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STRUCTURES OF MONO- AND BIS(2-BUTENYL)ZIRCONIUM COMPLEXES IN SOLUTION AND THREO SELECTIVE INSERTION REACTION OF ALIPHATIC ALDEHYDES

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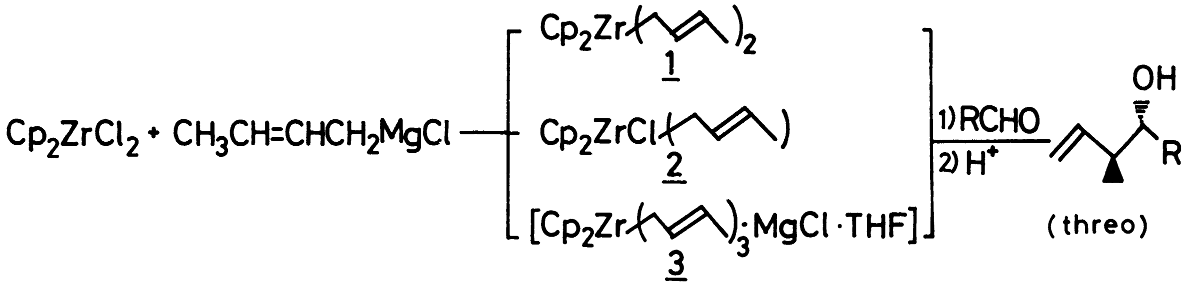
2-Butenyl group of $Cp_2ZrCl(C_4H_7)$, $Cp_2Zr(C_4H_7)_2$ and $[Cp_2Zr(C_4H_7)_3 \cdot MgCl \cdot THF]$ prepared from Cp_2ZrCl_2 and 2-butenylmagnesium chloride has essentially the (E)-configuration. These complexes react with aldehydes threo selectively at -78°C. $Zr(OR)_4/C_4H_7MgCl$ and $Ti(OR)_4/C_4H_7MgCl$ systems also serve as efficient reagents for threo selective synthesis of methylhomoallyl alcohols.

Diastereoselective synthesis of β-alkylhomoallyl alcohols via allylic metal compounds is one of the important subjects in the organic chemistry.[1] Recently, a butenylzirconium complex prepared *in situ* from 2-butenylmagnesium chloride and bis(cyclopentadienyl)zirconium chloride (Cp_2ZrCl_2) was reported by Y. Yamamoto et al. to be an efficient reagent for threo selective synthesis of β-methylhomoallyl alcohols.[2] Similar regioselective reaction was also found by us for the addition of ketones to Cp_2ZrCH_3((E)-2-butenyl).[3] The structural study and chemical characterization of these complexes are required to clarify the reaction pathway. This paper describes 1) preparation and the structure of 2-butenylzirconium complexes in solution and 2) diastereoselective reaction with aldehydes.

Bis(cyclopentadienyl)Zr(2-butenyl)$_2$ 1 was readily prepared by stirring a 1:2 mixture of Cp_2ZrCl_2 and 2-butenylmagnesium chloride (C_4H_7MgCl) in ether or THF at ambient temperature for 2 h. The yield was 90 %. The resulting complex 1 was isolated as pale yellow crystals (mp. 47°C) by recrystallization from hexane at -20°C.[4] This method, however, can not be applied to the preparation of pure Cp_2ZrCl(2-butenyl) 2, because the 1:1 reaction of Cp_2ZrCl_2 with C_4H_7MgCl in ether at -20~30°C gave a 95/5 mixture of 1 and 2. This is due to the insolubility of the

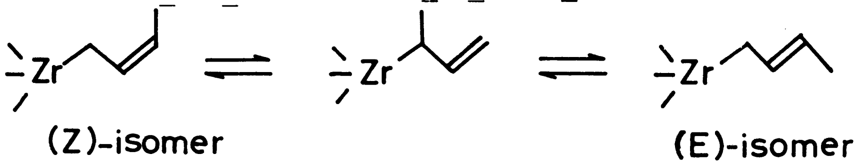
Cp_2ZrCl_2 in ether; i.e., ether soluble species $Cp_2ZrCl(C_4H_7)$ immediately react with C_4H_7MgCl to give 1. The corresponding reaction proceeds homogeneously at 0~20°C when THF was used as solvent but it also gave a mixture (1, 2 and $[Cp_2Zr(C_4H_7)_3 \cdot MgCl \cdot THF]$ 3) in 50/42/8 ratio as confirmed by the ^{1}H-NMR spectrum of the product.



(1)

Mono-2-butenylzirconium complex 2 was first prepared successfully by the disproportionation reaction; i.e., a 1:1 mixture of Cp_2ZrCl_2 and $Cp_2Zr(C_4H_7)_2$ was heated to 70°C for 10 h in THF and the product was recrystallized from hexane (mp. 78°C).[5] The complex 3 was obtained as orange crystals in 80 % yield by the 1:1 reaction of 1 with C_4H_7MgCl in THF at 20°C followed by recrystallization from THF at -20°C.[6] The chemical constitution of these complexes was determined by analysis of metal, NMR spectra and gas chromatographic analysis of the hydrolysis products.

The ^{1}H-NMR chemical shifts show that two butenyl groups of 1 and three butenyl groups of 3 are magnetically equivalent, respectively, and are bound to metal by σ-bond at CH_2 carbon. The proton-proton coupling constant, $J_{2,3}$, for 1, 2 and 3 are 15.5, 15.4 and 14.2 Hz, respectively, at -70°C to indicate that 2-butenyl group has essentially the (E)-configuration. The magnitude of the coupling constant of $J_{2,3}$ for 1, was 14.4 Hz at 30°C and increased to 16.0 Hz at -90°C in THF-d_8 suggesting that the equilibrium shown in eq. 2 exists and shifts to the right by lowering the temperature. The (E)/(Z) ratio for 1, 2 and 3 at -70°C was calculated to be 87/13, 85/15 and 55/45, assuming the coupling constants, 16.0 and 12.0 Hz for (E) and (Z)-species.[7] Similar equilibrium is known for C_4H_7MgCl in ether (E/Z ratio was 60/40).[8]



(2)

The results of reaction of complexes 1-3 with aliphatic aldehydes are shown in Table 1. The threo selectivities observed for 1, 2, and related complexes are quite similar to the values (73~88 %) reported for the butenylzirconium complex prepared *in situ*. The selectivity could be improved by lowering the reaction

Table 1. Threo Selective Insertion of Aldehydes to Zirconium Complexes[a)]

Complex	Reaction temp.(°C)	Threo selectivity		
		CH_3CHO	C_2H_5CHO	$i\text{-}C_3H_7CHO$
1	30	78	79	72
	0	80	81	77
	-78	88	89	82
	-110	91	92	86
2	-78	77	78	74
3	-78	58	66	55
$Cp_2ZrCH_3(C_4H_7)$[b)]	-78	81	90	76
$Cp_2Zr(OC_5H_{11})(C_4H_7)$[c)]	-78	90	90	89

a) One molar amount of aldehyde was added to the complexes. Yields were 87-95 %. b) Prepared from $Cp_2ZrCl(CH_3)$ and C_4H_7MgCl. c) Prepared from Cp_2ZrCl_2/lithium amylalkoxide/C_4H_7MgCl.

temperature (or increasing the (E)-2-butenylzirconium species) to -110°C. To understand the mechanism, the preparation of (Z)-isomer of 1 or 2 seems necessary to check whether the erythro-isomer is generated from the (Z)-isomer. However, preparation of (Z)-isomers of 1 or 2 by reaction of Cp_2ZrCl_2 with (Z)-2-butenylpotassium in THF at -20°C failed because it gave only the (E)-isomer. It should be noted that the corresponding(2-butenyl)titanocene species also proceed with highly threo selective addition to aldehydes.[9)]

To evaluate the role of auxiliary ligand in the zirconium complexes, we have examined the reaction of aldehyde with zirconium or titanium complexes bearing an OR ligand; i.e., $Zr(OR)_4/C_4H_7MgCl$ (R; C_2H_5, $i\text{-}C_4H_9$)[10)] or $Ti(OR)_4/C_4H_7MgCl$ (R; C_2H_5, $i\text{-}C_3H_7$, C_4H_9)[11)] which are readily available by the 1:1 reaction of $Zr(OR)_4$ or

Table 2. Stereoselective Reaction Using Metal Alkoxide Derivatives[a)]

Complex	Reaction temp.(°C)	Threo selectivity(%)		
		CH_3CHO	C_2H_5CHO	$i\text{-}C_3H_7CHO$
$Zr(OC_2H_5)_3(C_4H_7)$	30	70	78	80
	-78	79	84	83
	-110	90	93	83
$Zr(O\text{-}t\text{-}C_4H_9)_3(C_4H_7)$	-78	78	89	83
$Zr(S\text{-}t\text{-}C_4H_9)_3(C_4H_7)$	-78	75	80	72
$Ti(OC_2H_5)_4/C_4H_7MgCl$[b)]	-78	77	80	78
$Ti(O\text{-}i\text{-}C_3H_7)_4/C_4H_7MgCl$[b)]	-78	80	85	87
$Ti(OC_4H_9)_4/C_4H_7MgCl$[b)]	-78	80	82	80

a) Molar ratio of aldehyde/complex is 1.0. The product yield was 90-95%.
b) 1/1 mixture was prepared at -20°C.

$Ti(OR)_4$ with C_4H_7MgCl in THF at -20°C. The threo selectivity obtained with these systems (Table 2) is comparable to the results observed for 1 and 2. Thus, metal alkoxides serve as a useful reagent for facile threo selective synthesis of β-methylhomoallyl alcohols. $Cp_2Zr(OC_{10}H_{19})_2$ and $Zr(OC_5H_{11})_4$ prepared from (+)-menthol or (+)-amyl alcohol were also useful as metal alkoxides but the asymmetric allylation was not observed. These results indicate that the steric effect of ligands is not essential for controlling the stereoselectivity. The strong M-O bonding character of Zr and extreme preference of the (E)-configuration is responsible for the observed high selectivity.

References

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4) ^1H-NMR of 1 at -70°C(d_8-toluene); 5.33(dt, $J_{2,3}$=15.5 Hz, CH), 5.29(s, Cp), 4.35(dq, CH), 1.77(d, J=6.4 Hz, CH_3), 1.43(d, J-10.0 Hz, CH_2). Found: Zr, 24.1% (metal oxide method). Calcd for $C_{18}H_{24}Zr$: Zr, 24.5%.
5) ^1H-NMR of 2 at 30°C(d_8-toluene); 5.82(s, Cp), 5.14(dt, J=15.0 Hz, CH), 4.99 (dq, CH). 1.97(d, J=7.9 Hz, CH_2), 1.84(d, J=6.2 Hz, CH_3). Found: Zr, 28.7% (metal oxide method). Calcd for $C_{14}H_{17}ZrCl$: Zr, 29.2%.
6) ^1H-NMR of 3 at 30°C(d_8-toluene); 5.33(s, Cp), 5.10(dt, $J_{2,3}$=14.2 Hz, CH), 4.37(dq, CH), 2.07(d, J=6.9 Hz, CH_3), 1.78(d, J=6.0 Hz, CH_3), 3.98 and 1.49 (m, THF). Found: Zr, 17.5; Mg, 4.6% (EDTA titration). Calcd for $C_{26}H_{39}Zr$-MgOCl; Zr, 17.6; Mg, 4.7%.
7) Values of $J_{2,3}$ for 2-butenyltrimethylsilane were used as standards. Although the values for (E)- and (Z)-isomers of the alkenylsilane are reported to be 15.5 and 12.0 Hz, respectively, we employed here $J_{2,3}$=16.0 Hz (the value obsereved at -90°C for 1) as the coupling const. for the (E)-isomer of 1-3. See, H. Sakurai, Y. Kudo, and H. Miyoshi, Bull. Chem. Soc. Jpn., 49, 1533 (1976).
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10) The constitution of an orange semi-solid obtained from the benzene extract was determined to be $Zr(OR)_3(C_4H_7)$ by gas chromatographic analysis of the hydrolysis product.
11) The reaction of $Ti(O\text{-}i\text{-}C_3H_7)_3/LiC_4H_7$ with PhCHO to give a threo-homoallyl alcohol was recently reported; L. Wilder and D. Seebach, Helv. Chim. Acta., 65, 1085 (1982).

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