalt have been used. Therefore, the use of earth-abundant Mn will be significantly important in the utility of these types of reactions.

We currently have a manuscript in revision that details this O–H bond weakening chemistry. A postdoc who was briefly supported by this grant joined my laboratory without any background in synthetic organic or organometallic chemistry. During her short stay with me she rapidly learned methods of inorganic chemistry and served as an incredible learning opportunity for her. She is now a postdoctoral scholar in a different department her at UB.

Another project that initially was meant to compliment our studies in developing new manganese catalysts with manganocene (MnCp₂). We were unable to advance this project, but before we abandoned it we did discover some interesting structural properties and published a paper on this work in *Dalton Transactions*; graduate student carried out this work with support from the PRF grant. This manuscript described the synthesis and characterization of eight new adduct complexes of MnCp₂ with varying degrees of hapticity that do not fit into the traditional ideal categories of eta-5, eta-3, etc. The structural characterization of these new compounds by XRD revealed that the deviation from idealized hapticity correlates with the steric properties of the adduct ligand. However, before this work there was no defined way to quantify this deviation and we endeavored to quantify the extent of ring slippage to clearly demonstrate the relationship. Our efforts were rewarded with a linear correlation between a new parameter that quantifies the extent of ring slippage (D in the manuscript) and the Tolman “cone angle” or the percent-buried volume parameter of the adduct ligand. Furthermore, density functional theory was used to demonstrate that crystal-packing effects do not contribute to a large extent. The geometric analyses of the molecules that enabled this study was fully described in the manuscript and we anticipate will serve as a blue print for future parameterization of non-idealized hapticity changes.



In short, the support received and used for graduate students, postdocs, and undergraduates was quite fruitful on both scientific and educational fronts. My postdoc in particular had no background in synthetic organometallic chemistry. Without these funds she would not have had sufficient time to learn the necessary skills to successfully carry out the studies that eventually served as the basis for a publication. Both graduate students were supported for a full semester, enabling them to carry out a significant amount of work that pushed my research program from the beginning stages into what is now a full-fledged program. The students supported are my first two students, so I'm pleased that they were able to see the fruits of their hard labor and the risk they took of joining an assistant professor's group. Finally, I was also supported during the summer, which aided in my efforts on the project and freed up time for grant writing.