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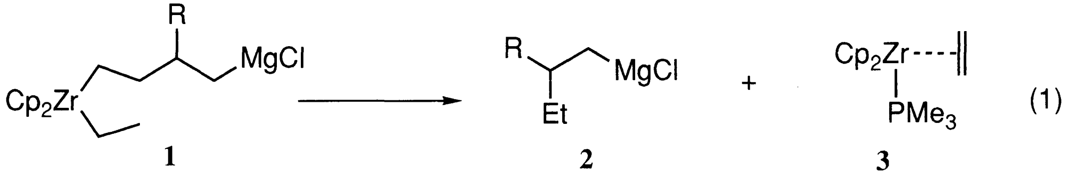
Factors Affecting the Unusual Reactivity Order in the β-Hydrogen Abstraction of Dialkylzirconocenes

Ei-ichi NEGISHI,* Thinh NGUYEN, John P. MAYE, Daniele CHOUEIRI,
Noriyuki SUZUKI,† and Tamotsu TAKAHASHI*†
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.
†Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444

Competitive β-hydrogen abstraction of "mixed" dialkylzirconocenes and kinetic measurements of decomposition of methyl(alkyl)zirconocenes reveal unexpected relative reactivity of alkyl groups as β-hydrogen donors, such as *s*-Bu > *t*-Bu ≥ Et > *n*-Bu > *i*-Bu, which correlate well in most cases with the reactivity order of: β-methyl > β-methylene > β-methine. Some mechanistically crucial features of the reaction are also discussed.

β-Hydrogen abstraction of dialkylzirconocenes to give the corresponding zirconocene-alkene complexes and alkanes has been shown to provide a convenient route to highly reactive zirconocene derivatives that are useful in both stoichiometric[1,2] and catalytic[3,4] reactions. While some aspects, such as the nondissociative nature,[5] of the reaction have been clarified, other puzzles have emerged for clarification. For example, the reaction of Cp_2ZrCl_2, where Cp = η^5-C_5H_5, with 2 equivalents of *t*-BuLi, which was shown to proceed via Cp_2Zr(Bu-*t*)(Bu-*i*), readily provides Cp_2Zr-isobutylene as a source of "Cp_2Zr". In sharp contrast, the corresponding reaction with 2 equivalents of *i*-BuLi gives Cp_2Zr(Bu-*i*)$_2$ as a relatively stable species.[6] In the reaction of 1-alkenes with ethylmagnesium derivatives catalyzed by Cp_2ZrCl_2, we have been led to conclude that



1 **2** **3**

a putative intermediate **1** regioselectively decomposes to give the observed products **2** and **3**.[3a] The potential synthetic significance vis-a-vis various puzzling results promoted us to investigate the scope and nature of the β-hydrogen abstraction reaction of dialkylzirconocenes and related species. For late transition metal dialkyls, similar thermal decomposition reactions of unsymmetrical dialkylplatinum complexes have been reported.[7]

Chloro(alkyl)zirconocenes, prepared by either hydrozirconation[8] of alkenes or treatment of Cp_2ZrCl_2 with alkyllithiums[6] (one equivalent), were treated with one equivalent each of alkyllithiums[9] to generate *in situ* a series of "mixed" dialkylzirconocenes. All chloro(alkyl)zirconocenes and most of the "mixed" dialkylzirconocenes herein reported were generated in ≥90% yields, as judged by ^{1}H NMR analysis of their Cp signals. The β-abstraction reaction of dialkylzirconocenes was also monitored by ^{1}H NMR spectroscopy in the presence of 1-2 equivalents of PMe_3. The experimental results summarized in Table 1 exhibit some unusual order of reactivity of alkyl groups as β-hydrogen donors. Thus, analysis of the products of competitive β-abstraction reaction of Cp_2Zr(Et)R, where R is *n*-Bu, *i*-Bu, *s*-Bu, and *t*-Bu has revealed the reactivity order: *s*-Bu > *t*-Bu >

Table 1. Thermal Decomposition of Dialkylzirconocenes in the Presence of PMe_3

	$Cp_2ZrR^1R^2$		Yield of $Cp_2Zr(alkene^i)(PMe_3)$ / %a)		
entry	R^1	R^2	$i = 1$	$i = 2$	total
1	Et	*n*-Bu	88	12	100
2	Et	*n*-Decyl	73	<3	73-76
3	Et	*i*-Bu	90	<2	90-92
4	Et	*n*-Hex(Et)$CHCH_2$	70	<2	70-72
5	Et	*s*-Bu	8	86b)	94
6	Et	*t*-Bu	12	53	65
7	Et	$PhCH_2CH_2$	28	52	80
8	*n*-Decyl	*i*-Bu	90	5	95
9	*n*-Decyl	*s*-Bu	<2	95b)	95-97
10	*n*-Decyl	*t*-Bu	9	82	91
11	*n*-Dodecyl	$PhCH_2CH_2$	10	87	97
12	*n*-Hex(Et)$CHCH_2$	*t*-Bu	<2	63	63-65

a)$Alkene^i$ ($i = 1$ and 2) are produced from R^i ($i = 1$ and 2), respectively. The products were stereoisomeric mixtures of the distal and proximal isomers except for $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$. The combined amounts of the two isomers are shown. b)Only 1-butene complex was formed. See Ref.10.

Table 2. The First-Order Rate Constants for the β-Hydrogen Abstraction Reaction of Cp_2ZrMeR

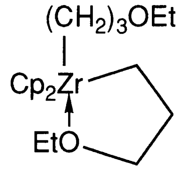
	Rate constant (10^2 x k_1) / min^{-1} a)			
R of Cp_2ZrMeR	in the presence of PMe_3		in the absence of PMe_3	
s-Bu	3.65 (0 °C)		3.90 (0 °C)	
t-Bu	0.61 (0 °C)		0.52 (0 °C)	
Et	0.84 (0 °C)	5.23 (20 °C)	0.52 (0 °C)	5.05 (20 °C)
n-Bu		0.75 (20 °C)		0.83 (20 °C)
i-Bu		0.17 (20 °C)		0.19 (20 °C)

a)The error range in each case was <10%.

Et > *n*-Bu > *i*-Bu. Kinetic measurements of the first-order β-abstraction reaction of $Cp_2Zr(Me)R$ prepared by treatment of $Cp_2Zr(Me)Cl$[11a)] with one equivalent of RLi (Table 2) have further confirmed the reactivity. Clearly, the order of reactivity shown above does not correlate with the overall steric requirements of alkyl groups. On the other hand, all of the results in Table 1 and 2 with the exception of those cases where the $PhCH_2CH_2$ group is involved are in agreement with the generalization that *the reactivity of alkyl ligands as β-hydrogen donors correlates with the degree of substitution at the β-carbon centers and that it decreased in the order: β-methyl > β-methylene > β-methine.* A few additional comments are in order. First, there has been no sign of any interaction between Cp_2Zr-alkene-PMe_3 complexes with alkanes formed as byproducts. In this sense, the reaction must be essentially irreversible, and the observed results are kinetic rather than thermodynamic in nature. Second, the reaction rates are virtually unaffected by PMe_3 (Table 2). This conclusion has been further supported by the finding that addition of PMe_3 to Cp_2ZrMe_2 did not cause any detectable shift of the ^1H NMR Cp signal, indicating that even the sterically least demanding dialkylzirconocene, i.e., Cp_2ZrMe_2, does not detectably interact with PMe_3. Thus, the role of PMe_3 is merely to trap and stabilize the β-abstraction products in the form of Cp_2Zr-alkene-PMe_3. Third, the greater reactivity of $PhCH_2CH_2$ relative to that of Et is anomalous, but it may readily be accommodated by invoking benzylic stabilization. While predictive comparison within one category e.g., β-methyl containing Et, *s*-Bu, and *t*-Bu, remains to be difficult, this study permits some rationalization and prediction of the course of β-hydrogen abstraction of dialkylzirconocenes.

A typical procedure for β-hydrogen abstraction reaction of dialkylzirconocenes is as follows. Pure $Cp_2Zr(CH_3)Cl$ was prepared by treatment of $(Cp_2ZrCl)_2O$ with trimethylaluminum.11b) Ethyllithium was cleanly prepared from ethyl iodide and *t*-BuLi in ether.9) To a solution of $Cp_2Zr(CH_3)Cl$ prepared above in THF was added 1 equiv of ethyllithium at -78 °C and the mixture was stirred for 1h. $Cp_2Zr(Me)Et$ was obtained in 90% yield. Its NMR spectra for identification of these species were obtained at -20 °C because β-abstraction reaction gradually proceeds at higher temperature. Its ^1H NMR spectrum in a mixture of C_6D_6, THF, ether and pentane (4 : 4 : 1 : 1; 0.08 mol dm^{-3}) showed singlet peak assigned to Cp at 5.96, and singlet peak at -0.30 for methyl group attached to zirconium, and a peak for methylene of ethyl group at 0.30 ppm as a quartet with 8 Hz of coupling constant. Methyl peak of ethyl group was covered with solvent signals. The ^{13}C NMR spectrum cleanly showed four peaks of $Cp_2Zr(Me)Et$ at 110.80, 44.11, 30.12 and 16.69 ppm. To this solution of $Cp_2Zr(Me)Et$ was added 1.1 equiv of trimethylphosphine, if used, at -78 °C. The β-hydrogen abstraction reaction of $Cp_2Zr(Me)Et$ was monitored at 20 °C or 0 °C by ^1H NMR spectroscopy. Characteristic peaks for ethylene complexes10) appeared and grew as β-abstraction proceeded. Decrease of the Cp signal of $Cp_2Zr(Me)Et$ was observed to determine the rate constant. The rate constants for β-hydrogen abstraction of $Cp_2Zr(Me)Et$ were 5.23×10^{-2} min^{-1} (20 °C) and 0.84×10^{-2} min^{-1} (0 °C) in the presence of PMe_3 and 5.05×10^{-2} min^{-1} (20 °C) and 0.52×10^{-2} min^{-1} (0 °C) in the absence of PMe_3. During the reactions, formation of Cp_2ZrMe_2 due to disproportionation reaction of $Cp_2Zr(Me)Et$ was not observed.

The following results shed some light on the mechanism of the reaction. First, treatment of Cp_2ZrCl_2 with 3 equivalents of *n*-BuLi in THF at -28 °C followed by warming to 22 °C produced after 24 h a 50% yield of $LiCp_2Zr(Bu\text{-}n)_3$ which displayed a ^1H NMR singlet at δ 5.80 ppm for the Cp groups and only five ^{13}C NMR signals at δ 14.25, 30.38, 36.28, 42.52, 110.66 ppm. It showed no sign of decomposition for at least 48 h at 22 °C. Treatment of Cp_2ZrCl_2 with 2 equivalents of 3-ethoxypropyllithium11) yielded $Cp_2Zr(CH_2CH_2CH_2OEt)_2$. Its rate of decomposition was 700 times as slow as that of $Cp_2Zr(Bu\text{-}n)_2$. It is likely that the γ-ethoxy group participates in chelation leading to the observed stabilization, as in **4**. The two examples shown above point to the significance of the Zr valence shell empty orbital. Second, β-hydrogen abstraction of **5**12) in the presence of PMe_3 produced in 90% combined yield Cp_2Zr-alkene-PMe_3 complexes showing two predominant ^1H NMR signals at δ 5.34 and 5.36 ppm. However, it was not feasible to determine the ratio of **6a** to **6b**. Treatment of



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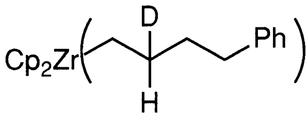

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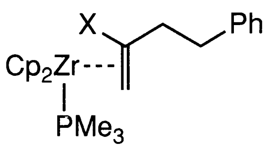
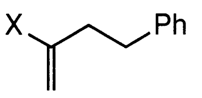
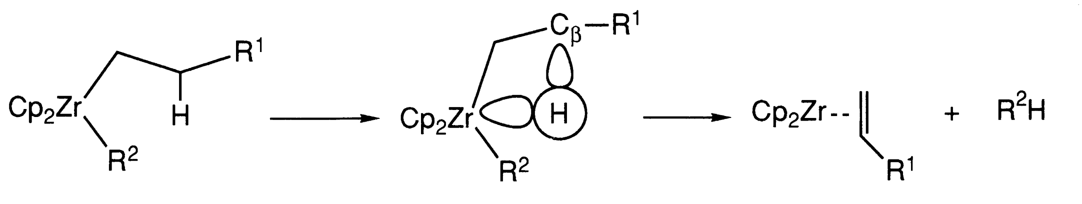


6 (**a**: X = H, **b**: X = D)



7 (**a**/**b** = 1/ 5.7)



(2)

this mixture with iodine released two expected alkenes **7a** and **7b** in 82% combined yield in a ratio of 1 to 5.7, indicating $k_H/k_D = 5.7$. Coupled with the first-order kinetics and the previously reported nondissociative nature of the reaction,$^{5)}$ the results presented above strongly support the mechanism involving agostic interaction of a H-C$_\beta$ bond with Zr (Eq. 2), which provides a rational basis for the predictive reactivity order herein presented.

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