

## Catalytic Hydrogenation of Alkenes Using Zirconocene-Alkene Complexes

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Hydrogenation reactions of alkenes were catalyzed by zirconium-alkene complex derivatives which were prepared from  $\text{Cp}_2\text{ZrCl}_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) and  $n$  equiv. of  $\text{RR}'\text{CHCH}_2\text{M}$  ( $\text{M} = \text{MgX}$  or  $\text{Li}$ ). By the use of three or more equiv. of  $\text{EtMgBr}$  relative to  $\text{Cp}_2\text{ZrCl}_2$ , the product yield of hydrogenation of 1-decene was remarkably improved most likely due to the stabilization of the  $\text{Zr(II)}$  species.

Although many reactions of zirconium(II) complexes have been reported,<sup>1)</sup> catalytic reactions using these complexes are rare. Furthermore, catalytic cycles involving these  $\text{Zr(II)}$  species have not been clearly demonstrated. Recently we have developed a catalytic cycle for C-C bond formation reactions of zirconocene-alkene complexes by the selective transmetalation of zirconacyclopentanes derivatives and demonstrated that the cycle involves zirconium-alkene complexes.<sup>2)</sup> Since then we have investigated catalytic reactions using zirconocene-alkene complexes which can be quantitatively prepared in situ by the reaction of  $\text{Cp}_2\text{ZrCl}_2$  with 2 equiv. of  $\text{RR}'\text{CHCH}_2\text{M}$  ( $\text{M} = \text{MgX}$  or  $\text{Li}$ ).<sup>3)</sup> In this paper, we describe hydrogenation reactions of alkenes catalyzed by the system  $\text{Cp}_2\text{ZrCl}_2 / n \text{RR}'\text{CHCH}_2\text{M}$  ( $\text{M} = \text{MgX}$  or  $\text{Li}$ ).

Catalytic hydrogenation of alkenes using  $\text{Zr(IV)}$  ( $d^0$ ) species such as  $\text{Cp}_2\text{ZrH}_2$ ,<sup>4)</sup>  $\text{Cp}_2\text{Zr(H)Cl}$ ,<sup>4)</sup>  $(\text{RCp})_2\text{ZrMe}_2$ ,<sup>5)</sup> and  $\text{Cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)$ <sup>6)</sup> have been reported. Several mechanisms for hydrogenation catalyzed by  $\text{Zr(IV)}$  species have been proposed. One involves hydrogenation of zirconium(II) species<sup>4)</sup> and another involves direct interaction between  $\text{H}_2$  and  $\text{Zr(IV)}$  species.<sup>7)</sup> Although oxidative addition of  $\text{H}_2$  to  $\text{Zr(II)}$  species have been found,<sup>8)</sup> catalytic hydrogenation using  $\text{Zr(II)}$  species has not been demonstrated. Hydrogenation reactions of alkenes with Ziegler-Natta catalyst systems consisting of zirconium compounds and aluminum derivatives have also been reported.<sup>9)</sup> This system led to the competitive hydrogenation of terminal alkenes with polymerization, which was quite different from our results (*vide infra*).

A typical reaction was carried out as follows. To a mixture of  $\text{Cp}_2\text{ZrCl}_2$  (0.2 mmol) and tetrahydrofuran (THF) (5  $\text{cm}^3$ ) was added 3 equiv. of  $\text{EtMgBr}$  in THF (0.6 mmol, 1.0  $\text{mol dm}^{-3}$ , 0.6  $\text{cm}^3$ ) at  $-78^\circ\text{C}$ . After stirring it for 1 h at  $-78^\circ\text{C}$ , the mixture was warmed to room temperature and stirred for 1 h at room temperature. Hydrogen gas was slowly bubbled through the solution. And then 1 mmol of 1-decene was added to the mixture. The mixture was stirred at  $50^\circ\text{C}$  for 1 h under hydrogen (1 atm). The product was checked by

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Table 1. The Effect of the Ratio of EtMgBr/Cp<sub>2</sub>ZrCl<sub>2</sub> on Catalytic Hydrogenation Reactions of 1-Decene<sup>a)</sup>

EtMgBr/Cp <sub>2</sub> ZrCl <sub>2</sub>	Conversion of 1-decene/%		Yield of decane/%	
	1 h	24 h	1 h	24 h
1	4	6	0	0
2	29	30	27	24
3	97	100	95	98
4	91	95	73	92
8	13	97	8	80
3b)	-	100	-	83

a) Zr:1-decene = 0.2 : 1, Solvent: THF, Temperature: 50 °C. H<sub>2</sub> : 1 atm b) Zr:1-decene = 0.02 : 1, H<sub>2</sub> : 5 atm.

GC and NMR spectroscopy, and their yields were determined by GC.

A mixture of 2 equiv. of EtMgBr and Cp<sub>2</sub>ZrCl<sub>2</sub>, which affords zirconocene-ethylene complex in situ, was not effective for hydrogenation of 1-decene as was expected. Interestingly, however, when 3 equiv. of EtMgBr was used, the yield of hydrogenated product was remarkably improved. The effect of the ratio, EtMgBr/Cp<sub>2</sub>ZrCl<sub>2</sub>, on the hydrogenation of 1-decene was notable as shown in Table 1. The use of 1 equiv. of EtMgBr did not give the product even after 24 h. An excess of EtMgBr beyond 3 equiv. retarded the hydrogenation reaction. The optimum ratio of EtMgBr to Cp<sub>2</sub>ZrCl<sub>2</sub> under conditions used here was 3.

Internal alkenes such as 2-octene,  $\beta$ -methylstyrene and cyclooctene gave lower yields, 52, 40, and 5%, respectively, than terminal alkenes after 24 h. This is in sharp contrast to the Ziegler-Natta catalysts systems, (-)-(EBTHI)ZrMe<sub>2</sub>/[Al(Me)-O-]<sub>n</sub> (EBTHI = ethylenebis(tetrahydro-1-indenyl)) which gives better yields of hydrogenated product for internal alkenes than for terminal alkenes.<sup>9c)</sup> Hydrogenation reactions of 1-decene

Table 2. Hydrogenation of 1-Decene Catalyzed by the System Consisting of Cp<sub>2</sub>ZrCl<sub>2</sub> / 3 Equiv. of Various Grignard or Organolithium Reagents<sup>a)</sup>

Reagent	Conversion of 1-decene/%	Yield of decane/%
MeMgBr	3	1
MeLi	5	5
EtMgBr	100	98
n-PrMgBr	100	96
iso-PrMgBr	81	59
n-BuMgCl	84	71
n-BuLi	100	97

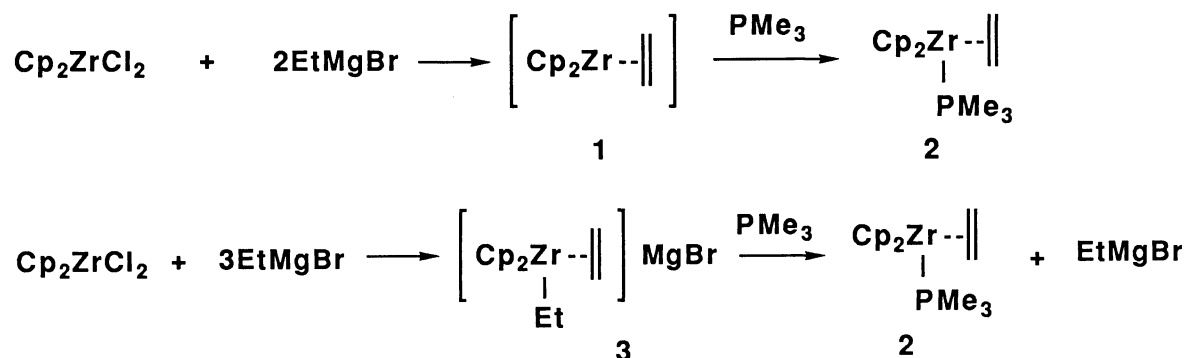
a) Cp<sub>2</sub>ZrCl<sub>2</sub>:Reagent:1-decene = 0.2:0.6:1, Temperature: 50 °C, Solvent: THF, Time:24 h.

using 3 equiv. of other Grignard or organolithium reagents were summarized in Table 2.

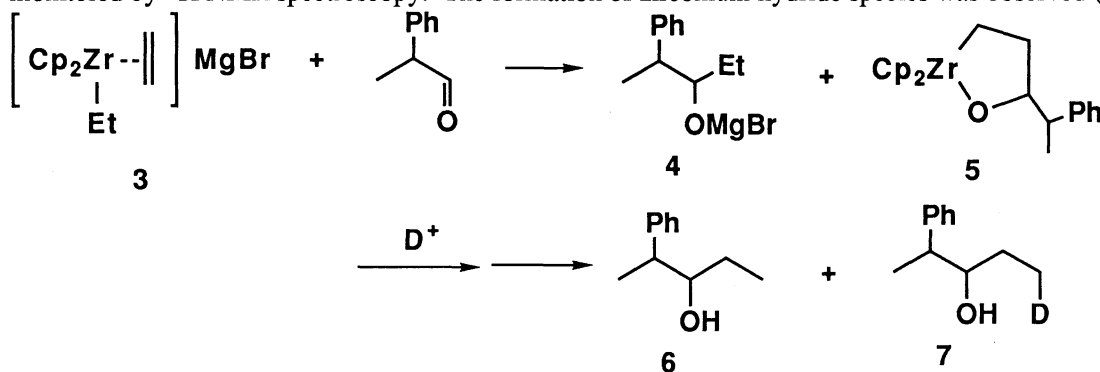
The reaction of MeMgBr with Cp<sub>2</sub>ZrCl<sub>2</sub> gave a good yield of Cp<sub>2</sub>ZrMe<sub>2</sub> based on Zr. This Zr(IV) species was not active for hydrogenation of 1-decene under conditions used here. Since Cp<sub>2</sub>ZrMe<sub>2</sub> cannot decompose via reductive  $\beta$ -elimination to give a Cp<sub>2</sub>Zr(II) species, those Cp<sub>2</sub>Zr(IV) species capable of producing Cp<sub>2</sub>Zr(II) must be required for hydrogenation.

In order to investigate the zirconium species formed in the reaction of Cp<sub>2</sub>ZrCl<sub>2</sub> with an excess of EtMgBr, the following reactions were carried out. It is known that the reaction of Cp<sub>2</sub>ZrCl<sub>2</sub> with 2 equiv. of EtMgBr gave zirconocene-ethylene complex Cp<sub>2</sub>Zr(CH<sub>2</sub>=CH<sub>2</sub>)(PMe<sub>3</sub>) **2** in high yield in the presence of

$\text{PMe}_3$ .<sup>3d)</sup> In the absence of  $\text{PMe}_3$ , novel species  $\text{Cp}_2\text{Zr}(\text{CH}_2=\text{CH}_2)$  **1** was detected. Its  $^1\text{H}$  NMR spectrum showed a singlet peak at 5.5 ppm assigned to the Cp protons and a singlet at 0.7 ppm assignable to ethylene protons. Addition of 1 equiv. of  $\text{PMe}_3$  to this led to disappearance of both peaks at 5.5 ppm and 0.7 ppm and appearance of signals of **2**. In the  $^1\text{H}$  NMR spectrum of **2**, the two  $\text{CH}_2$  moieties of the ethylene ligand are not equivalent because of coordination of  $\text{PMe}_3$ . On the other hand  $^1\text{H}$  NMR spectrum of **1** showed that those two  $\text{CH}_2$  moieties are equivalent. Various reactions of the complex **1** have already been reported.<sup>2,10)</sup>



The reaction of  $\text{Cp}_2\text{ZrCl}_2$  with 3 equiv. of  $\text{EtMgBr}$  afforded a novel species **3**, which was tentatively assigned to a zirconate complex  $[\text{Cp}_2\text{ZrEt}(\text{CH}_2=\text{CH}_2)]\text{MgBr}$ . Its  $^1\text{H}$  NMR spectrum revealed a characteristic broad singlet at 5.3 ppm assignable to the Cp protons. When 4 or 8 equiv. of  $\text{EtMgBr}$  was added to  $\text{Cp}_2\text{ZrCl}_2$ , the formation of the same complex was observed. Treatment of **3** with  $\text{PMe}_3$  gave **2** in 93% yield along with the formation of free  $\text{EtMgBr}$  in 66%. The reaction of **3** with 2-phenylpropanal can, in principle, give two products **4** and **5**. Deuterolysis of the reaction mixture with 1 equiv. of 2-phenylpropanal predominantly gave **6** in 73% yield. Deuterated compound **7** was obtained only in 9% yield. This indicates that the ethyl group on Zr reacted with the aldehyde faster than the ethylene ligand. In fact, the reaction of **3** with 2 equiv. of 2-phenylpropanal gave **7** in 66% yield based on Zr after deuterolysis and usual work-up. These results further support the formation of the Zr(II) complex **3**. Although two broad peaks at 0.51 ppm and -0.50 ppm assignable to its ethylene ligand were seen, ethyl ligand was not clearly detected in its  $^1\text{H}$  NMR spectrum. Low temperature NMR study did not give further informations. Therefore, an analogous ate complex  $[\text{Cp}_2\text{ZrPh}(\text{CH}_2=\text{CH}_2)]\text{MgBr}$  **8** was prepared by the reaction of  $\text{Cp}_2\text{ZrPh}_2$  with  $\text{EtMgBr}$ . The complex **8** gave **2** in 76% yield on treatment with  $\text{PMe}_3$ . Its  $^1\text{H}$  NMR spectrum showed a Cp signal at 5.30 ppm, two triplets at 0.32 ppm and -0.15 ppm assignable to the ethylene ligand and multiplet signals for the phenyl group at 6.8-7.2 ppm. Isolation of **3** and **8** has not yet been successful. Reaction of **3** with hydrogen gas was monitored by  $^1\text{H}$  NMR spectroscopy. The formation of zirconium hydride species was observed (Cp: 5.6 ppm,



Zr-H: -3.6 ppm).<sup>11)</sup> However, the detailed mechanism of hydrogenation reactions and full characterization of **3** and **8** must await further study.

In order to make clear the difference between the results with 2 equiv. of EtMgBr and those with 3 equiv. of EtMgBr, the stabilities of **1** and **3** were investigated. Decomposition of **1** and **3** apparently obeyed the first-order rule, and the rate constants were  $1.3 \times 10^{-2} \text{ min}^{-1}$  and  $2.5 \times 10^{-3} \text{ min}^{-1}$  at 23 °C, respectively. In the case of 4 equiv. of EtMgBr, the complex **3** was more stable. Decomposition rate constant was  $9.9 \times 10^{-4} \text{ min}^{-1}$ .

The results obtained suggested the following. Hydrogenation of alkenes under the conditions used here requires the Zr(II) species as catalyst precursors. However, the 16 electron species **1** is not stable enough to induce hydrogenation in high yields. The presence of the third equiv. of EtMgBr (EtMgBr/Cp<sub>2</sub>ZrCl<sub>2</sub> = 3) afforded **3**, which can act as a stabilized form of **1**. A further excess of EtMgBr, however, retards the reaction of Zr(II) with hydrogen presumably due to further stabilization of the Zr(II) species.

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