## **Oxidative Addition of 2-Haloalkene to Zirconocene**

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Alkenylzirconocene compounds, which are easily prepared by the hydrozirconation of alkynes, have been very useful intermediates in organic synthesis.<sup>2-4</sup> Hydrozirconation of terminal alkynes regio- and stereoselectively affords alkenylzirconocene compounds of type I.<sup>2,3</sup> Even though compound II is formed in situ, it immediately isomerizes to I in the presence of Cp<sub>2</sub>ZrHCl.<sup>2,3c</sup> Consequently, an alkenylzirconocene of type II cannot be obtained by this method.



To prepare a type II compound, we have investigated novel oxidative addition reactions of 2-haloalkenes to Zr(II).<sup>5,6</sup> In this paper, we report the formation of an alkenylzirconocene of type II by the reaction of a 2-haloalkene with Cp<sub>2</sub>ZrBu<sub>2</sub> (Cp<sub>2</sub>Zr equivalent, Negishi reagent),7 together with its X-ray structure. We also report one-pot carbon-carbon bond formation reactions of 2-haloalkenes via oxidative addition to zirconocene (eq 1).

1a	Cp <sub>2</sub> ZrBu <sub>2</sub> > 2a	Phi cet. Pd(PPh <sub>3</sub> ) <sub>4</sub> + ZnCl <sub>2</sub>	Ph Ph	78% based on 1a: one-pot reaction	(1)
	98% yield				

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 (5) Preparation of trisubstituted monoalkenylzirconocene by a reaction

of Cp<sub>2</sub>ZrCl<sub>2</sub> with LiC(Ph)=CMe<sub>2</sub> was shown as unpublished results: Comprehensive Organometallic Chemistry; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 3, p 590. See also: Cardin, C. J.; Cardin, D. J.; Kelley, J. M.; Norton, R. J.; Roy, A. J. Organomet. Chem. 1977, 132, C23. However, a reaction of 1 equiv of CH<sub>3</sub>C(Li)=CH<sub>2</sub> with zirconocene dichloride was not clean under the conditions used here.

(6) An alkenylzirconocene complex of type II was prepared by a reaction of zirconium-molybdenum bimetallic acyl compounds with Cp2ZrMe2 and was spectroscopically characterized; see: Matchett, S. A.; Norton, J. R. Organometallics 1988, 7, 2228.

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Table 1. Oxidative Addition Reactions of Haloalkenes to Zirconocene

2-Haloalkene	Zirconium complex	Product	Yield/%
Ph.J. 18	Cp <sub>2</sub> ZrBu <sub>2</sub>	Cp <sub>2</sub> Zr Ci Ph 2a	98
H₃C CI 1b	Cp <sub>2</sub> ZrBu <sub>2</sub>	Cp2Zr CH3 2b	80(54)
H <sub>3</sub> C <sup>L</sup> Br <sup>10</sup>	Cp <sub>2</sub> ZrBu <sub>2</sub>	Cp <sub>2</sub> Zr CH <sub>3</sub> 2c Br	93(73)
H11Cs CI 1d	Cp <sub>2</sub> ZrBu <sub>2</sub>	Cp2Zr C5H11 2d	70
(N) ci 10	$Cp_2ZrBu_2$	Cp2Zt N 20	92(61)
16	(1-BuC5H4)2ZrBu2	(t-BuC₅H₄)₂Zt Cl Cl	83(62)

<sup>a</sup> NMR yields. Isolated yields are given in parentheses.

Compared with late transition metal chemistry, only a few examples of intermolecular oxidative addition reactions are known for zirconocene using alkyl halides,<sup>8-10</sup> arenes,<sup>9</sup> phosphorus compounds,<sup>11</sup> silanes,<sup>12</sup> and allyl ethers.<sup>13</sup> In some cases, further useful synthetic applications were reported,<sup>14</sup> but the oxidative addition intermediates have not been structurally characterized. In addition, there is no report of oxidative addition for alkenyl halides to zirconocene, to the best of our knowledge.

Treatment of 2-chloropropene (1b) with Cp<sub>2</sub>ZrBu<sub>2</sub>, which was prepared in situ from Cp<sub>2</sub>ZrCl<sub>2</sub> and 2 equiv of n-BuLi, gave the oxidative addition product 2b in 80% yield at room temperature. Cp<sub>2</sub>ZrBu<sub>2</sub> is known to act as a Cp<sub>2</sub>Zr equivalent at room temperature, since Cp<sub>2</sub>ZrBu<sub>2</sub> is converted quantitatively into the active species Cp<sub>2</sub>Zr(CH<sub>2</sub>=CH<sub>2</sub>Et). Results for other 2-haloalkenes are shown in Table 1. The oxidative addition reaction proceeded very cleanly, and the yields were good in all cases. The <sup>1</sup>H NMR spectrum of **2b** in  $C_6D_6$  showed two vinylidene protons at 5.61 and 5.32 ppm and a methyl group at 1.93 ppm; the Cp signal appeared at 5.86 ppm. Its <sup>13</sup>C NMR spectrum revealed two alkenyl carbons at 198.6 and 115.6 ppm, assignable to a carbon attached to zirconium and a vinylidene carbon, respectively. Cp carbons and a methyl carbon signals appeared at 112.9 and 30.8 ppm, respectively. The formation of bis(alkenyl)zirconium complexes was not observed under these conditions. However, in nonpolar solvents such as hexane, **2b** was gradually converted into a mixture of Cp<sub>2</sub>ZrCl<sub>2</sub> and a bis(alkenyl)zirconium compound because of the low solubility of  $Cp_2ZrCl_2$  in hexane.

To obtain good crystals for X-ray analysis, a t-Bu-substituted cyclopentadienyl ligand was used. The reaction of (t-BuC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>-ZrBu<sub>2</sub> with 1b in ether afforded 2f in 83% NMR yield, and recrystallization from n-hexane gave yellow crystals in 62%

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Figure 1. Structure of 2f. Selected bond lengths (Å) and angles (deg): Zr-C(2) 2.277(3), Zr-C(2.432(1)), C(2)-C(3) 1.342(6), C(1)-C(2) 1.492;  $Zr-C(2)-C(1) 123.3(3)^{\circ}$ ,  $Cl-Zr-C(2) 99.7(1)^{\circ}$ ,  $C(1)-C(2)-C(3) 118.6(3)^{\circ}$ .

isolated yield (eq 2). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2f were



very similar to those of **2b**.<sup>15</sup> The structure of **2f**, an alkenylzirconocene compound of type **II**, is shown in Figure 1.<sup>16</sup> The bond length of C(2)-C(3), 1.343(6) Å, is slightly longer than usual bond lengths of alkenylzirconocenes (1.217(9)-1.339(3) Å).<sup>16</sup> There are no agostic interactions between Zr and CH<sub>2</sub> or CH<sub>3</sub> groups of **2f** since their distances are 3.141(4) and 3.338-(4) Å, respectively. It is noteworthy that the bond angle of Zr-C(2)-C(3), 118.1(3)°, is, as expected, larger than those of alkenylzirconocenes with agostic interactions between C<sub>β</sub>-H and Zr (88.7(4)-108.8(3)°)<sup>16a,g</sup> but significantly smaller than those Communications to the Editor

Scheme 1



**Table 2.** One-Pot Catalytic Carbon-Carbon Bond Formation

 Reactions of Haloalkenes via Oxidative Addition to Zirconocene

Haloalkene	Catalyst	Reagent	Product	Yield/%ª
1 a	CuCl/LiCl	i Ci	Ph	83
1 a	Pd(PPh3)4/ZnCl2	PhI	Ph	78
1 d	Pd(PPh3)4/ZnCl2	PhCOCI	C5H11 Ph	63

<sup>a</sup> Based on haloalkenes. All catalytic reactions were carried out after treatment of the haloalkenes with 1 equiv of Cp<sub>2</sub>ZrBu<sub>2</sub>.

of alkenylzir conocenes without agostic interactions  $(137.4(3) - 144.2(5)^\circ)$ .<sup>16a,g</sup>

A plausible mechanism for the oxidative addition of 2-haloalkenes to zirconocene is shown in Scheme 1.

The oxidative addition products 2a-f did not undergo isomerization from type II to type I in solution.<sup>17</sup> Several carbon-carbon bond formation reactions of 2 were investigated. The palladium-catalyzed coupling reaction<sup>18</sup> and coppercatalyzed allylation<sup>19</sup> of 2 gave satisfactory results and could be carried out in one pot. It is not necessary to isolate the intermediate. Selected one-pot reactions are shown in Table 2. It is noteworthy that the isomerization from type II to type I was not observed during the one-pot reactions.

1-Haloalkenes such as  $\beta$ -bromostyrene and 1-bromooctene also afforded oxidative addition products **3** and **4** in 63% and 65% yields, respectively.<sup>20</sup> However, phenyl halides such as



phenyl iodide, bromide, and chloride did not give oxidative addition products.

Supporting Information Available: Experimental details and analytical data for all compounds and crystallographic data, positional and thermal parameters, and lists of bond lengths and angles for 2f (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(20) J values of olefinic protons of 3 and 4 were 19 and 18 Hz, respectively, which indicated the *trans* configuration.

<sup>(15)</sup> **2f**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, Me<sub>4</sub>Si)  $\delta$  1.30 (s, 9H), 1.95 (t, J = 1.3Hz, 3H), 5.26–5.29 (m, 2H), 5.32–5.34 (m, 1H), 5.69–5.71 (m, 2H), 5.72–5.73 (m, 1H), 5.82–5.84 (m, 2H), 6.35–6.38 (m, 2H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, Me<sub>4</sub>Si)  $\delta$  31.0, 31.3, 33.3, 105.1, 109.0, 112.8, 115.5, 119.3, 142.9, 197.7. Anal. Calcd for C<sub>21</sub>H<sub>31</sub>ClZr: C, 61.50; H, 7.62; Cl, 8.64. Found: C, 61.35; H, 7.65; Cl, 8.58.

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