Preparation of ethylene-bridged Group 14 metal–zirconocene complexes

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Abstract

The reactions of the zirconocene–ethylene complex $Cp_2Zr(CH_2=CH_2)(PMe_3)$ with Group 14 metal chlorides or alkoxides give ethylene-bridged group 14 metal–zirconocene complexes. A reaction mechanism via a five-membered intermediate which involves direct coupling of ethylene and single bonding is proposed. © 2000 Elsevier Science S.A. All rights reserved.
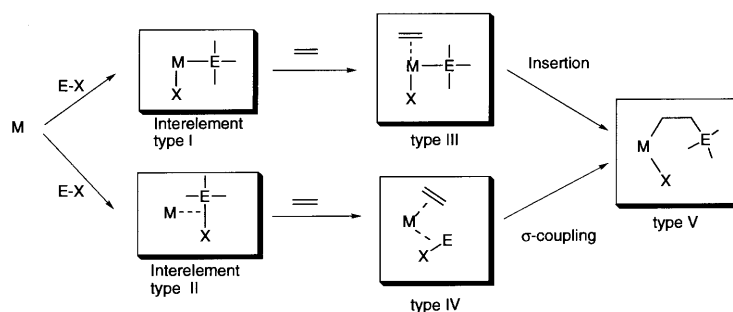
Keywords: Zirconocene; Ethylene complexes; Tin; Germanium; Silyl; Ethylene-bridged; σ-coupling

1. Introduction

The following two types of inter-element compounds should be considered as reactive species when a low valent transition metal M is treated with Group 14 metal compounds E–X [1–5] as shown in Scheme 1. Both type I and type II afford the same product type V via types III and IV, respectively, in the reaction with olefins. Reaction of type I compound with olefin is well known as insertion of olefin [6]. For example, for transition metal catalyzed hydrosilation of olefins, generally this type of insertion giving type V is accepted as the key step of the catalytic reactions. On the other hand, σ-coupling between olefin and E–X on a transition metal as shown by type IV to give type V is very rare.

Recently we have investigated the reactions of zirconocene–ethylene complexes [7]. This complex reacts with various unsaturated compounds such as alkynes, alkenes and ketones [8]. In all the cases five-membered zirconacycles are formed. However the reaction of olefin complexes with a single bond has not been intensively investigated [7b,9]. If the reaction with a single bond (σ-coupling) occurs as well as the case of unsaturated bonds, it is expected that A–B single bond cleavage occurs to give a zirconocene complex (type V) as shown in Scheme 2.

Scheme 1.

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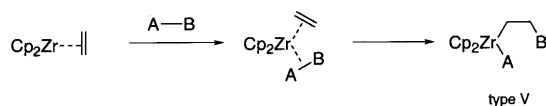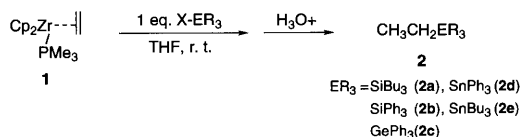
Scheme 2.

2. Results and discussion

2.1. Reaction of zirconocene ethylene complex 1 with Group 14 metal compounds: formation of 2a–2e

Zirconocene–ethylene complex $Cp_2Zr(CH_2=CH_2)$ (PMe_3) (1) was prepared by treatment of Cp_2ZrCl_2 with two equivalents of EtMgBr followed by addition of PMe_3 [7a]. As shown in Scheme 3, the reaction of the zirconocene–ethylene complex 1 with group 14 metal compounds afforded ethylated compounds 2 after hydrolysis. Yields are shown in Table 1 [10].

2.2. Formation of 4a–4e

Deuterolysis of the reaction mixture of 1 and Ph_3SiCl was performed and resulted in the formation of $DCH_2CH_2SiPh_3$ (2b-d) with 93% D incorporation (Scheme 4). This indicates that the ethylene-bridged silicon–zirconocene complex 4b was formed in situ.

Formation of zirconocene complex 4b was observed by NMR spectroscopy. The ^{1}H-NMR spectrum of 4b showed a singlet at 6.05 ppm assigned to Cp protons. Its chemical shift is reasonable for zirconium(IV) species. The ^{13}C-NMR spectrum of 4b shows three signals besides phenyl carbons at 113.13, 45.11, 17.87 ppm assignable to Cp, $ZrCH_2$ and CH_2Si, respectively. The Cp signal at around 113 ppm is consistent with that of

zirconium(IV) compounds. The low field shift to 45.11 ppm of the methylene carbon is characteristic of the methylene attached to zirconocene as usually observed. Complex 4b was also prepared by hydrozirconation of vinyltriphenylsilane. The NMR spectra of 4b prepared from vinyltriphenylsilane were consistent with that prepared from 1 and triphenylsilyl chloride. Deuterolysis of the complex 4b prepared from vinyltriphenylsilane gave 2b-d in 84% yield with 97% D incorporation.
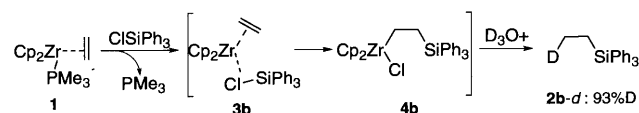
Ethylene-bridged complexes containing germanium and tin 4c–4e were also prepared by the reaction of 1 with tin and germanium compounds, respectively (Scheme 5). The tin–zirconium complexes were not so stable compared with 4b. The ethylene-bridged tin–zirconium complexes could also be prepared by the hydrozirconation reaction of vinyltriphenyltin or vinyltributyltin.
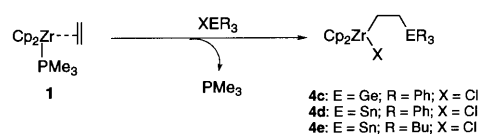
2.3. Spectral data of 4b–4e

Characteristic NMR data for the ethylene-bridged tin–zirconium or germanium–zirconium complexes are similar to those of 4b as summarized in Table 2. For comparison, chemical shifts of hydrolysis products are also shown in Table 2. It is notable that the satellite peaks of methylene carbons due to ^{117}Sn and ^{119}Sn were observed. The satellite peaks on DEPT spectra are shown in Fig. 1. The DEPT spectra of the complexes 4d and 4e clearly indicate zirconium and tin are connected by ethylene. These complexes were not stable. They gradually decomposed in solution at room temperature.

2.4. Reaction mechanism for the formation of 4b–4e

As a plausible mechanism of the formation of the ethylene-bridged complexes, two pathways A and B are shown in Scheme 6. Path A involves oxidative addition of the E–X bond to zirconocene(II), and then the ethylene molecule inserts into the Zr–E bond to give the ethylene-bridged complex. On the other hand, in path B, the σ-coupling of the E–X bond occurs with an

Scheme 3.

Table 1
Reaction of 1 with Group 4 metal compounds

$X–ER_3$	Reaction time	Yield (%) [a]	Product
$Cl–SiBu_3$	12 h	71 (49)	2a
$Cl–SiPh_3$	6 h	82 (42)	2b
$Cl–GePh_3$	10 min	93 (82)	2c
$Cl–SnPh_3$	10 min	99 (73)	2d
$Cl–SnBu_3$	1 h	92 (44)	2e
$Bu_3Sn–O–SnBu_3$	1 h	69	2e
$MeO–SnBu_3$	1 h	61	2e

[a] Yields were determined by GC after hydrolysis. Isolated yields are shown in parentheses.

Scheme 4.

Scheme 5.

Table 2
^{1}H and ^{13}C-NMR chemical shifts of ethylene bridged complexes **3** and hydrolysis products **2** [a]

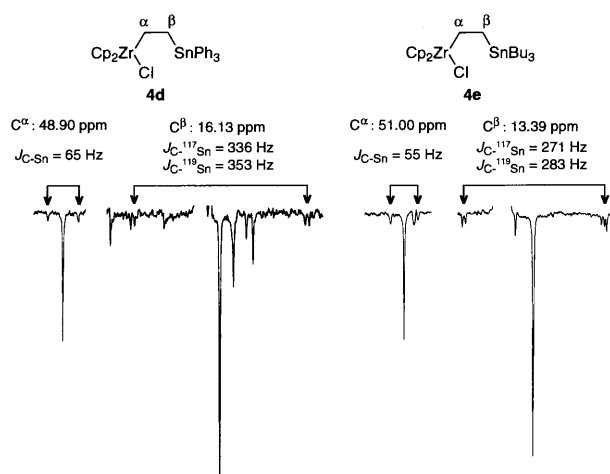| ER$_3$	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)			^{13}C-NMR (ppm)	
	Cp	Cp	Cα	Cβ	Cα′	Cβ′
SiPh$_3$ **4b**	6.05	113.13	45.11	17.87	7.76	5.08
GePh$_3$ **4c**	6.03	113.07	46.54	19.30	9.10	6.30
SnPh$_3$ **4d**	6.11	113.11	48.90 (65 Hz)	16.13 (336, 353 Hz)	1092 (26 Hz)	3.04 (388.406 Hz)
SnBu$_3$ **4e**	6.14	113.11	51.00 (55 Hz)	13.39 (271 283 Hz)	11.07 (23 Hz)	0.85 (305, 319 Hz)

[a] Coupling constants J_{C-Sn} are shown in parentheses.

Fig. 1.

ethylene on zirconocene. It is known that an ethylene insertion reaction to the Zr–Si bond has been reported using CpCp*Zr[Si(SiMe$_3$)$_3$]Cl or Cp*Cl$_2$ZrSi(SiMe$_3$)$_3$ [6]. However, it is also well known that no ethylene insertion took place with biscyclopentadienylzirconium complexes, Cp$_2$Zr(SiMe$_3$)(Cl) and Cp$_2$Zr[Si(SiMe$_3$)$_3$]Cl [1m]. In addition, insertion of olefin to the Zr–Ge or Zr–Sn bond is not known according to our knowledge. It should also be noted that the ethylene is a strong ligand and stays on zirconocene during the reaction. Therefore, the results obtained here suggest that the reaction of **1** with the E–X bond proceeds via path B.
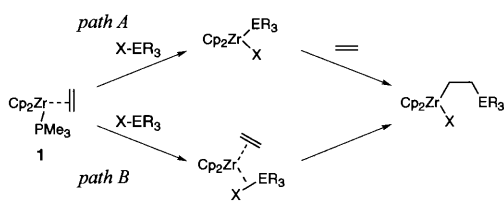
Scheme 6.

3. Experimental

Unless otherwise noted, all starting materials were commercially available and were used without further purification. Cp$_2$ZrCl$_2$ was purchased from Nichia Corporation. EtMgBr (0.95 M, THF solution) was purchased from Kanto Chemicals Co., Ltd. Ph$_3$SiCl, Ph$_3$SnCl, *n*-Bu$_3$SnCl and (*n*-Bu$_3$Sn)$_2$O were purchased from Tokyo Chemical Industry Co., Ltd. PMe$_3$ (1.0 M, THF solution), Ph$_3$GeCl and *n*-Bu$_3$SnOMe were purchased from Aldrich Chemical Co., Inc. Bu$_3$SiCl was obtained from Shin-etsu Chemical Industry Co., Ltd. Cp$_2$Zr(H)Cl was prepared by reaction of Cp$_2$ZrCl$_2$ with LiAlH$_4$ [11]. All reactions were carried out under a positive pressure of dry N$_2$. THF was refluxed and distilled over sodium and benzophenone under a nitrogen atmosphere. ^{1}H- and ^{13}C-NMR spectra were recorded for CDCl$_3$ (containing 1% Me$_4$Si) solutions on a Bruker ARX-400 NMR spectrometer. GC analyses were performed on Shimadzu GC-14A or 14B equipped with fused silica capillary column Shimadzu CBP1-M25-025 and Shimadzu C-R6A chromatopac integrator. GC yields were determined using suitable hydrocarbons as internal standards.

*3.1. A representative procedure for the reaction of zirconocene–ethylene complex with Group 14 metal compounds: reaction of zirconocene–ethylene complex stabilized by PMe$_3$ with Ph$_3$SnCl and formation of ethyltriphenyltin (**2d**)*

To a solution of Cp$_2$ZrCl$_2$ (292 mg, 1.0 mmol) in THF (5 ml) was added EtMgBr (2.1 ml, 0.96 M, 2.0 mmol) at −78°C and the reaction mixture was stirred at −78°C for 1 h. And then, at −78°C, PMe$_3$ (1.2 ml, 1.0 M, 1.2 mmol) was added and the mixture was stirred at room temperature for 3 h. To the mixture was added Ph$_3$SnCl (385 mg, 1.0 mmol) at room tempera-

ture and this was stirred for 10 min. The mixture was quenched with 3N HCl aq. followed by extraction with hexane. The organic layer was dried over MgSO$_4$. After concentration, column chromatography on silica gel (hexane as eluent) afforded the title compound as a white solid. GC yield was 99% and isolated yield was 73%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 1.37 (t, $J = 7.7$ Hz, 3H), 1.43–1.58 (m, 2H), 7.33–7.36 (m, 9H), 7.52–7.55 (m, 6H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 3.04 ($J_{C-^{117}Sn} = 388$ Hz, $J_{C-^{119}Sn} = 406$ Hz), 10.92 ($J_{C-Sn} = 26$ Hz), 128.45 ($J_{C-Sn} = 47$ Hz), 128.81 ($J_{C-Sn} = 10$ Hz), 137.08 ($J_{C-Sn} = 34$ Hz), 138.87 ($J_{C-^{117}Sn} = 460$ Hz, $J_{C-^{119}Sn} = 482$ Hz).

3.1.1. Formation of ethyltributylsilane (2a)

A colorless liquid. GC yield 71%, isolated yield 49%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 0.48–0.52 (m, 8H), 0.87–0.94 (m, 12H), 1.24–1.33 (m, 12H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 4.18, 7.54, 11.88, 13.80, 26.23, 26.90.

3.1.2. Ethyltriphenylsilane (2b)

A white solid. GC yield 82%, isolated yield 42%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 1.11 (t, $J = 7.8$ Hz, 3H), 1.38 (q, $J = 7.8$ Hz, 2H), 7.33–7.42 (m, 9H), 7.52 (dd, $J = 1.6$, 7.7 Hz, 6H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 5.08, 7.76, 127.84, 129.34, 135.24, 135.68.

3.1.3. Ethyltriphenylgermane (2c)

A white solid. GC yield 93% and isolated yield 82%. NMR spectra were compared to an authentic sample [12].

3.1.4. Ethyltributyltin (2e)

A colorless liquid. GC yield 92%, isolated yield 44%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 0.76–0.83 (m, 8H), 0.89 (t, $J = 7.3$ Hz, 9H), 1.16 (t, $J = 8.0$ Hz, 3H), 1.27–1.33 (m, 6H), 1.46–1.50 (m, 6H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 0.85 ($J_{C-^{117}Sn} = 305$ Hz, $J_{C-^{119}Sn} = 319$ Hz), 8.48 ($J_{C-^{117}Sn} = 299$ Hz, $J_{C-^{119}Sn} = 313$ Hz), 11.07 ($J_{C-Sn} = 23$ Hz), 13.75, 27.49 ($J_{C-Sn} = 51$ Hz), 29.37 ($J_{C-Sn} = 20$ Hz).

3.1.5. 2-Deuteroethyltriphenylsilane (2b-d)

The reaction was carried out in the same way as described above using Ph$_3$SiCl. The reaction mixture was stirred for 6 h at room temperature, and then quenched with 20% DCl–D$_2$O instead of 3N HCl. GC yield was 68% and isolated yield was 49% with 93% deuterium incorporation. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 1.09 (tt, $J = 1.7$, 7.8 Hz, 2H), 1.37 (t, $J = 7.8$ Hz, 2H), 7.32–7.42 (m, 9H), 7.52 (dd, $J = 1.5$, 7.7 Hz, 6H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 4.95, 7.46 (t, $J_{C-D} = 20$ Hz), 127.81, 129.32, 135.20, 135.65.

3.2. Hydrozirconation of vinyltriphenylsilane: alternative method for the preparation of 2-deuteroethyltriphenylsilane (2b-d)

To a solution of vinyltriphenylsilane (286 mg, 1.0 mmol) in THF (5 ml), Cp$_2$Zr(H)Cl (387 mg, 1.5 mmol) was added at room temperature and stirred for 6 h. The mixture was quenched with 20% DCl–D$_2$O and isolated in the same way as described above. Isolated yield was 84% with 97% deuterium incorporation.

3.3. NMR measurement of ethylene-bridged Group 14 metal–zirconocene complexes (4b–4e)

After the preparation of complexes 4b–4e by the reactions described above, the reaction mixtures (0.2 ml) with C$_6$D$_6$ (0.4 ml) were measured by ^{1}H-NMR, ^{13}C-NMR and DEPT. For complexes 4d and 4e it took around 8 h to observe the satellite peaks derived from ^{117}Sn and ^{119}Sn on DEPT, and an excess amount (3 mmol) of Ph$_3$SnCl or Bu$_3$SnCl was used to avoid the decomposition of complexes.

3.3.1. 2-Triphenylsilylethylzirconocene chloride (4b)

Characteristic NMR signals: ^{1}H-NMR (C$_6$D$_6$–THF, Me$_4$Si) δ 1.12–1.17 (m, 2H), 6.05 (s, 10H). ^{13}C-NMR (C$_6$D$_6$–THF, Me$_4$Si) δ 17.87, 45.11, 113.13.

3.3.2. 2-Triphenylgermylethylzirconocene chloride (4c)

Characteristic NMR signals: ^{1}H-NMR (C$_6$D$_6$–THF, Me$_4$Si) δ 1.11–1.17 (m, 2H), 1.93–1.97 (m, 2H), 6.03 (s, 10H). ^{13}C-NMR (C$_6$D$_6$–THF, Me$_4$Si) δ 19.30, 46.54, 113.07.

3.3.3. 2-Triphenylstannylethylzirconocene chloride (4d)

Characteristic NMR signals: ^{1}H-NMR (C$_6$D$_6$–THF, Me$_4$Si) δ 1.40–1.46 (m, 2H), 1.95–2.01 (m, 2H), 6.11 (s, 10H). ^{13}C-NMR (C$_6$D$_6$–THF, Me$_4$Si) δ 16.13 ($J_{C-^{117}Sn} = 336$ Hz, $J_{C-^{119}Sn} = 353$ Hz), 48.90 ($J_{C-Sn} = 65$ Hz), 113.11.

3.3.4. 2-Tributylstannylethylzirconocene chloride (4e)

Characteristic NMR signals: ^{1}H-NMR (C$_6$D$_6$–THF, Me$_4$Si) δ 6.14 (s, 10H). ^{13}C-NMR (C$_6$D$_6$–THF, Me$_4$Si) δ 13.39 ($J_{C-^{117}Sn} = 271$ Hz, $J_{C-^{119}Sn} = 283$ Hz), 51.00 ($J_{C-Sn} = 55$ Hz), 113.11.

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