Formation of Ethylene-Bridged Bimetallic Zirconocene Complexes by Coupling of Cp_2ZrEt_2 and Cp_2ZrX_2 (X = Cl or Br)

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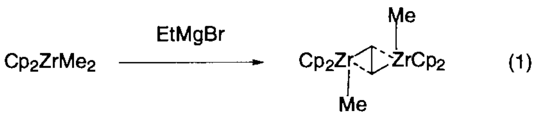
Cp_2ZrEt_2 reacted with one equiv of Cp_2ZrX_2 (X = Cl or Br) in THF to afford ethylene-bridged bimetallic zirconocene complexes, $(Cp_2ZrX)_2(CH_2CH_2)$ (X = Cl (**2a**), or Br (**2b**)), in high yields. The structure of **2b** was determined by X-ray analysis. Reactions of **2a**–**b** with various anions Y^- gave a series of ethylene-bridged bimetallic zirconocene complexes, $(Cp_2ZrY)_2(CH_2CH_2)$ (Y = Ph, Me, Bu, CH_2SiMe_3) in good to high yields.

Bimetallic zirconocene complexes containing a side-on bridged ethylene ligand are attractive, since they have ethylene and alkyl groups on zirconocene simultaneously, and also they have unusual penta-coordinate carbons.[1–4] Kaminsky et al. have reported that when Cp_2ZrCl_2 was treated with Et_3Al, $(Cp_2ZrCl\text{-}AlEt_3)_2(CH_2CH_2)$ was formed.[1] Recently, we have reported that $(Cp_2ZrMe)_2(CH_2CH_2)$ (**1**) was formed by addition of a Grignard reagent, EtMgBr, to a zirconocene complex Cp_2ZrMe_2.[2]



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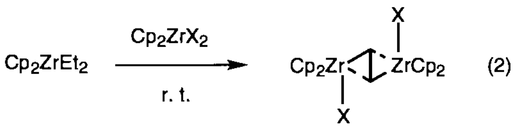
This Grignard method was applied to the synthesis of similar types of complexes $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}ZrEt]_2\text{-}(CH_2CH_2)$ by Royo et al.[3] and $(Cp_2ZrEt)_2(CH_2CH_2)$ by Fischer, Walther, and co-workers.[4] The structures of all these complexes have been confirmed by X-ray analysis. This Grignard method we developed has synthetical limitations inasmuch as it can introduce only an Et group or a Me group as Y in $(Cp_2ZrY)_2(CH_2CH_2)$. Therefore, we investigated the development of a general method for the synthesis of a series of $(Cp_2ZrY)_2(CH_2CH_2)$ where Y is an anionic ligand. In this paper we would like to report a new coupling method of two zirconocene complexes Cp_2ZrEt_2 and Cp_2ZrX_2 (X = Cl or Br) for the formation of bimetallic halide derivatives, $(Cp_2ZrX)_2(CH_2CH_2)$ (X = Cl or Br) which can be conveniently converted into a series of ethylene-bridged bimetallic zirconocene complexes $(Cp_2ZrY)_2(CH_2CH_2)$ by reaction with anions Y^-.



X = Cl or Br

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As shown in eq (2), when Cp_2ZrEt_2 was treated with one equiv of Cp_2ZrCl_2, an ethylene-bridged bimetallic complex $(Cp_2ZrCl)_2(CH_2CH_2)$ (**2a**) was obtained as a yellow solid in high yield. A typical procedure is as follows. To a THF solution of Cp_2ZrEt_2 was added one equiv of Cp_2ZrCl_2 at –20 °C. The mixture was warmed up to room temperature to give yellow precipitates in 91% isolated yield. Its ^1H NMR spectrum showed characteristic bridged-ethylene protons at –0.45 ppm as a singlet and Cp protons at 5.62 ppm. In its ^{13}C NMR spectrum, two signals appeared at 11.68 ppm and 106.65 ppm assignable to ethylene carbons and Cp carbons, respectively. These NMR spectra were characteristic of the ethylene-bridged bimetallic zirconocene complexes.[5]

An analogous complex, $(Cp_2ZrBr)_2(CH_2CH_2)$ (**2b**) was obtained in 76% isolated yield as orange crystals when Cp_2ZrBr_2 was used instead of Cp_2ZrCl_2. Its ^1H and ^{13}C NMR spectra were almost the same as that of **2a**.[6] The structure of **2b** was determined by X-ray crystallography as shown in Figure 1.[7] The C–C bond length of ethylene was 1.48 Å in **2b**. This number is almost comparable to those in other bimetallic zirconocene-ethylene complexes such as $(Cp_2ZrMe)_2(CH_2CH_2)$ (**1**) (1.47 Å),[2] $(Cp_2ZrEt)_2(CH_2CH_2)$ (1.50 Å)[4] and $[\{(\eta^5\text{-}C_5H_3)_2(SiMe_2)_2\}\text{-}ZrEt]_2(CH_2CH_2)$ (1.48 Å),[3] and is relatively shorter than that in $(Cp_2ZrClAlEt_3)_2(CH_2CH_2)$ (1.55 Å).[1] Compared with a monometallic zirconocene(II)-ethylene complex the C–C bond length of the ethylene in **2b** is almost the same as that in $Cp_2Zr(CH_2CH_2)(PMe_3)$ (1.49 Å).[8]

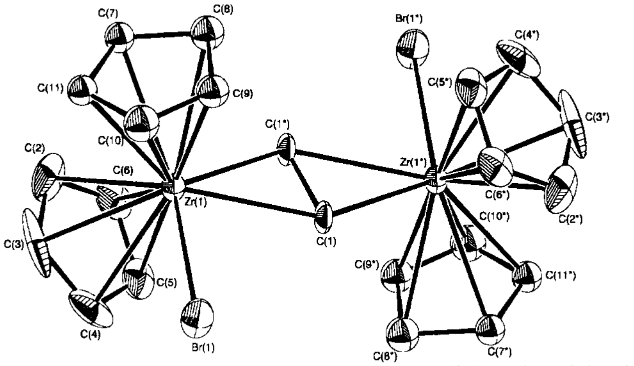
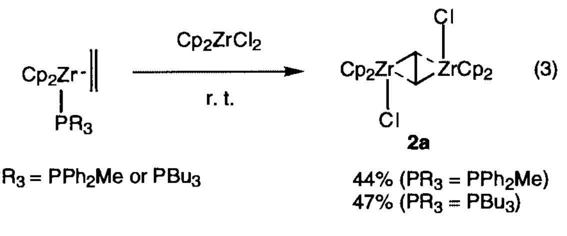


Figure 1. Structure of $(Cp_2ZrBr)_2(CH_2CH_2)$ (**2b**). Selected bond distances (Å) and bond angles (deg): Zr(1)-C(1), 2.516(6); Zr(1)-C(1*), 2.331(6); Zr(1)-Br(1), 2.7123(9); C(1)-C(1*), 1.48(1); Zr(1)-C(1)-C(1*), 65.5(4); Zr(1)-C(1*)-C(1), 79.1(4); C(1)-Zr(1)-C(1*), 35.4(3); C(1)-Zr(1)-Br(1), 81.0(1).

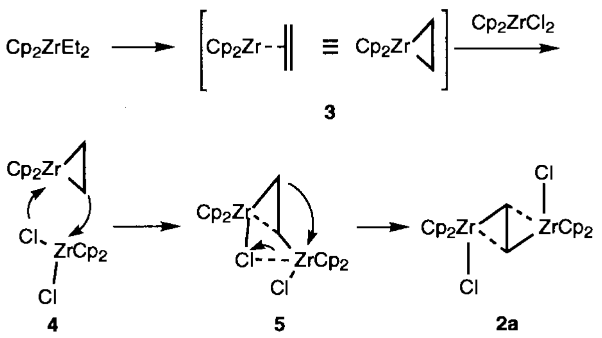
We have reported that Cp_2ZrEt_2 can be cleanly converted into a zirconocene-ethylene complex in situ at room temperature. Therefore, we tried the reaction of zirconocene-ethylene phos-



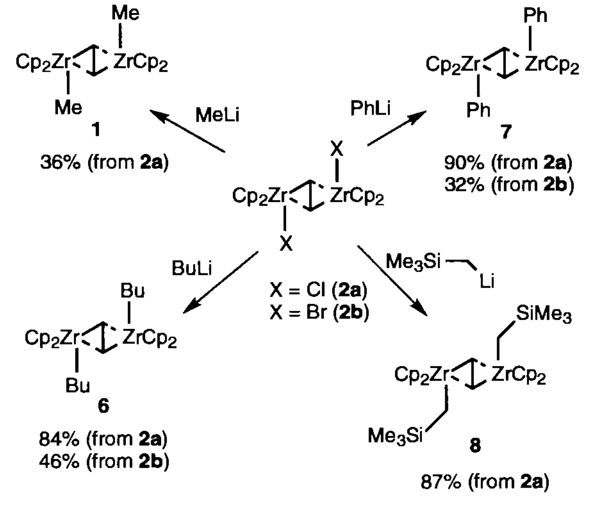
phine complexes, $Cp_2Zr(CH_2{=}CH_2)(PBu_3)$ or $Cp_2Zr(CH_2{=}CH_2)(PPh_2Me)$[9] with Cp_2ZrCl_2. As expected, bimetallic complex **2a** was formed in 47% and 44%, respectively, as shown in eq (3).

This result clearly showed that bimetallic zirconocene-ethylene complexes were formed by the coupling reaction of the zirconocene-ethylene complex, $Cp_2Zr(CH_2{=}CH_2)$, with Cp_2ZrCl_2. The reaction mechanism for the formation of **2** from the monometallic zirconocene-ethylene complex **3** is not elucidated yet, but the following mechanism can explain the formation of **2a** (Scheme 1). Initially, a zirconocene-ethylene complex **3** is generated from Cp_2ZrEt_2, and Cp_2ZrCl_2 interacts with **3** to form an intermediate (**5**). One of the ethylene carbons coordinates to the zirconium metal of Cp_2ZrCl_2 while Cl in Cp_2ZrCl_2 simultaneously coordinates to the other Zr. Successive nucleophilic attack of the other ethylene carbon to Zr metal with elimination of the bridged Cl from the Zr metal affords **2a** as shown in Scheme 1.

Scheme 1.



Scheme 2.



The bimetallic complexes **2a** and **2b** can be converted into various analogous complexes by reaction with nucleophiles such as lithium reagents. Representative procedure is as follows. To a suspension of **2a** was added two equiv of PhLi at –78°C and wamed up to room temperature. After stirring it for 1h, $(Cp_2ZrPh)_2(CH_2CH_2)$ (**7**) was afforded as yellow precipitates. Results are summarized in Scheme 2. When **2a** was treated with MeLi, $(Cp_2ZrMe)_2(CH_2CH_2)$ (**1**) was obtained in 36% yield. The reaction with *n*-BuLi, and Me_3SiCH_2Li gave $(Cp_2ZrBu)_2(CH_2CH_2)$ (**6**), and $(Cp_2ZrCH_2SiMe_3)_2(CH_2CH_2)$ (**8**) in high yields, respectively.[10–12] These bimetallic complexes **1**, **2** and **6**–**8** have relatively poor solubility in organic solvents. The reaction of **2b** with lithium reagents gave rather lower yields of products. When the first nucleophile reacts with **2a** or **2b**, mono-substituted intermediates $(Cp_2ZrR)(Cp_2ZrX)(CH_2CH_2)$ are formed. The stability of these intermedates might depend on the halogen ligand X.

Further investigation on the coupling reaction of two different zirconocene complexes for the formation of bimetallic zirconocene complexes is now in progress.

References and Notes

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5 Compound data for **2a**: Isolated as a yellow solid (91%). ^1H NMR (C_6D_6–THF, Me_4Si) δ –0.45 (s, 4H), 5.62 (s, 20H); ^{13}C NMR (C_6D_6–THF, Me_4Si) δ 11.68, 106.65. Anal. Calcd for $C_{22}H_{24}Cl_2Zr_2$: C, 48.77; H, 4.47; Cl, 13.09%. Found: C, 49.19; H, 4.76; Cl, 12.63%.

6 Compound data for **2b**: Isolated as orange crystals (76%). ^1H NMR (C_6D_6–THF, Me_4Si) δ –0.44 (s, 4H), 5.61 (s, 20H); ^{13}C NMR (C_6D_6–THF, Me_4Si) δ 11.68, 106.65. Anal. Calcd for $C_{22}H_{24}Br_2Zr_2$: C, 41.90; H, 3.84; Br, 25.34%. Found: C, 42.69; H, 4.06; Br, 24.38%.

7 Crystal data for **2b**: $C_{22}H_{24}Br_2Zr_2$, MW = 630.69, monoclinic, space group $P2_1/n$, a = 11.0744(7) Å, b = 8.0860(5) Å, c = 13.2223(8) Å, β = 113.397(1)°, V = 1086.7(1) Å^3, Z = 2, d_{calcd} = 1.927 g/cm^3, R = 0.049, R_w = 0.077 for 1899 reflections ($I > 2\sigma(I)$). A cyclopentadienyl ring was found to be disordered, and this was resolved into two half-occupancy orientations (C(7)–C(11) and C(12)–C(16)). C(12)–C(16) atoms were omitted for clarity in Figure 1.

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10 Compound data for **6**: Isolated as yellow solid (24%). NMR yield 84%. Characteristic NMR signals are as follows. ^1H NMR (C_6D_6–THF, Me_4Si) δ –0.44 (s, 4H) (for ethylene), 5.62 (s, 20H) (for *Cp*). ^{13}C NMR (C_6D_6–THF, Me_4Si) δ 106.67 (for *Cp*).

11 Compound data for **7**: Isolated as yellow solid (60%). NMR yield 90%. ^1H NMR (C_6D_6–THF, Me_4Si) δ 0.18 (s, 4H), 5.76 (s, 20H), 6.92–7.42 (m, 10H). ^{13}C NMR (C_6D_6–THF, Me_4Si) δ 12.99, 107.42, 123.34, 126.92, 136.27, 141.87.

12 Compound data for **8**: Isolated as yellow solid (57%). NMR yield 87%. ^1H NMR (C_6D_6–THF, Me_4Si) δ –0.36 (s, 4H), –0.28 (s, 4H), 0.32 (s, 18H), 5.50 (s, 20H); ^{13}C NMR (C_6D_6–THF, Me_4Si) δ 4.82, 15.23, 17.69, 106.93.