Reaction of a Zirconocene-Ethylene Complex with Group 14 Metal Chlorides or Alkoxides

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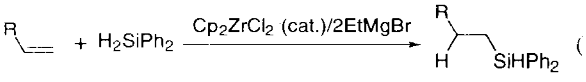
A zirconocene-ethylene complex $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$ reacted with R_3EX (E = Si, Ge, Sn; R = Ph or Bu; X = Cl, OEt, or OER_3) to give R_3EEt in high yields after hydrolysis. The reaction mixture of the ethylene complex with Bu_3SnCl further reacted with phenylacetylene to give homoallyltin compounds. When the reaction mixture was treated with Ph_3SnCl or Ph_3GeCl instead of phenylacetylene, Ph_3SnEt or Ph_3GeEt was obtained in high yields after hydrolysis *via* the replacement of the β-$SnBu_3$ moiety.

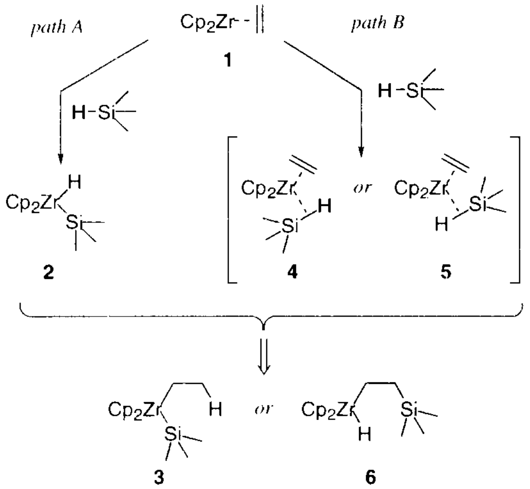
Recently we have reported the hydrosilylation reaction of olefins catalyzed by the Cp_2ZrCl_2/Grignard system (eq. 1).[1] Although the oxidative addition products of a silane to zirconocene were isolated,[1a] there are still several possible ways for the hydrosilation reaction.



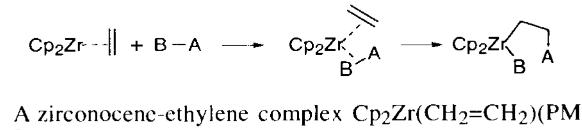
(1)

In addition to the mechanism of the olefin insertion[1a,2] of **2** to give **3** or **6** (path A), one possible mechanism involves a five membered intermediate **4** and **5** (path B) giving **3** and **6** without oxidative addition of silanes (Scheme 1). In order to understand the possibility of this reaction from **5** to **6**, we attempted the reaction of a zirconocene ethylene complex with silyl, germyl and stannyl compounds.

Scheme 1.

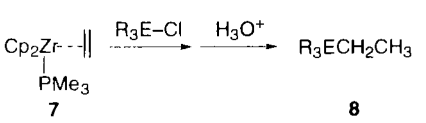


Recently we have investigated the reactions of zirconocene-ethylene complexes[3] with various unsaturated compounds such as alkynes, alkenes, and ketones.[4] These reactions afforded five membered zirconacycles. However, the reaction of the olefin complexes with an A–B single bond has not been intensively investigated.[3b,5] This reaction does not give a five membered ring compound since the A–B bond is cleaved during the reaction as shown in eq. 2.



(2)

A zirconocene-ethylene complex $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$ (**7**)[2] reacted with various group 14 metal compounds to give the ethylated products **8** after hydrolysis in high yields (eq. 3).[6] Table 1 shows the results of reactions of **7** in THF at room temperature with group 14 metal chlorides or alkoxides.



7 **8** (3)

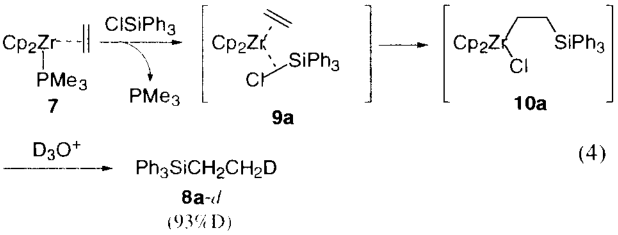
(E = Si, Ge, Sn; R = alkyl, Ph)

Table 1. Reaction of $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$ (**7**) with group 14 metal chlorides or alkoxides

Entry	X–ER$_3$	Time	Product	Yield/%[a]
1	$Cl\text{-}SiBu_3$	12 h	$EtSiBu_3$	71
2	$Cl\text{-}SiPh_3$	6 h	$EtSiPh_3$ (**8a**)	82
3	$Cl\text{-}GePh_3$	10 min	$EtGePh_3$ (**8b**)	93
4	$Cl\text{-}SnPh_3$	10 min	$EtSnPh_3$ (**8c**)	99
5	$Cl\text{-}SnBu_3$	1 h	$EtSnBu_3$ (**8d**)	92
6	$Bu_3Sn\text{-}O\text{-}SnBu_3$	1 h	$EtSnBu_3$ (**8d**)	69
7	$EtO\text{-}SnBu_3$	1 h	$EtSnBu_3$ (**8d**)	61

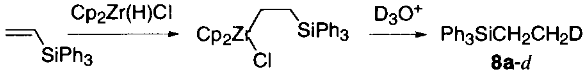
[a] Yields were determined by GC after hydrolysis.

Deuterolysis of the reaction mixture of **7** and Ph_3SiCl gave $DCH_2CH_2SiPh_3$ (**8a**-*d*) with 93% D incorporation. This suggests that this reaction proceeded *via* the five membered intermediate **9a** to give triphenylsilylethylzirconocene compound **10a** as shown in eq. 4.



(4)

The formation of **10a** in the C_6D_6/THF/hexane solution was observed by NMR. The ^{13}C-NMR spectrum of **10a** shows three signals except phenyl carbons at 113.13, 45.11, 17.87 assignable to Cp, $Zr\underline{C}H_2$ and $\underline{C}H_2Si$, respectively. The low field shift to 45.11 ppm of the methylene carbon is characteristic of the methylene attached to zirconocene as usually observed. In order to verify the structure of **10a**, a hydrozirconation reaction of vinyltriphenylsilane was carried out as shown in eq. 5.[7] The ^{13}C-NMR spectrum of the zirconium containing product was identical to that of the intermediate **10a**.



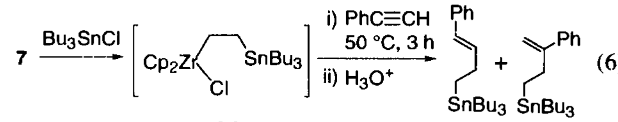
(5)

8a-*d*

84% (97%D)

Reactions of **7** with Ph$_3$GeCl and R$_3$SnCl were also carried out and monitored by NMR. In their ^{13}C-NMR spectra, Cp and two ethylene carbons appeared at 113.07, 46.54, 19.30 (**10b**, for Ph$_3$GeCl) and 113.02, 48.92, 18.62 (**10c**, for Ph$_3$SnCl), respectively. These spectra were consistent with that of **10a**. Therefore, similar types of compounds to **10a** were also formed in the case of Sn and Ge. These intermediates **10b** and **10c** were not stable. They gradually decomposed in solution at room temperature. The yields of EtSnPh$_3$ and EtGePh$_3$ obtained after hydrolysis decreased to around 40% after 3 h. The reaction intermediate **10d** which was obtained by the reaction of **7** with Bu$_3$SnCl was also unstable under conditions used here.

It was surprising that the reaction intermediate of **10d** with one equiv of phenylacetylene for 3 h at 50 °C afforded a mixture of two regio isomers of homoallyltin compounds **11** after hydrolysis in 41% combined yields with a ratio of 1.3 to 1 (eq. 6). When an internal alkyne such as 3-hexyne was used instead of phenylacetylene, the corresponding homoallyltin compound was obtained only in 18% yield along with the formation of a homocoupling of 3-hexyne in 43% yield after hydrolysis.



(6)

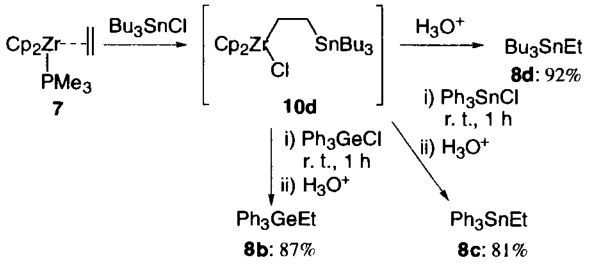
10d

11

41% (1.3:1)

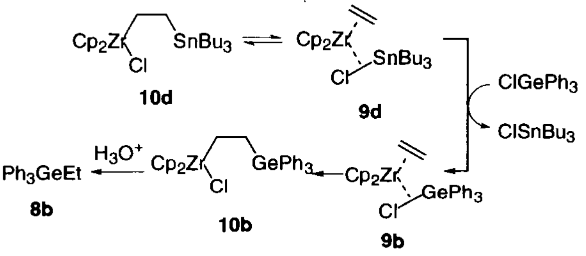
During the course of our further investigation of the reactivity of **10d**, we found another surprising result. When the reaction intermediate **10d** was treated with Ph$_3$GeCl and Ph$_3$SnCl for 1 h at room temperature, the products *via* replacement of the β-SnBu$_3$ moiety, **8b** (87%) and **8c** (81%) were obtained, respectively, after hydrolysis (Scheme 2).

Scheme 2.



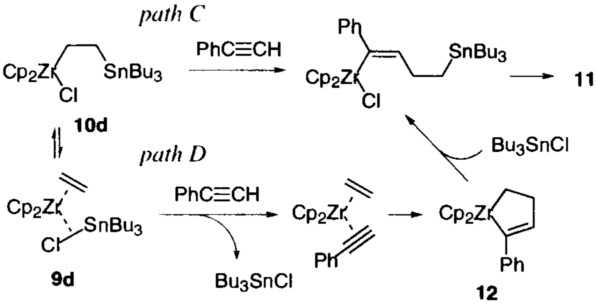
This transformation without loss of the bridging ethylene can be explained by the existence of an equilibrium between **10d** and **9d** (Scheme 3). A plausible mechanism involves the replacement of the Bu$_3$SnCl moiety in **9d** by Ph$_3$GeCl to give **9b** which, in turn, affords EtGePh$_3$ after hydrolysis *via* **10b**. It is noteworthy that the reactions of **10b** or **10c** with Bu$_3$SnCl did not give EtSnBu$_3$ after hydrolysis.

Scheme 3.



From the results obtained here, it is possible to consider two reaction mechanisms (path C and D) to explain the formation of homoallyltin compounds in the reaction of phenylacetylene with the intermediate **10d** as shown in Scheme 4. Since we have reported the formation of a zirconacyclopentene by the reaction of an ethylene complex with an alkyne[4d,e] and a selective reaction of the zirconacyclopentene with organotin chlorides giving homoallyltin compounds after hydrolysis,[8] the path D is more likely over path C. However, the path C which involves an insertion reaction of an alkyne into the zirconium-carbon bond in **10d** cannot be ruled out.

Scheme 4.



Further investigations are still in progress in this area.

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