

Earth Abundant Manganese Catalysed Sustainable Chemical Transformations

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Conclusion

Conventional methods for creating carbon-carbon bonds and transforming organic functional groups often rely on organohalides and other organometallic reagents, which generate stoichiometric waste. To overcome the drawbacks of these traditional techniques, transition metal-based catalysis has emerged as a viable alternative, adhering to "green chemistry" principles. Over the last two decades, there has been a growing interest in the synthesis and reactivity of organometallic complexes due to their essential role in developing more eco-friendly protocols for key chemical transformations. Pincer complexes are notable for their unique blend of stability and reactivity, enabling them to withstand high temperatures, which makes them particularly useful in homogeneous catalysis. Given that manganese is the third most abundant transition metal, extensive research has been conducted on the synthesis and reactivity of its pincer complexes. This thesis aims to highlight significant reactions involving C-C bond formation and organic functional group transformations, with a focus on alkylation, (de)hydrogenation, hydration, and deamination reactions.

Chapter 1 explores the significance of manganese complexes and their distinctive reactivity, specifically "metal-ligand cooperation." It also discusses the acceptorless dehydrogenative coupling (ADC) and borrowing hydrogen (BH) strategies, which facilitate the formation of new C-C and C-N bonds. Following these approaches, important literature on manganese complexes is reviewed, covering (de)hydrogenation and C-C and C-N alkylation reactions.

Chapter 2 outlines the use of a phosphine-free, quinoline-based pincer manganese catalyst (**Mn-1**) for the α -alkylation of methyl ketones, utilizing primary alcohols as alkyl substitutes. This C-C bond formation occurs through a hydrogen auto-transfer process, with water being the only by-product, making the method atom efficient. Studies using electronic structure theory have supported the proposed mechanism.

In Chapter 3, the text discusses an Earth-abundant Mn-PNP pincer complex (**Mn-2**) that catalyzes the terpenylation of both cyclic and acyclic ketones and the secondary alcohol 1-phenylethanol, using isoprenoid derivatives such as prenol, nerol, phytol, solanesol, and E-farnesol as allyl substitutes. These C-C coupling reactions are environmentally friendly and atom-economic, proceeding through the dehydrogenation of alcohols via a hydrogen autotransfer method facilitated by metal-ligand cooperation.

Chapter 4 highlights the importance of formate salt, a vital chemical with a wide range of uses. This study introduces the first instance of formate synthesis catalyzed by a base metal, utilizing a simultaneous dehydrogenation and transfer hydrogenation approach. The reaction is facilitated by a pincer Mn complex with a PNP ligand (PNP = bis(2-(diphenylphosphanyl)ethyl)amine). The method developed is sustainable, atom-efficient, and employs renewable resources such as methanol and bicarbonates. The manganese-based pincer complex (**Mn-2**) catalyzes the reaction in two stages: methanol dehydrogenation and bicarbonate transfer hydrogenation, producing formate salts in the presence of a mild base. Dehydrogenated methanol also aids in formate production when a base is present. A maximum turnover number (TON) of up to 2640 was achieved for producing formate salt from the reaction between potassium bicarbonate and methanol.

In Chapter 5, the conversion of nitriles to primary amides using a manganese complex with a bidentate phosphine ligand DPPP (1,3-bis(diphenylphosphanyl)propane) under mild conditions is demonstrated. This process yields good to excellent isolated amounts of the

corresponding primary amides, showcasing substrate versatility with notable functional group tolerance. The substrates include a wide range of (hetero)aromatic and aliphatic nitriles. Based on experimental mechanistic insights, a likely reaction pathway is proposed.

Chapter 6 presents the first example of manganese-based non-pincer complexes for the oxidative deamination of amines to carboxylic acids. The reaction is catalyzed by the **Mn-8** complex [DAFO-Mn(CO)₃Br], where DAFO (4,5-diazafluoren-9-one) serves as a bidentate ligand. The reaction occurs in the presence of NaOH as a base, producing NH₃ and H₂ as the only by-products. Dehydrogenative homo-coupling of primary amines derivatives to form symmetrical secondary imines was also explored, yielding good amounts of the corresponding homo-coupled products. Stoichiometric reactions and mechanistic studies supported a mechanistic pathway based on metal-ligand cooperation.

In summary, effective catalytic methods for alkylation, (de)hydrogenation, hydration, and deamination have been established, which are both atom-efficient and environmentally friendly. Commonly available alcohols serve as alkylation agents, replacing methods that generate waste. Methanol acts as a hydrogen donor in the (de)hydrogenation process. Water is employed as a sustainable substrate in hydration and deamination reactions. Across all reactions discussed in the thesis, water and/or molecular hydrogen are the sole byproducts, thus supporting sustainable and green chemistry or serving as substrates (Scheme 7.1). We propose that manganese pincer complexes could effectively replace their precious metal counterparts in facilitating new C-C bond formation and standard organic transformations. Typically, phosphine ligands lead to costly and moisture-sensitive complexes. Consequently, the development of phosphine-free pincer ligands, particularly NNN or NN ligands, and their corresponding metal complexes using manganese precursors with ancillary ligands like carbonyl (e.g., Mn(CO)₅Br) will be pursued. Investigating the reactivity of these complexes will aid in understanding small molecule activation and addressing other synthetic challenges.



Figure 7.1. Alkylation, (de)hydrogenation, hydration and deamination reactions developed using manganese catalysts.