

PRF#: 57861-DN13

Title: Photodehydrogenative Coupling of Aromatic Hydrocarbons with a Manganese Catalyst

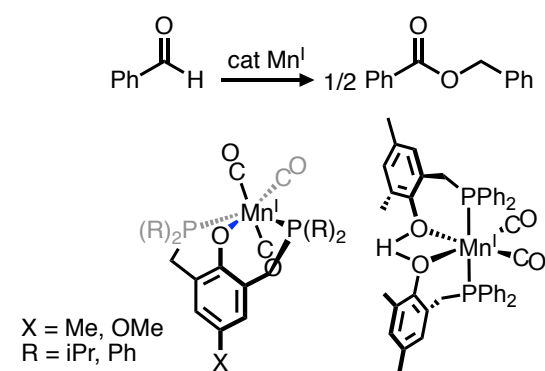
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## PROGRESS REPORT NARRATIVE

### Summary

Since the start of the second year of the project, our efforts shifted away from photochemical transformations to those involving catalytic (de)hydrogenations and catalyzed Tishchenko reactions. These were spurred on by our efforts in developing better platforms for photochemical coupling reactions, but we found the systems were better suited for thermochemically controlled reactions. As part of this work, we developed novel bis- and mono-phosphine phenol ligands that coordinate to manganese, the complexes of which catalyze the Tishchenko reaction. We also developed a phenylglycine derived beta-amino phosphine supported Mn catalyst that is a chemoselective transfer hydrogenation catalyst for chalcones and allylic alcohol isomerization. These catalysts are still underdeveloped and serve as our main motivation moving forward in this area.

### Scientific Details Related to the Project



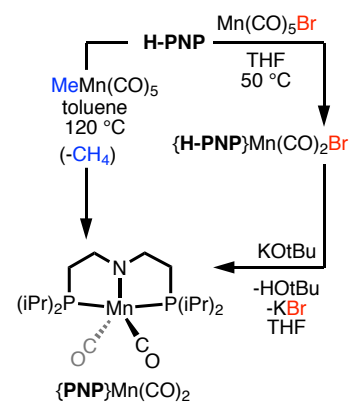
**Figure 1.** Summary of work using phenolic phosphine Mn(I) complexes and catalyzed Tishchenko reaction.

transformations. Unfortunately, the complexes did not have exciting photochemistry (pun-intended), typically resulting in phosphine dissociation and dimerization to insoluble material. However, we did discover that the parent **POPMn(CO)<sub>3</sub>** complex was a catalyst for aldehyde disproportionation (**Figure 1**), resulting in catalytic ester formation in the Tishchenko named reaction. This work was published in *Dalton* shortly after the first year of the project ended.<sup>4</sup>

The area of Mn(I) in catalysis has been very active since Milstein and Beller published the first Mn-based dehydrogenation and hydrogenation catalysts. We noted that the only synthon for these Mn(I) pincer catalysts was  $\text{Mn}(\text{CO})_5\text{Br}$  and demonstrated in another report that  $\text{MeMn}(\text{CO})_5$  is also an excellent synthon. Importantly, the use of the  $\text{MeMn}(\text{CO})_5$  starting material provides rapid access to the active 16-electron active catalyst, whereas use of  $\text{Mn}(\text{CO})_5\text{Br}$  often requires an extra activation step and sometimes does not coordinate the ligand under catalytically relevant conditions (**Figure 2**). This work was published in *Dalton Trans.*<sup>5</sup>

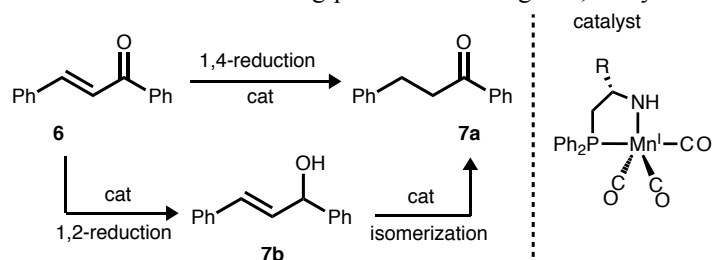
Continuing the work with the phenolic phosphine ligands, we noted that the Tishchenko reaction catalysis proceeded precisely twice as fast with the dimerized precursor as the parent monomeric **POPMn(CO)<sub>3</sub>** complex. This indicated that a phosphine dissociated under catalytic conditions, and therein prompted our preparation of a bidentate mono-phosphine phenol ligand and additionally studied its coordination chemistry with Mn(I). This work revealed many interesting coordination chemistry that is now published in *Inorg. Chem.* as a Forum Article that further discusses some of the challenges in Mn(I) organometallic catalysis.<sup>7</sup>

At the end of the first year of the project, we had completed the work related to the tetramer complex. This work is published in three papers.<sup>1,2,6</sup> The key finding is that the CO photolysis of the tetrameric complex induces a weakening of the O–H bonds so much so that spontaneous release of H-atoms results. This is likely the cause of the C–C bond coupling we observed, wherein the resulting  $\text{Mn}^{\text{II}}$  ions that form from loss of H-atom facilitate a Friedel-Crafts like reaction. We briefly explored this hypothesis but were unable to produce large quantities of coupled material. It was our thought that the failure to produce a catalyst for C–C coupling was related to the instability of the  $\text{Mn}^{\text{II}}$  complexes formed immediately after CO photolysis and H-atom loss. This inspired our design of a bis-phosphine phenol ligand (**HPOP**) to stabilize the reactive species. Using the **HPOP** ligand we prepared several new Mn(I) complexes and explored its catalytic properties for a variety of



**Figure 2.** Summary of work using  $\text{MeMn}(\text{CO})_5$  as a synthon instead of  $\text{MnBr}(\text{CO})_5$ .

In addition to our work using phenolic-based ligands, last year we began to prepare beta-amino phosphine ligands.



**Figure 3.** We discovered the first examples of manganese catalyzed allylic alcohol isomerization. The same catalysts are also efficient transfer hydrogenation catalysts for ketones, and chemoselective 1,4-transfer hydrogenation catalysts for chalcones.

This work was inspired by a certain paper by Evgeny Pidko, wherein they used a glycine-derived beta-amino phosphine ligand to support Mn(I) catalysts in ester hydrogenation. We followed suit and rationalized that a benzylamine would impart greater stability to the catalyst. During this work, we discovered that these beta-amino phosphine ligands, especially the phenylglycine derived ligand, were excellent supports for Mn(I) catalyzed transfer hydrogenation of ketones, chemoselective reduction of chalcones to saturated ketones, and allylic alcohol isomerization reactions. The latter two represent a first in Mn(I) catalyzed reactions

and is currently undergoing peer review (**Figure 3**).<sup>8</sup>

In addition to the scientific work that this PRF grant funded, several students' academic calendar support was covered and many other students' summer salaries were covered. The second-year funds did not cover any postdoctoral or undergraduate researchers. The lead PI received travel support to present the research funded by the project at ACS National Meetings and Gordon Research Conference.

#### Impact of Research Support on Career

The PRF funds enabled continuation of active research after startup funds had expired. The students and the PI used travel funds for dissemination of the project findings to the scientific community at ACS national meetings and Gordon Research Conferences. The published work benefited both the PI and students in furthering career, as publications are a primary metric of success. The two students who received semester salary used this time to work on their dissertation project and are currently expected to graduate within the year. Therefore, the PRF grant supported these students' projects that will enable them to obtain postdoctoral fellowships or industrial positions. The PI's career benefited greatly from the PRF fund because obtaining external funding serves as evidence of a successful independent career.

#### Bibliography (published work supported by PRF DNI 57861-DN13)

1. Kadassery, K. J.; Dey, S. K.; Friedman, A. E.; Lacy, D. C. *Inorg. Chem.* **2017**, *56*, 8748-8751.
2. Kadassery, K. J.; Dey, S. K.; Cannella, A. F.; Surendhran, R. Lacy, D. C. *Inorg. Chem.* **2017**, *56*, 9954-9965.
3. Cannella, A. F.; Dey, S. K. MacMillan, S. N.; Lacy, D. C. *Dalton Trans.* **2018**, *47*, 5171-5180.
4. Kadassery, K. J.; MacMillan, S. N.; Lacy, D. C. *Dalton. Trans.* **2018**, *47*, 12652-12655.
5. Kadassery, K. J.; Lacy, D. C. *Dalton Trans.* **2019**, *48*, 4467-4470.
6. Kadassery, K. J.; Sethi, K.; Lacy, D. C. *Inorg. Chem.* **2019**, *58*, 4679-4685.
7. Kadassery, K. J.; MacMillan, S. N.; Lacy, D. C. *Inorg. Chem.* **2019**. 10527-10535.
8. Vigneswaran, V.; Lacy, D. C. **2019**, available on ChemRxiv. DOI: <https://doi.org/10.26434/chemrxiv.9396266.v1>