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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 Cp_2ZrCl_2 ($Cp = \eta^5\text{-}C_5H_5$) and n equiv. of $RR'CHCH_2M$ (M = MgX or Li). By the use of three or more equiv. of EtMgBr relative to Cp_2ZrCl_2, the product yield of hydrogenation of 1-decene was remarkably improved most likely due to the stabilization of the Zr(II) species.

Although many reactions of zirconium(II) complexes have been reported,1) catalytic reactions using these complexes are rare. Furthermore, catalytic cycles involving these 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.2) Since then we have investigated catalytic reactions using zirconocene-alkene complexes which can be quantitatively prepared in situ by the reaction of Cp_2ZrCl_2 with 2 equiv. of $RR'CHCH_2M$ (M = MgX or Li).3) In this paper, we describe hydrogenation reactions of alkenes catalyzed by the system Cp_2ZrCl_2 / n $RR'CHCH_2M$ (M = MgX or Li).

Catalytic hydrogenation of alkenes using Zr(IV) (d^0) species such as Cp_2ZrH_2,4) $Cp_2Zr(H)Cl$,4) $(RCp)_2ZrMe_2$,5) and $Cp_2ZrH(CH_2PPh_2)$6) have been reported. Several mechanisms for hydrogenation catalyzed by Zr(IV) species have been proposed. One involves hydrogenation of zirconium(II) species4) and another involves direct interaction between H_2 and Zr(IV) species.7) Although oxidative addition of H_2 to Zr(II) species have been found,8) catalytic hydrogenation using 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.9) 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 Cp_2ZrCl_2 (0.2 mmol) and tetrahydrofuran (THF) (5 cm^3) was added 3 equiv. of EtMgBr in THF (0.6 mmol, 1.0 mol dm^{-3}, 0.6 cm^3) at -78 °C. After stirring it for 1 h at -78 °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 °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 $EtMgBr/Cp_2ZrCl_2$ on Catalytic Hydrogenation Reactions of 1-Decene[a)]

$EtMgBr/Cp_2ZrCl_2$	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
3[b)]	-	100	-	83

a)Zr:1-decene = 0.2 : 1, Solvent: THF, Temperature: 50 °C. H_2 : 1 atm b) Zr:1-decene = 0.02 : 1, H_2 : 5 atm.

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

A mixture of 2 equiv. of EtMgBr and Cp_2ZrCl_2, 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, $EtMgBr/Cp_2ZrCl_2$, 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_2ZrCl_2 under conditions used here was 3.

Internal alkenes such as 2-octene, β-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)$ZrMe_2$/$[Al(Me)\text{-}O\text{-}]_n$ (EBTHI = ethylenebis(tetrahydro-1-indenyl)) which gives better yields of hydrogenated product for internal alkenes than for terminal alkenes.[9c)] Hydrogenation reactions of 1-decene using 3 equiv. of other Grignard or organolithium reagents were summarized in Table 2.

Table 2. Hydrogenation of 1-Decene Catalyzed by the System Consisting of Cp_2ZrCl_2 / 3 Equiv. of Various Grignard or Organolithium Reagents[a)]

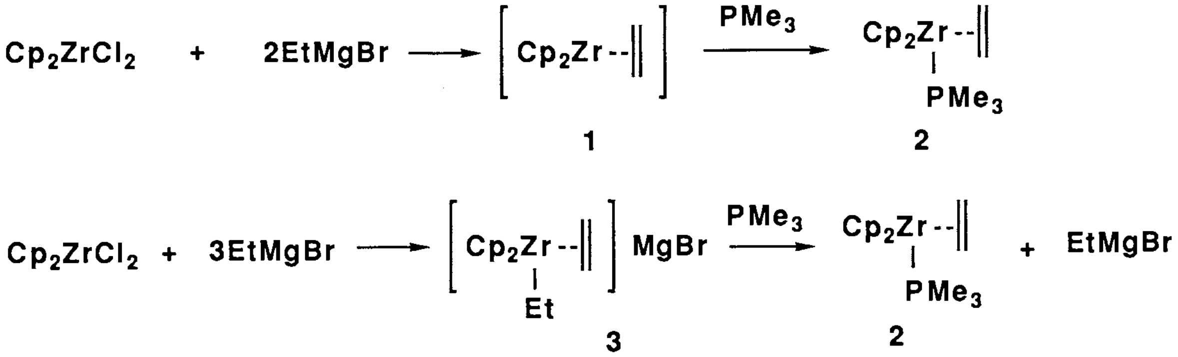
Reagent	Conversion of 1-decene/%	Yield of decane/%
MeMgBr	3	1
MeLi	5	5
EtMgBr	100	98
n-PrMgBr	100	96
iso-PrMgBr	81	59
n-BuMgCl	84	71
n-BuLi	100	97

a)Cp_2ZrCl_2:Reagent:1-decene = 0.2:0.6:1, Temperature: 50 °C, Solvent: THF, Time:24 h.

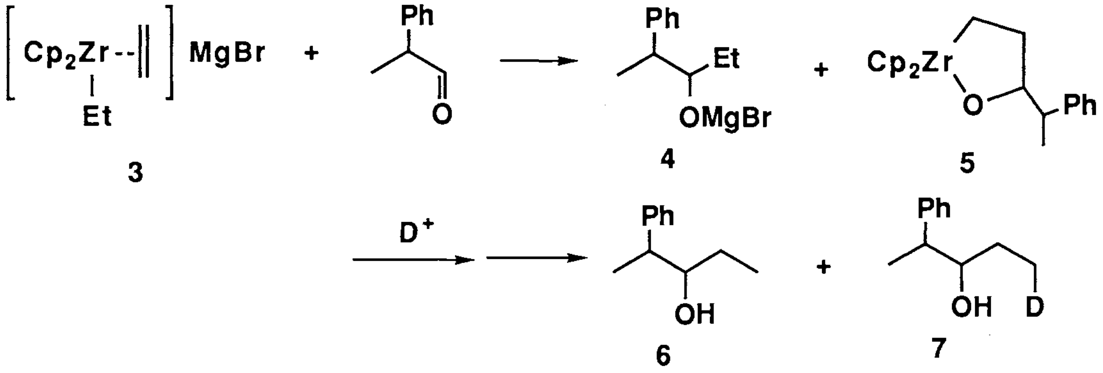
The reaction of MeMgBr with Cp_2ZrCl_2 gave a good yield of Cp_2ZrMe_2 based on Zr. This Zr(IV) species was not active for hydrogenation of 1-decene under conditions used here. Since Cp_2ZrMe_2 cannot decompose via reductive β-elimination to give a $Cp_2Zr(II)$ species, those $Cp_2Zr(IV)$ species capable of producing $Cp_2Zr(II)$ must be required for hydrogenation.

In order to investigate the zirconium species formed in the reaction of Cp_2ZrCl_2 with an excess of EtMgBr, the following reactions were carried out. It is known that the reaction of Cp_2ZrCl_2 with 2 equiv. of EtMgBr gave zirconocene-ethylene complex $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$ **2** in high yield in the presence of

PMe_3.[3d)] In the absence of PMe_3 , novel species $Cp_2Zr(CH_2{=}CH_2)$ **1** was detected. Its ^1H 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 PMe_3 to this led to disappearance of both peaks at 5.5ppm and 0.7 ppm and appearance of signals of **2**. In the ^1H NMR spectrum of **2**, the two CH_2 moieties of the ethylene ligand are not equivalent because of coordination of PMe_3. On the other hand ^1H NMR spectrum of **1** showed that those two CH_2 moieties are equivalent. Various reactions of the complex **1** have already been reported.[2,10)]



The reaction of Cp_2ZrCl_2 with 3 equiv. of EtMgBr afforded a novel species **3**, which was tentatively assigned to a zirconate complex $[Cp_2ZrEt(CH_2{=}CH_2)]MgBr$. Its ^1H NMR spectrum revealed a characteristic broad singlet at 5.3 ppm assignable to the Cp protons. When 4 or 8 equiv. of EtMgBr was added to Cp_2ZrCl_2, the formation of the same complex was observed. Treatment of **3** with PMe_3 gave **2** in 93% yield along with the formation of free 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 ^1H NMR spectrum. Low temperature NMR study did not give further informations. Therefore, an analogous ate complex $[Cp_2ZrPh(CH_2{=}CH_2)]MgBr$ **8** was prepared by the reaction of Cp_2ZrPh_2 with EtMgBr. The complex **8** gave **2** in 76% yield on treatment with PMe_3. Its ^1H 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 ^1H NMR spectroscopy. The formation of zirconium hydride species was observed (Cp: 5.6 ppm,



Zr-H: -3.6 ppm).[11] 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 1.3×10^{-2} min^{-1} and 2.5×10^{-3}min^{-1} at 23 °C, respectively. In the case of 4 equiv. of EtMgBr, the complex **3** was more stable. Decomposition rate constant was 9.9×10^{-4} 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_2ZrCl_2 = 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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