Designing Transition Metal Catalysts for Sustainable Transfer Hydrogenation

Seunghyeon Lee[a], Youn-Joo Cheong[a], Hye-Young Jang[a],*

[a]*Department of Energy System Research, Ajou University, Suwon, KS001, KOREA*

**Hye-Young Jang:hyjang2@ajou.ac.kr*

Abstract: Transfer hydrogenation is a method that transfer hydrogen atom to organic compounds using transition metal catalysts in the absence of H_2 gas. Because of glycerol's varied advantages, research about the transformation of glycerol has been conducted actively. We aimed the reduction of organic compounds using glycerol as a sustainable hydrogen source in the presence of iridium catalysts. We have synthesized a couple of iridium catalysts and performed transfer hydrogenation of acetophenone and glycerol. Detailed conditions will be discussed in this presentation.

Keywords: Transfer hydrogenation, Glycerol, Acetophenone

1. Introduction

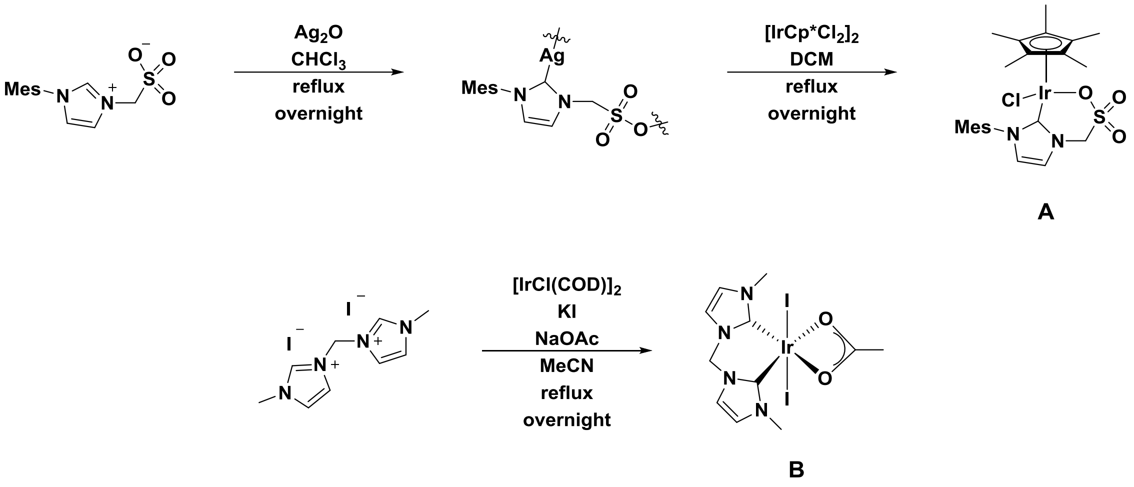
Recent interests regarding the utilization of glycerol as a sustainable chemical resource have been increasing. Glycerol is the byproduct of biofuel processes, and the development of the chemical transformation of glycerol would provide benefits in chemical industries. Glycerol also has many chemical advantages. For example, it is non-flammable, non-toxic, and high boiling point property rather than other alcohols such as MeOH and EtOH. It can dissolve inorganic salt, acid, base, metal complex, and organic compounds.1), 2), 3) In this study, we use glycerol as a reductant for transfer hydrogenation, where various organic compounds including acetophenone are converted to reduced compounds and glycerol also is converted to useful chemicals such as D-lactic acid.

2. Experimental (or Theoretical)

The ligands were prepared according to literature procedures4) and other reagents, including $[Ir(COD)Cl]_2$ are commercially available and were used as received. One of the catalysts that we have used as a basic conceptual structure is methylenebis((N-methyl)imidazole-2-ylidene)acetate(diiodo)Ir(III). This catalyst was synthesized from methylenebis((N-methyl)imidazole diiodide (104 mg, 0.24 mmol), $[Ir(COD)Cl]_2$ (79 mg, 0.12 mmol), KI(156 mg, 0.94 mmool) and NaOAc(115 mg, 1.4 mmol). Gradient column chromatography (SiO_2; first CH_2Cl_2 then CH_2Cl_2/acetone, 8:1) gave the titled product as an orange solid (33 mg, 21%), which was recrystallized from CH_2Cl_2/Et_2O.6) General procedure for the transfer hydrogenation of acetophenone and glycerol is as follows. Acetophenone (0.5 mmol), catalyst (2.5 mol%), and base (0.5 mmol) in 0.8ml of glycerol was stirred at 100 ℃ during 15h. The conversion was detected by GC based on 1-phenylethanol produced.

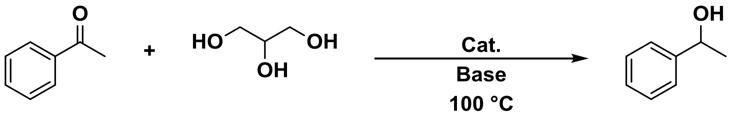
3. Results and discussion

We synthesized various catalysts based on the known NHC-Ir catalyst. Known catalysts are synthesized following literature procedures. 5), 6) (Figure 1).



Scheme 1. Synthesis of NHC-Ir catalysts

We performed transfer hydrogenation of acetophenone and glycerol. The results are shown in Table 1. Catalyst B having a biscarbene ligand shows higher conversion than catalyst A involving a carbene-oxygen ligand. Using the strong base, the conversion is a little bit increased. According to our result, the ligand effect is much more important than the basicity of bases.



Entry	Catalyst	Base	GC conversion (%)
1	A	KOH	16
2	A	Na^{t}OPen	15
3	B	KOH	48
4	B	Na^{t}OPen	43

Table 1. Result of Transfer Hydrogenation

4. Conclusions

We have synthesized various Ir catalysts involving different structured-NHC carbene ligands. These catalysts have been employed to transfer hydrogenation of acetophenone and glycerol to show the effect of ligands on transfer hydrogenation reactions.

References

1. Corrado Crotti, Erica Farnetti and Nicol Guidolin,, Green Chem, 12 (2012) 2225.
2. Yang Li, Martin Nielsen, Bin Li, Pierre H. Dixneuf, Henrik Junge and Matthias Beller, Green Chem. 17 (2015) 193.
3. A. Azua, J.A. Mata, and Eduardo Peris, Organometallics 30 (2011) 5532.
4. S.G. Meier, W. Sarfet, J.M. Junquera-Hernandes, M. Delgado, D. Tordera, E. Orti, H.J. Bolink, F. Kessler, R. Scopelliti, M. Gratzel, M. K. Nazeeruddin and E. Baranoff, J. Mater. Chem. C 1 (2013) 58.
5. A. Rajaraman, A. R. Sahoo, F. Hild, C.Fischmeister, M. Achard and C. Bruneau, Dalton Trans 44 (2015) 17467.
6. M. Alvrecht, J.R. miecznikowski, A. Samuel, J. W. Faller, and R. H Crabtree, Organometallics 21 (2002) 3596.