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## 主 論 文 の 要 旨

論文題目

Development of Selective Hydrogenation of Chemically Inert Carbonyl Compounds using (PNNP)Ir Complexes

((PNNP)Ir錯体触媒を用いた化学的に不活性なカルボニル化合物の選択的水素化反応の開発)

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## 論 文 内 容 の 要 旨

The three chapters as outlined in this thesis accounts for the development of systems applicable for the selective reduction of carbonyl compounds to alcohols utilizing (PNNP)Ir complexes. Within each of the three chapters of these thesis, key challenges in the hydrogenation of carbonyl compounds were undertaken and overcome utilizing new strategies for clean reduction of carbonyl compounds in conjunction with sterically robust and multi-functional (PNNP)Ir complexes.

The first chapter of this thesis accounts for the development of a highly efficient and selective system generally applicable to the selective reduction of carboxylic acids to terminal alcohols. In previous works for the development of systems for reduction of carboxylic acids, the challenges regarding the inherent stability and tendency of carboxylic acids to undergo a wide range of side reactions have limited the achieved selectivity and substrate scope. In chapter 1 of this thesis, is presented a novel approach to the selective reduction of carboxylic acids to alcohols. In the presence of a Lewis acid additive and excess amount of alcohol, smooth esterification of parent carboxylic acid was achieved to yield ester intermediates. In the presence of the (PNNP)Ir complexes, the ester

intermediates were smoothly hydrogenated to yield their corresponding terminal alcohols in high yield. This method was also applicable to a wide range of dicarboxylic acids, which are highly challenging substrates due to their tendency to undergo oligomerization and polyesterification. Our methodology allowed for the selective hydrogenation of linear dicarboxylic acids of various carbon chain-length, achieving by far the largest substrate scope for dicarboxylic acid hydrogenation when comparing to state-of-the-art systems. Furthermore, the methodology allowed for the one-pot reduction of oxalic acid and glycolic acid to ethylene glycol, thus paving the way for a novel production method for the generation of ethylene glycol from biomass-derived chemicals.

In the second chapter of this thesis are presented the results of investigation into utilization of (PNNP)Ir complexes for direct hydrogenation of CO<sub>2</sub> to MeOH. The hydrogenation of CO<sub>2</sub> to MeOH has attracted significant attention in the past decades due to the possibility of directly transforming waste CO<sub>2</sub> into the valuable commodity chemical MeOH. Previous works for homogeneous hydrogenation of CO<sub>2</sub> to MeOH have suffered from low catalyst stability, and particularly, catalyst deactivation in presence of *in situ* generated CO is well reported. In order to overcome these issues, we pursued a strategy of hydrogenation in alcohol solvent in the presence of catalytic amounts of base additive NaH. This strategy proved fruitful, as unprecedented catalytic stability was obtained under these conditions, as the (PNNP)Ir complexes were found to achieve high turnover numbers reaction temperatures of ~200 °C and pressures of 7–10.4 MPa for prolonged reaction time of >72 hours. To better understand the impact of the reaction conditions for the selectivity for MeOH in this system, gaseous products were quantified, and it was discovered that NaH had a highly beneficial impact on increasing selectivity of MeOH over CO in this system. Based on mechanistic studies, it was concluded that NaH served a dual role in this system, firstly in increasing the concentration of catalytically active Ir-species for hydrogenation, and secondly, in catalyzing carbonylation of solvent EtOH with *in situ* formed CO. By tweaking the reaction conditions in regards to concentration of NaH and total pressure, the highest TON of any homogeneous system for CO<sub>2</sub> to MeOH hydrogenation, in the absence of amine additives, was

achieved, at high catalyst concentrations.

In the third chapter of this thesis, the development of a system for ketone and ester hydrogenation utilizing (PNNP)Ir complexes in presence of photoirradiation is accounted for. Generally speaking, hydrogenation of carbonyl compounds is an energy intensive process requiring harsh conditions regarding temperature and pressure, and one the main drawbacks of the (PNNP)Ir complexes utilized in chapters 1 and 2 of this thesis is their requirement for high reaction temperature and pressure. In addition to their properties for thermal hydrogenation, the (PNNP)Ir complexes also exhibit useful photo-chemical properties, and can act as photosensitizers, stabilizing charges spurred on by photonic energy by metal-to-ligand charge-transfer. In chapter three, these properties were successfully utilized to achieve photo-induced hydrogenation of ketones, aldehydes and esters at mild conditions. In the presence of photoirradiation, the (PNNP)Ir complexes underwent activation, likely through partial hydrogenation of their ligands, to generate catalytically active species which were found to be efficient for carbonyl compound hydrogenation at far milder conditions compared to when the hydrogenation was conducted in absence of photo-irradiation. Mechanistic studies utilizing a combination of electrospray ionization mass spectroscopy and UV-Vis absorption spectroscopy supported a proposed pathway for catalyst activation, and thus, not only was a system for very mild hydrogenation of carbonyl compounds developed, but additionally, new mechanistic insight generally applicable to homogeneous catalysts for carbonyl compound hydrogenation was elucidated, with potential applications for new catalyst design.

In conclusion, the utilization of (PNNP)Ir complexes in conjunction with the development of new strategies for carbonyl compound reduction was found to be highly fruitful, and the methodologies as presented in this thesis allowed for unprecedented substrate scope for the general reduction of carboxylic acids to alcohols, remarkable catalyst turnover in selective hydrogenation of CO<sub>2</sub> to MeOH, as well as very mild reduction of esters to alcohols, while simultaneously providing new mechanistic evidence with implication to next-generation design of carbonyl reduction catalysts.