Reaction of Alkenylzirconocenes with Dialkylzirconocenes: Unexpected Formation of Bimetallic (μ-Alkynyl)zirconocene Complexes

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Summary: Reaction of alkenylzirconocenes $Cp_2ZrX(MeC{=}CH_2)$ (X = Cl, Br) with dialkylzirconocenes Cp_2ZrR_2 (R = Me, Et, Bu) yielded the unexpected bimetallic zirconocene complexes $Cp_2Zr(\mu\text{-}X)(\mu\text{-}C{\equiv}CCH_3)ZrCp_2$ (X = Cl, Br). Its structure (X = Cl) was determined by X-ray crystallography. The monitoring of the reaction of Cp_2ZrBu_2 with $Cp_2ZrBr(MeC{=}CH_2)$ revealed that the first step of this reaction was an exchange reaction of the Bu and Br groups.

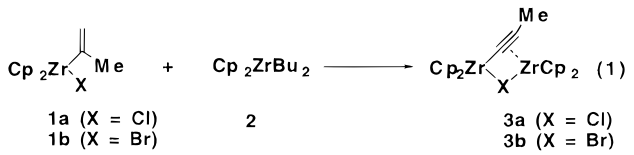
Introduction

Bimetallic electrophilic transition-metal complexes are attractive because of the potential for both metal centers to interact simultaneously with an organic molecule. Recently, we have reported the formation of the alkenylzirconocene complex $Cp_2ZrX(MeC{=}CH_2)$ (X = Cl (**1a**), Br (**1b**)) by oxidative-addition reactions of 2-halopropenes.[4] During subsequent reactivity studies we found the unexpected formation of bimetallic (μ-alkynyl)zirconocene complexes by the reaction of alkenylzirconocenes with dialkylzirconocenes. In this paper we wish to report the formation of the bimetallic zirconocene−alkynyl complex $Cp_2Zr(\mu\text{-}X)(\mu\text{-}C{\equiv}CCH_3)ZrCp_2$ (X = Cl (**3a**), Br (**3b**)) by the reaction of **1a** or **1b** with Cp_2ZrR_2 (R = Me, Et, Bu).

Results and Discussion

Erker and co-workers reported that the alkenyl-bridged zirconocene bimetallic complex $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}CH{=}CHPh)ZrCp_2$ and the alkynyl-bridged complex $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C{\equiv}CR)ZrCp_2$, can be prepared by the reactions of alkenylzirconocene $Cp_2ZrCl(CH{=}CHPh)$[5] and alkynylzirconocene $Cp_2ZrCl(C{\equiv}CR)$,[6] respectively, with "Cp_2Zr^{II}", which was produced *in situ* from Cp_2ZrPh_2 or $Cp_2ZrPh(CH{=}CHPh)$.[5]

Dibutylzirconocene is known as a source of "Cp_2Zr^{II} equivalent" (Negishi reagent).[7] Therefore, when alkenylzirconocene **1a**[4] was treated with Cp_2ZrBu_2 (**2**), we expected the formation of Erker's type of *alkenyl*-bridged complexes. However, the alkenyl-bridged complex $Cp_2Zr(\mu\text{-}X)(\mu\text{-}CMe{=}CH_2)ZrCp_2$ (**4**) was not formed, and complex **3a** was obtained unexpectedly, as shown in eq 1. The complex **3a** obtained here showed the same NMR data of the complex which was prepared by the reaction of an alkynylzirconocene with "Cp_2Zr".[6] Since the X-ray structure of this complex has not been reported, we determined its structure to verify the molecular geometry and identity.



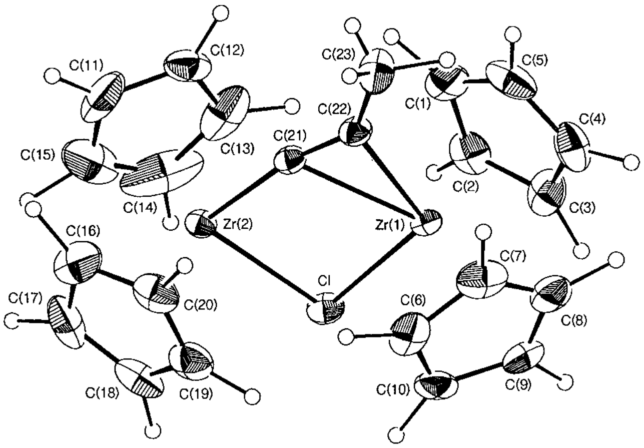


Figure 1. Perspective view of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C{\equiv}CCH_3)ZrCp_2$ (**3a**).

X-ray Crystal Structure of 3a. The molecular structure of the complex **3a** is shown in Figure 1. Crystallographic data and selected bond distances and angles are listed in Tables 1 and 2, respectively. Figure 1 clearly indicates that this complex contains two Zr atoms and a bridging alkynyl group. The Zr(1)−Zr(2) bond distance (3.4650(4) Å) is much larger than the sum of the Zr van der Waals radii (3.10 Å).[6] The C(21)−C(22) bond distance (1.286(4) Å) is slightly longer than for μ-C≡CR ligands (R = Ph, $SiMe_3$) in group 4 complexes, e.g., $[(C_5H_4CH_3)_2Zr]_2(\mu\text{-}C{\equiv}CPh)_2$ (1.261(2) Å),[6,8a]

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Table 1. Crystallographic Data for $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C{\equiv}CCH_3)ZrCp_2$ (3a)

complex	**3a**
formula	$C_{23}H_{23}ClZr_2$
fw	517.3
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	16.402(1)
b, Å	7.978(1)
c, Å	16.545(1)
β, deg	112.96(1)
Z	4
V, Å^3	1993(5)
μ(Mo Kα), cm^{-1}	11.69
cryst color	orange
cryst habit	prismatic
cryst size, mm^3	$0.2 \times 0.4 \times 0.4$
d_{calcd}, g/cm^3	1.72
diffractometer	Enraf-Nonius CAD-4
λ(Mo Kα), Å	0.710 73
T, K	293
scan range	$0.70 + 0.35 \tan \theta$
scan mode	$\omega - 2\theta$
scan speed, deg/min	variable
2θ range, deg	$2 \le 2\theta \le 60$
rflns measd	$0 \le h \le 23, 0 \le k \le 11, -23 \le l \le 23$
no. of rflns measd	5797
no. of rflns obsd ($\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$)	4829
R^a	0.040
$R_w{}^b$	0.049
S	1.89

[a] $R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o \rvert$. [b] $R_w = [\sum w \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2 / \sum w \lvert F_o\rvert]^{1/2}$; $w = [\sigma^2(F_o) + \{0.015(F_o)\}^2]^{-1}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Cp_2Zr(\mu\text{-}X)(\mu\text{-}C{\equiv}CCH_3)ZrCp_2$ (3a)

	Bond Distances		
Zr(1)−Zr(2)	3.4650(4)	Zr(2)−C(21)	2.121(3)
Zr(1)−Cl	2.6555(8)	C(21)−C(22)	1.286(4)
Zr(1)−C(21)	2.396(3)	C(22)−C(23)	1.490(5)
Zr(1)−C(22)	2.261(3)	C−C bond dist in Cp	1.28(2)−1.487(8)
Zr(2)−Cl	2.5563(9)		
	Bond Angles		
Cl−Zr(1)−C(21)	84.19(7)	Zr(2)−C(21)−C(22)	168.2(3)
Cl−Zr(1)−C(22)	116.09(8)	Zr(1)−C(22)−C(21)	79.8(2)
C(21)−Zr(1)−C(22)	31.9(1)	Zr(1)−C(22)−C(23)	139.0(2)
Cl−Zr(2)−C(21)	92.48(8)	C(21)−C(22)−C(23)	141.2(3)
Zr(1)−Cl−Zr(2)	83.31(2)	C−C−C bond angles in Cp	104.7(5)−111.4(5)
Zr(1)−C(21)−Zr(2)	100.0(1)		

$(Cp_2Zr)_2(\mu\text{-}C{\equiv}CSiMe_3)_2$ (1.249(7) Å),[8b] $Cp_2Zr(\mu\text{-}C{\equiv}CSiMe_3)(\mu\text{-}PhC{\equiv}C)ZrCp_2$ (1.247(4), 1.246(5) Å),[8c] and $Cp_2Zr(\mu\text{-}C{\equiv}CSiMe_3)(\mu\text{-}SiMe_3C{\equiv}C)Ni(PPh_3)$ (1.284(13) Å).[8d] However, this distance is substantially shorter than the C−C double bond of the μ-alkenyl group in $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}CH{=}CHPh)ZrCp_2$ (1.42(1) Å).[5] The two Zr−Cl bond distances, 2.656(8) and 2.556(9) Å, are consistent with those for the bridged Cl atom between the two Zr atoms (2.538(2) and 2.629(2) Å) in $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}CH{=}CHPh)ZrCp_2$.[5] The bond angle C(21)−C(22)−C(23) was 141.2(3)°, which is in a reasonable range for a bridging alkynyl C−C triple bond (134−148°).[8]

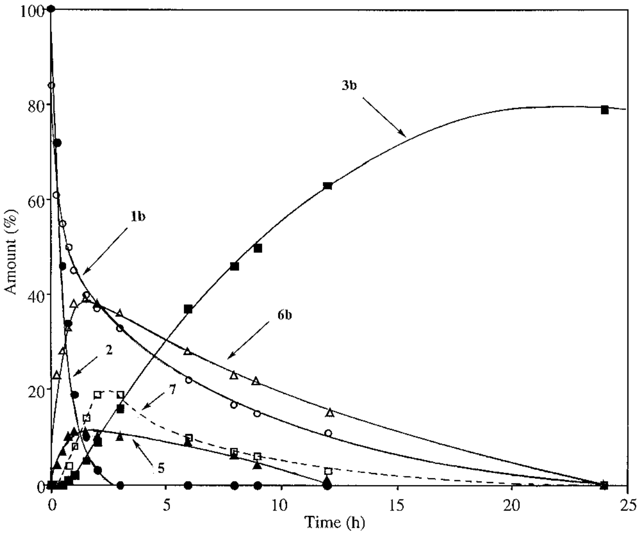
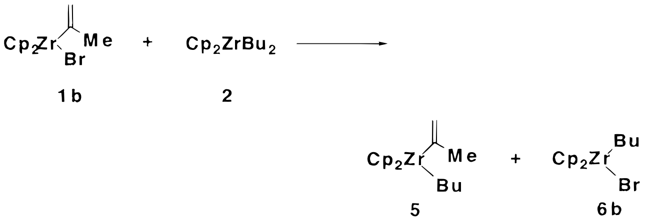
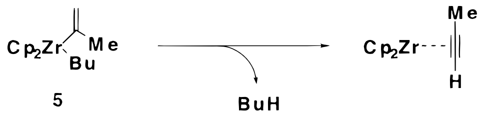


Figure 2. Reaction of $Cp_2Zr(MeC{=}CH_2)Br$ (**1b**) with Cp_2ZrBu_2 (**2**).

Mechanism. Since the result obtained here was quite puzzling to us, we followed the reaction of **1b** with **2** by ^1H NMR spectroscopy. The result is summarized in Figure 2. When 1 equiv of **2** is added to **1b**, two Cp signals at 6.11 and 5.93 ppm for **1b** and **2**, respectively, decrease after mixing. Two new peaks at 6.08 and 6.14 ppm assignable to the Cp groups of $Cp_2Zr(MeC{=}CH_2)Bu$ (**5**) and $Cp_2ZrBuBr$ (**6b**), respectively, emerge and grow to some extent (40% and 10% yields, respectively, after 1 h). These new peaks were consistent with those of the authentic samples **5** and **6b** prepared *in situ*. The formation of **5** and **6b** indicates that an exchange reaction of the Bu group of **2** with Br of **1b** occurs to give **5** and **6b**.



The two Cp peaks of **5** and **6b** at 6.08 and 6.14 ppm gradually decrease after 2 h and completely disappear after 24 h. The decrease of the peak assignable to **5** can be explained by β-hydrogen abstraction of **5**, giving a propyne complex. Actually, **5** prepared from **1b** and BuMgCl or BuLi gave $Cp_2Zr(CH_3C{\equiv}CH)(PMe_3)$ in the presence of PMe_3. The ^1H NMR spectrum of this propyne complex in THF showed the Cp signal, the Me group, and the terminal H of the propyne group at 5.28, 2.93, and 7.11 ppm, respectively, and the Me group of PMe_3 at 1.02 ppm. It is consistent with the known 1-hexyne complex $Cp_2Zr(C_4H_9C{\equiv}CH)(PMe_3)$, which shows the Cp signal, the terminal H of hexyne, and the Me group of PMe_3 at 5.29, 7.14, and 0.98 ppm, respectively.[9] In the absence of PMe_3, **5** reacted with 4-octyne to give 4-propyl-2,4-octadiene after hydrolysis. These data reveal that the formation of a propyne complex is reasonable. After 45 min, a new singlet at 5.78 ppm (compound **7**) appears. We tentatively assigned this compound **7** to the propyne complex or the oxidative-addition product **8**; however, unfortunately, complex **7** could not be fully characterized.



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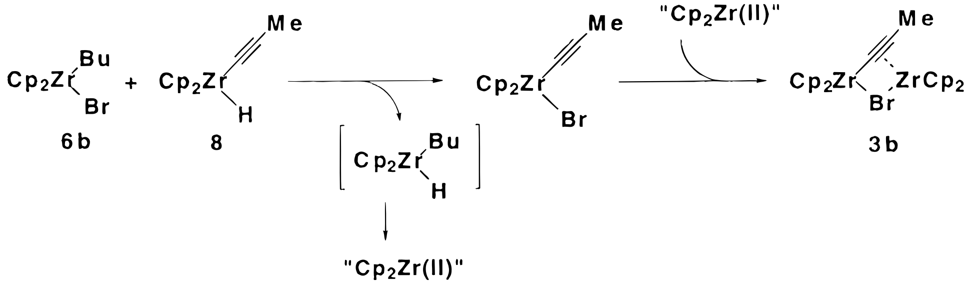
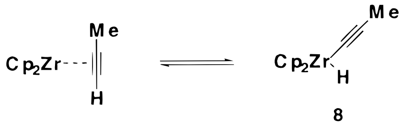
Scheme 1



This singlet peak at 5.78 ppm gradually increases to 20% yield after 2 h and then gradually decreases. After 24 h, it disappears.

The Cp signals of the final product **3b** appear at 5.36 and 5.47 ppm and gradually grow. The formation of **3b** from the propyne complex is not clear yet. However, the following two reactions are plausible. Oxidative addition of propyne to zirconocene gives $Cp_2ZrH(C{\equiv}CMe)$ (**8**):[10]



Further reaction of **6b** with **8** can provide the final product **3b** via an exchange reaction of Br of **6b** and the hydride of **8** (Scheme 1).

If there is no other reaction path, the rates of decrease of **1b** and **2** should be the same. However, as shown in Figure 2, the two rates were different, since **2** decomposes to Cp_2Zr^{II} species as already known.

The total amount of the Bu group of all the zirconium species gradually decreased. The decrease is attributed to a β-hydrogen abstraction reaction. In comparison with the rate of decrease of the Bu group, the exchange reaction rate of the Bu group of **2** with the Br group of **1b** was much faster.

In order to clarify this point, we carried out similar reactions of **1a** with other dialkylzirconocenes such as Cp_2ZrR_2 (R = Me, Et). Even with Cp_2ZrMe_2, the same product **3a** was obtained as we expected, even though the yield of **3a** was low (23%) and a higher reaction temperature (50 °C) was required. This is because the first alkyl−Br exchange step is very slow in the case of Cp_2ZrMe_2.

In addition, even after consumption of **2**, **1b** still reacts to give **3b**. This indicates that there must be several other reaction paths from **1b** to **3b**. Actually, formation of several small peaks, which could not be characterized, was also observed in ^{1}H NMR spectra during the reaction. Although we could not elucidate other reaction paths, the results we obtained above revealed that Cp_2ZrBu_2 did not play the usual role as a source of "zirconocene" equivalent but behaved as a dialkylzirconocene in the first step of this reaction.

Experimental Section

General Information. All reactions were carried out under a nitrogen atmosphere using standard Schlenk tube techniques. Diethyl ether, tetrahydrofuran (THF), and hexane were distilled over sodium and benzophenone. Zirconocene dichloride was purchased from Aldrich Chemical Co., Inc. Methyllithium (ether solution), ethylmagnesium bromide (THF solution), and *n*-butyllithium (hexane solution) were purchased from Kanto Chemicals Co., Ltd. 2-Bromo-1-propene, 2-chloro-1-propene, and 5-decyne were purchased from Tokyo Chemical Industry Co., Ltd. Complexes **1a** and **1b** were prepared by our method.[4]

NMR spectra were recorded on a JEOL EX-280 FT NMR spectrometer. Tetramethylsilane (TMS) was used as the reference for ^{1}H and ^{13}C NMR.

Reaction of Alkenylzirconocene 1a with Dialkylzirconocene Cp_2ZrR_2 (R = Me, Et, Bu): Formation of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C{\equiv}CCH_3)ZrCp_2$ (3a). To a solution of **1a** in ether, which was prepared from Cp_2ZrCl_2 (292 mg, 1.0 mmol) in 10 mL of ether, *n*-butyllithium (2.0 mmol in hexane solution), and 2-chloropropene (85 μL, 1.0 mmol), was added Cp_2ZrBu_2 generated from Cp_2ZrCl_2 (292 mg, 1.0 mmol) and 2.0 mmol of *n*-butyllithium (hexane solution) in 5 mL of ether. LiCl was removed through a frit, and the clear filtrate was allowed to stand at room temperature for 12 h. Dark red crystals precipitated from the solution. The crude product was recrystallized from THF to give pure dark red crystals of the title product **3a** (334 mg, 65% isolated yield). ^{1}H NMR (C_6D_6, $SiMe_4$): δ 2.63 (s, 3H, CH_3), 5.29 (s, 10H, C_5H_5), 5.38 (s, 10H, C_5H_5). ^{13}C NMR (CD_2Cl_2, $SiMe_4$): δ 21.27 ($^1J_{CH}$ = 127 Hz, CH_3), 104.04 ($^1J_{CH}$ = 157 Hz, C_5H_5), 105.60 ($^1J_{CH}$ = 158 Hz, C_5H_5), 177.94 (−C), 222.62 (−C). Anal. Calcd for $C_{23}H_{23}ClZr_2$: C, 53.40; H, 4.48; Cl, 6.85. Found: C, 53.20; H, 4.62; Cl, 7.01.[5] Dialkylzirconocenes (R = Me, Et) were used in a manner similar to the procedure described above for Cp_2ZrBu_2. Dialkylzirconocenes were prepared by the reaction of Cp_2ZrCl_2 with 2 equiv of either MeLi or EtMgBr in 5 mL of THF. The reaction of **1a** with Cp_2ZrMe_2 (50 °C, 24 h) and Cp_2ZrEt_2 (20 °C, 12 h) gave the same complex **3a** in 23% and 69% NMR yields, respectively.

Formation of $Cp_2Zr(\mu\text{-}Br)(\mu\text{-}C{\equiv}CCH_3)ZrCp_2$ (3b). This complex was prepared in the same manner as desribed above using 2-bromopropene instead of 2-chloropropene: orange crystals; isolated yield 63%. ^{1}H NMR (C_6D_6, $SiMe_4$): δ 2.64 (s, 3H, CH_3), 5.25 (s, 10H, C_5H_5)), 5.34 (s, 10H, C_5H_5). ^{13}C NMR (CD_2Cl_2, $SiMe_4$): δ 21.18 ($^1J_{CH}$ = 127 Hz, CH_3), 103.64 ($^1J_{CH}$ = 161 Hz, C_5H_5), 105.24 ($^1J_{CH}$ = 161 Hz, C_5H_5), 176.87 (−C−), 222.74 (−C−). Anal. Calcd for $C_{23}H_{23}BrZr_2$: C, 49.17; H, 4.13; Br, 14.22. Found: C, 49.54; H, 4.33; Br, 13.85.

X-ray Analysis of $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C{\equiv}CCH_3)ZrCp_2$ (3a). An orange crystal (dimensions 0.2 × 0.2 × 0.4 mm) suitable for X-ray diffraction studies was sealed in a capillary tube and mounted on an Enraf-Nonius CAD-4 diffractometer (Mo Kα, λ = 0.710 73 Å) equipped with a graphite monochromator. The cell dimensions were obtained by least-squares refinement of the setting angles for 25 reflections. Crystallographic data: fw 517.3, monoclinic, space group $P2_1/c$, $Z = 4$, a = 16.402(1) Å, b = 7.978(1) Å, c = 16.545(1) Å, β = 112.96(1)°, V = 1993(5) Å^3, D_{exptl} = 1.72 g cm^{-3}, and μ(Mo Kα) = 11.69 cm^{-1}. Diffraction data were collected in the $\omega-2\theta$ mode. A total of 5797 reflections ($2\theta_{max}$ = 60°) were measured, of which 4829 reflections were unique with $|F_o| > 3\sigma(|F_o|)$. The structure was

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solved by direct methods (SHELX-86[11]) and refined by full-matrix least-squares techniques using Xtal3.2[12] software on a Fujitsu S-4/5 workstation. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at the calculated positions with isotropic displacement parameters of their parent carbon atoms. Refinement of positional and thermal parameters led to convergence with $R(F) = \sum|F_o - F_c|/\sum|F_o| = 0.040$, $R(wF) = (\sum w(F_o - F_c)^2/\sum w(F_o)^2)^{1/2} = 0.049$, and GOF = 1.89.

Monitoring the Reaction of 1b with 2 by ^{1}H NMR. To a solution of 1.0 mmol of **1b** in 3 mL of THF was added at 0 °C Cp_2ZrBu_2 (**2**) generated from Cp_2ZrCl_2 (1.0 mmol, 292 mg) and 2.0 mmol of *n*-BuLi (hexane solution) in 3 mL of THF. A small amount of the mixture (0.35 mL) was transferred into a NMR tube containing 0.20 mL of C_6D_6 at −78 °C. ^{1}H NMR spectra of the mixture were measured at 15 °C. Yields were determined by integration of Cp signals of the zirconium species using mesitylene as an internal standard. ^{1}H NMR (C_6D_6 + THF, $SiMe_4$): **1b**, δ 6.11 (s, Cp); **2**, δ 5.93 (s, Cp); **5**, δ 6.08 (s, Cp); **6b**, δ 6.14 (s, Cp); **7**, δ 5.78 (s, Cp). Cp signals in ^{13}C NMR (C_6D_6 + THF, $SiMe_4$): **1b**, δ 113.38; **2**, δ 110.67; **5**, δ 111.14; **6b**, δ 111.96.

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Supporting Information Available: Tables of all atomic coordinates and equivalent isotropic and anisotropic displacement parameters for complex **3a** and a figure giving ^{1}H NMR spectra of the reaction mixture of **1b** and **2** (4 pages). Ordering information is given on any current masthead page.

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