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Reaction of Dimethylzirconocene with Alkylmagnesium Halides as a Potentially General Method for Preparing Zirconocene-Alkene Complexes

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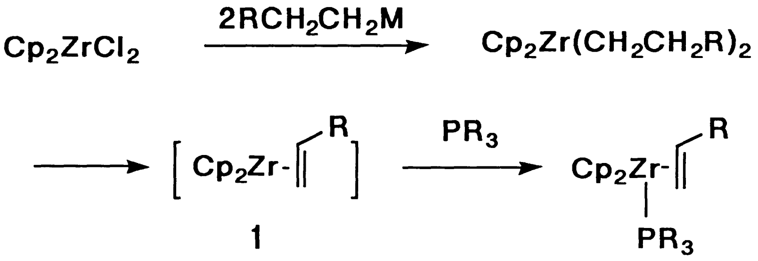
Addition of one equivalent of RCH_2CH_2MgX to Cp_2ZrMe_2 ($Cp = C_5H_5$) in the presence of PMe_3 led to a transmetalation reaction to afford zirconocene-alkene complexes $Cp_2Zr(RCH=CH_2)(PMe_3)$ in good yields along with the formation of MeMgX.

Since we prepared a zirconocene-stilbene complex as the first example[1-3] of zirconocene-alkene complexes, these compounds have been prepared by (i) β-hydrogen abstraction and elimination of an alkane from dialkylzirconocenes,[4-6] (ii) displacement of a ligand of zirconocene(II) complexes Cp_2ZrLL' (L, L' = phosphine or alkene) with an alkene,[1-3,7] and (iii) β,γ-carbon-carbon bond cleavage of zirconacyclopentane compounds.[8] These three methods have afforded stable zirconocene-alkene-phosphine complexes in moderate to good yields; for example, $Cp_2Zr(CH_2=CH_2)(PMe_3)$ was obtained in 95,[4] 47,[7] and 87%[8] yields by the method (i), (ii) and (iii), respectively. It has also been demonstrated that in the absence of phosphine, reactive zirconocene-alkene species **1**, which could be quantitatively generated in situ by the method (i), can serve as "zirconocene" equivalent, not only for cyclization reactions of enynes,[1,3] diynes,[1,3,9] dienes[10] and others[11] but also for highly selective carbon-carbon bond formation



Scheme 1.

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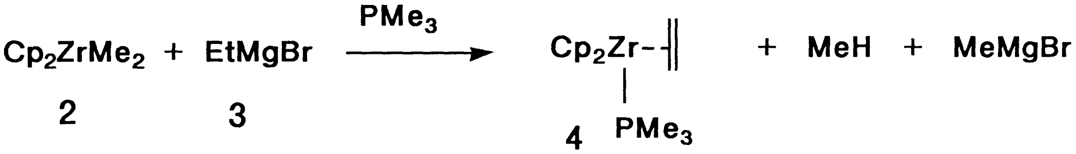
between two alkenes.[12)] However, the method (i) requires two equivalents of Grignard or lithium reagents to prepare dialkylzirconocenes from Cp_2ZrCl_2 as shown in Scheme 1. Since only one of the two alkyl groups is converted into the alkene on zirconium, the maximum yield based on the lithium or Grignard reagents cannot exceed 50%, even though the reactions proceed in excellent yields based on zirconium. This is a critical limitation of method (i) from the viewpoint of organic synthesis, and it prompted us to develop an alternative method for obtaining zirconocene-alkene complexes requiring only one equivalent of such reagents.



Scheme 2.

On treatment of dimethylzirconocene (**2**) with one equivalent of ethylmagnesium bromide (**3**) in THF at room temperature, zirconocene-ethylene complex $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$ (**4**) was obtained in 95% yield in the presence of trimethylphosphine along with the formation of MeMgBr (74%). The complex **4** was identified by its characteristic NMR spectra. Addition of one equivalent of MeOH to the reaction mixture at -78 °C selectively quenched MeMgBr which can be obstructive to further reactions of the zirconocene-alkene complexes obtained here. When n-propyl and n-butyl Grignard reagents were used instead of ethyl Grignard reagent, the corresponding propylene and 1-butene complexes $Cp_2Zr(RCH{=}CH_2)(PMe_3)$ were obtained in 77% (R = Me) and 70% (R = Et), respectively. When one equivalent of n-BuLi was added in place of n-BuMgCl, only 31% of the butene complex was formed after 12 h at room temperature. These results are summarized in Table 1.

A typical procedure is as follows. To a mixture of 0.292 g (1 mmol) of Cp_2ZrCl_2 and 4 cm^3 of THF were added two equivalents of methyllithium (1.1 M, 1.82 cm^3, 2.0 mmol) in ether at -78 °C. It was stirred for 1 h at the same temperature, and then gradually warmed to room temperature with

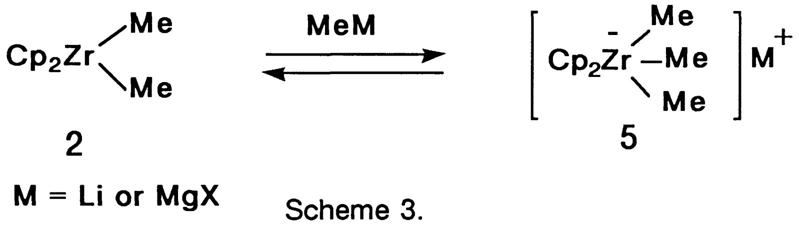
Table 1. Preparation of zirconocene-alkene complexes by the reaction of Cp_2ZrMe_2 with one equivalent of alkylmetals in the presence of PMe_3

RM	Time/h	Products	Yield[a)]/%
EtMgBr	1	$Cp_2Zr(CH_2{=}CH_2)(PMe_3)$	78
EtMgBr	3	$Cp_2Zr(CH_2{=}CH_2)(PMe_3)$	95
n-PrMgBr	3	$Cp_2Zr(MeCH{=}CH_2)(PMe_3)$	77
n-BuMgCl	3	$Cp_2Zr(EtCH{=}CH_2)(PMe_3)$	70
n-BuLi	12	$Cp_2Zr(EtCH{=}CH_2)(PMe_3)$	31

a) Yields were determined by ^1H-NMR spectroscopy.

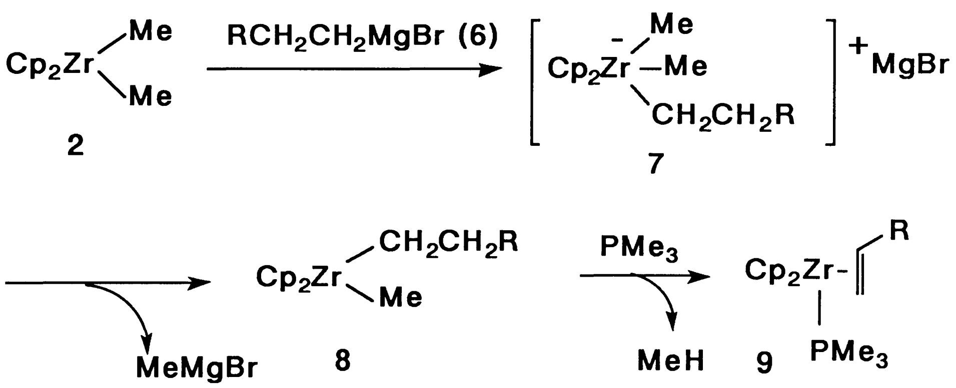
stirring. Dimethylzirconocene (**2**) was quantitatively formed in situ. To this were added ethylmagnesium bromide in THF (0.99 M, 1.01 cm^3, 1.0 mmol) and PMe_3 (1.0 M, 1.2 cm^3, 1.2 mmol). After stirring the mixture at room temperature for 3 h, zirconocene-ethylene trimethylphosphine complex **4** was obtained in 95% yield. The reaction was monitored by ^{1}H-NMR spectroscopy (400 MHz). A singlet at δ 5.94 assigned to Cp of Cp_2ZrMe_2 and a new doublet at δ 5.06 assignable to Cp of **4** were observed. The latter grew at the expense of the peak at δ 5.94. A singlet ascribed to the methyl group of MeMgX emerged at δ -1.3. There was no build up of any intermediate compounds during the course of the reaction.

In order to investigate the possible role of ate complexation, we examined the reaction of **2** with MeMgBr or MeLi. The ^{1}H-NMR spectrum of a mixture of **2** and MeMgBr showed no evidence of the formation of novel species such as zirconate complex **5**. An equilibrium should exist, however, between the complexes **2** and **5** as shown in Scheme 3, since the addition of EtMgBr or n-BuMgCl to **2** liberated MeMgX (X = Br or Cl). In contrast, in the case of lithium reagent Razuvaev suggested the formation of unstable ate complexes $Li[Cp_2ZrR_2R']$ when Cp_2ZrR_2 (R = Me or Ph) reacted with R'Li (R' = Ph or Me).[13]



Scheme 3.

The available data strongly suggest the following mechanism for this reaction, which involves the formation of an ate-complex **7** from **2** and an alkylmagnesium halide **6**, liberation of methylmagnesium halide from **7** affording **8**, β-hydrogen abstraction and elimination of the alkyl group of **8** with concomitant formation of methane to produce **9**, in the presence of a phosphine.



Scheme 4.

Zirconocene-alkene complexes, such as $Cp_2Zr(CH_2{=}CH_2)$, prepared in situ in the absence of a phosphine reacted with an equimolar amount of β-methylstyrene at room temperature to give a coupled product. After hydrolysis, 2-methylbutylbenzene was obtained in 51% yield with >99% regioselectivity via $Cp_2Zr(CH_2{=}CH_2)$.

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