

Biomass Building Blocks

Iridium Tetra(4-carboxyphenyl) Porphyrin, Calix[4]pyrrole and Tetraphenyl Porphyrin Complexes as Potential Hydrogenation Catalysts

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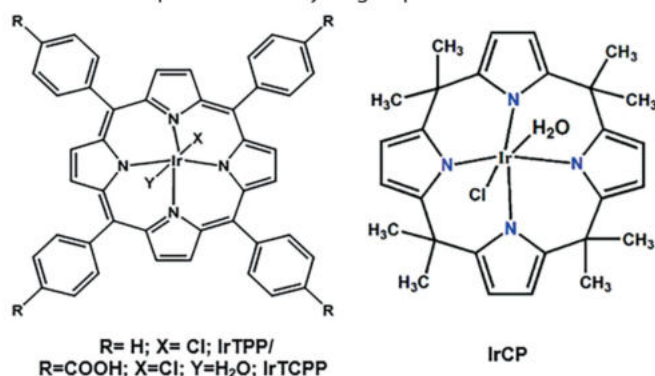
Abstract: Here we report the preparation of first examples of iridium-based organometallic macromolecules, viz., iridium-tetra(4-carboxyphenyl)porphyrin (IrTCPP), iridium-calix[4]pyrrole (IrCP) iridium-tetraphenylporphyrin (IrTPP), which are effective catalysts for hydrogenation of levulinic acid (LA) to γ -valerolactone (GVL) and 1,4-pentanediol under base free condi-

tions. The turnover number in the range of 1220–2850 is evident for the chosen reaction using iridium macromolecule based catalysts. The heterogenization of homogeneous IrTCPP, IrCP, and IrTPP result in stable reactivity of the catalysts for several runs.

Introduction

Iridium-based organometallic complexes have a similar chemistry as rhodium; they possess unique properties and are ideal catalysts for oxidative addition, hydrogenation, bond breaking, and bond making reactions in various chemical processes.^[1–5,6–9] Several iridium based organometallic complexes (iridium-olefin, arene, allyl, alkyl, and carbene complexes) have been extensively studied for hydrogenation, C–H activation, and oxidative addition.^[10,11] Vaska's catalyst^[12] and Crabtree's catalyst^[13–15] are the well-known examples of important iridium-based homogeneous catalysts used for oxidative addition and hydrogenation reactions. Recently, Bayram et al. reported the complete hydrogenation of benzene at room temperature using zero-valent iridium nanoparticles.^[8] Similarly, iridium hydride based complexes possessing various coordinating ligands have been shown to be potential catalysts for hydrogenation of ketones and alcohols.^[10] Also, iridium-containing pincer complex^[16,17] was shown as to be a promising catalyst for the conversion of biomass derivatives. Cyclo-metallated iridium complexes have also attracted great interest owing to their unique photophysical properties.^[18,19] At this juncture, to the best of our knowledge there are no reports on iridium-based macromolecules (Scheme 1). The development of such iridium complexes may broaden the scope as catalysts and may act as model molecules

for biological, photophysical and chemical activities.^[20,21] In other words, in recent years, great attention has been focused on the conversion of biomass into valuable chemicals, in which group VIII metal complexes play a vital role.^[16,17,22–24] In particular, hydrogenation of levulinic acid to γ -valerolactone and 1,4-pentanediol has a significant role as a green solvent, as well as an important intermediate in several fine chemical syntheses.^[25,26] Herein, we report the preparation of novel iridium-based macromolecules [iridium-tetra(4-carboxyphenyl)porphyrin (IrTCPP), iridium-calix[4]pyrrole (IrCP), iridium tetra-phenyl porphyrin (IrTPP) and subsequently, heterogenized on a functionalized molecular sieves support. The homogeneous (IrTCPP, IrTPP, IrCP) and heterogenized iridium complexes (SBA-AM-IrTCPP/IrTPP/IrCP) are explored as catalysts for the conversion of levulinic acid under phosphane, and base-free conditions with moderate temperature and hydrogen pressure.



Scheme 1. Representative examples of iridium based macromolecules.

Results and Discussion

All of the macromolecules were prepared using the Schlenk technique by treating nucleophile (pyrrole) and electrophile

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