1B3b

Synthesis of Iridium complexes with a Novel Pincer Type Tridentate Ligand and Application to Catalysts for Dehydrogenation of Alkanes

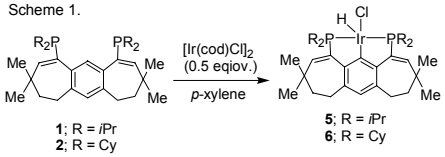
○Takuya Suguri[1], Yohsuke Yamamoto[1]

[1]Graduate School of Science, Hiroshima University

The development of effective systems for conversions of alkanes to the corresponding alkenes is one of the major goals in the field of homogeneous catalysis. In 1996, Kaska, Jensen, et al. reported that the $\{C_6H_3\text{-}2,6\text{-}[CH_2P(t\text{Bu})_2]_2\}IrH_2$ pincer complex catalyzes the transfer dehydrogenation of cyclooctane (COA) with *tert*-butylethylene (TBE) in neat substrate solution to form cyclooctene (COE) and *tert*-butylethane (TBA).[1a] In further studies, bis(phosphinite) pincer type complexes $\{p\text{-X-}C_6H_2\text{-}2,6\text{-}[OP(i\text{Pr})_2]_2\}IrHCl$ has been synthesized and these complexes exhibit high catalytic activities.[1b]

We will report synthesis of novel pincer type complexes which have a fused 7-6-7 ring system and application of the iridium complexes. In order to obtain novel pincer type iridium complexes, pincer type ligands **1**-**4** (R = *i*Pr, Cy (= cyclohexyl), Xyl (= 3,5-dimethylphenyl), Ph) were synthesized, respectively. Iridium complexes **5**-**8** were obtained from these pincer ligands by refluxing with $[Ir(cod)Cl]_2$ in *p*-xylene (Scheme 1, 2). With the newly prepared iridium complexes in hand, the catalytic activity of the iridium complexes **5**, **6** for dehydrogenation of alkanes was investigated. Cyclooctane or *n*-octane is used as a substrate for dehydrogenation, and *tert*-butylethylene or 2-norbornene (NBE) was used as a hydrogen acceptor (Scheme 3). The results of the catalytic experiments are summarized in Table 1. We have found one of the iridium complexes, **5**, exhibits the most active catalytic ability in the field of transfer dehydrogenation of alkanes by homogeneous catalyst.

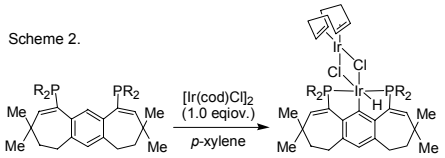
Scheme 1.



1; R = *i*Pr
2; R = Cy

5; R = *i*Pr
6; R = Cy

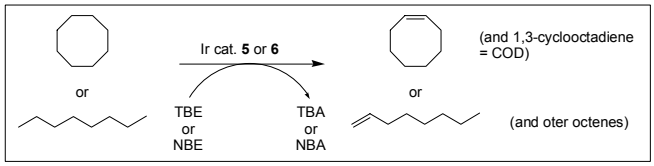
Scheme 2.



3; R = Ph
4; R = Xyl

7; R = Ph
8; R = Xyl

Scheme.3



(TBE = *tert*-butylethylene NBE = 2-norornene
TBA = *tert*-butylethane NBA = norborane)

Table 1.

cat.	substrate	H_2 acceptor	temp(°C)	time(h)	total TON
5 (0.01 mol%)[a]	COA	TBE	200	1	3600 (COE : COD = 83 : 17)[b]
6 (0.03 mol%)[a]	COA	TBE	200	1	0
5 (1.0 mM)[a]	*n*-Octane	NBE (2.0 M)	150	12	1500[b, c]
6 (1.0 mM)[a]	*n*-Octane	NBE (0.5 M)	150	1	0

[a] NaO*t*Bu was added to generate catalytic active spieces. [b] ^{1}H NMR was used to determine the TONs. [c] TONs were estimated from the ratio of NBE and NBA.

1 (a) M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska, and C. M. Jensen, *Chem. Commun.*, 2083 (1996). (b) I. Göttker-Schnetmann, P. White, and M. Brookhart, *J. Am. Chem. Soc.*, **126**, 1804 (2004).