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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.[2–4] Hydrozirconation of terminal alkynes regio- and stereoselectively affords alkenylzirconocene compounds of type **I**.[2,3] Even though compound **II** is formed *in situ*, it immediately isomerizes to **I** in the presence of Cp_2ZrHCl.[2,3c] 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).[5,6] In this paper, we report the formation of an alkenylzirconocene of type **II** by the reaction of a 2-haloalkene with Cp_2ZrBu_2 (Cp_2Zr 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),

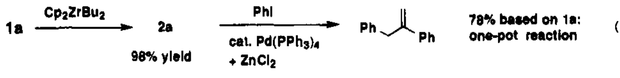
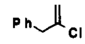
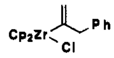
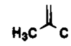
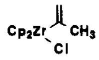
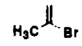
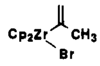
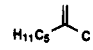
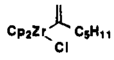
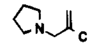
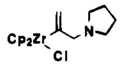
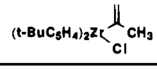
 (1)

Table 1. Oxidative Addition Reactions of Haloalkenes to Zirconocene

2-Haloalkene		Zirconium complex	Product		Yield/%
	**1a**	Cp_2ZrBu_2		**2a**	98
	**1b**	Cp_2ZrBu_2		**2b**	80(54)
	**1c**	Cp_2ZrBu_2		**2c**	93(73)
	**1d**	Cp_2ZrBu_2		**2d**	70
	**1e**	Cp_2ZrBu_2		**2e**	92(61)
1b		$(\iota\text{-BuC}_5H_4)_2ZrBu_2$		**2f**	83(62)

[a] 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,[8–10] arenes,[9] phosphorus compounds,[11] silanes,[12] and allyl ethers.[13] In some cases, further useful synthetic applications were reported,[14] 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_2ZrBu_2, which was prepared *in situ* from Cp_2ZrCl_2 and 2 equiv of n-BuLi, gave the oxidative addition product **2b** in 80% yield at room temperature. Cp_2ZrBu_2 is known to act as a Cp_2Zr equivalent at room temperature, since Cp_2ZrBu_2 is converted quantitatively into the active species $Cp_2Zr(CH_2{=}CH_2Et)$. 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 ^1H 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 ^{13}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_2ZrCl_2 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 $(t\text{-BuC}_5H_4)_2ZrBu_2$ with **1b** in ether afforded **2f** in 83% NMR yield, and recrystallization from *n*-hexane gave yellow crystals in 62%

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(2) For a review, see: Labinger, J. A. '*Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, p 667.

(3) (a) Labinger, J. A.; Hart, D. W.; Seibert, W. E.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (c) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. (d) Loots, M. J.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 8045. (e) Yoshifuji, M.; Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1977**, 1303.

(4) (a) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729. (b) Negishi, E.; Van Horn, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 3168. (c) Okukado, N.; Van Horn, D. E.; Klima, W. E.; Negishi, E. *Tetrahedron Lett.* **1978**, 1027. (d) Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252. (e) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393.

(5) Preparation of trisubstituted monoalkenylzirconocene by a reaction of Cp_2ZrCl_2 with $LiC(Ph){=}CMe_2$ 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 $CH_3C(Li){=}CH_2$ 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 Cp_2ZrMe_2 and was spectroscopically characterized; see: Matchett, S. A.; Norton, J. R. *Organometallics* **1988**, *7*, 2228.

(7) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(8) Williams, G. M.; Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 3660.

(9) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

(10) Demerseman, B.; Buquet, G.; Bigorne, M. *J. Organomet. Chem.* **1977**, *132*, 223.

(11) Gell, K. I.; Schwartz, J. *Inorg. Chem.* **1980**, *19*, 3207.

(12) (a) Kreutzer, K. A.; Fisher, R. A.; Davis, W. A.; Spaltenstein, E.; Buchwald, S. L. *Organometallics* **1991**, *10*, 4031. (b) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M. Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564.

(13) (a) Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E. *Tetrahedron Lett.* **1989**, 5105. (b) Ito, H.; Taguchi, T.; Hanzawa, Y. *Tetrahedron Lett.* **1992**, *33*, 1295.

(14) For example, see: (a) Ito, H.; Ikeuchi, Y.; Taguchi, T.; Hanzawa, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5469. (b) Ito, H.; Motoki, Y.; Taguchi, T.; Hanzawa, Y. *J. Am. Chem. Soc.* **1993**, *115*, 8835.

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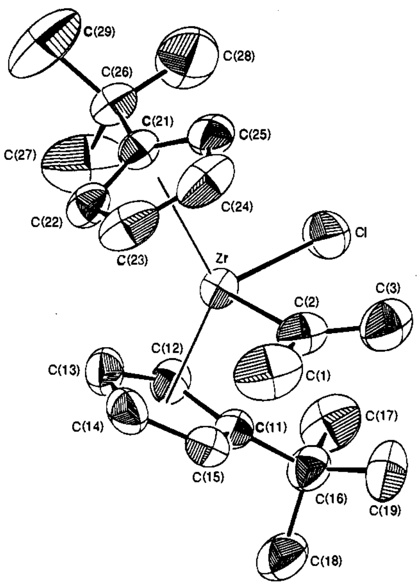


Figure 1. Structure of **2f**. Selected bond lengths (Å) and angles (deg): Zr–C(2) 2.277(3), Zr–Cl 2.432(1), C(2)–C(3) 1.342(6), C(1)–C(2) 1.492; Zr–C(2)–C(1) 123.3(3)°, Cl–Zr–C(2) 99.7(1)°, C(1)–C(2)–C(3) 118.6(3)°.

isolated yield (eq 2). The ^1H and ^{13}C NMR spectra of **2f** were

$$(t\text{-}BuC_5H_4)_2ZrCl_2 \xrightarrow[0°C,\ 3h]{2n\text{-}BuLi,\ -78°C,\ in\ ether} (t\text{-}BuC_5H_4)_2ZrBu_2 \xrightarrow[\text{yellow crystals}]{1b} 2f \qquad (2)$$

very similar to those of **2b**.[15] The structure of **2f**, an alkenylzirconocene compound of type **II**, is shown in Figure 1.[16] 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).[16] There are no agostic interactions between Zr and CH_2 or CH_3 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_β-H and Zr (88.7(4)–108.8(3)°)[16a,g] but significantly smaller than those of alkenylzirconocenes without agostic interactions (137.4(3)–144.2(5)°).[16a,g]

Scheme 1

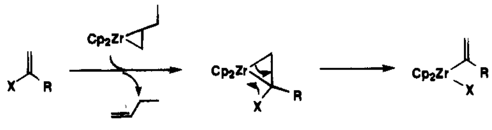
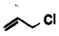
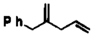
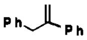
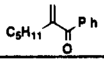


Table 2. One-Pot Catalytic Carbon–Carbon Bond Formation Reactions of Haloalkenes via Oxidative Addition to Zirconocene

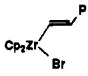
Haloalkene	Catalyst	Reagent	Product	Yield/%[a]
1a	CuCl/LiCl			83
1a	$Pd(PPh_3)_4/ZnCl_2$	PhI		78
1d	$Pd(PPh_3)_4/ZnCl_2$	PhCOCl		63

[a] Based on haloalkenes. All catalytic reactions were carried out after treatment of the haloalkenes with 1 equiv of Cp_2ZrBu_2.

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.[17] Several carbon–carbon bond formation reactions of **2** were investigated. The palladium-catalyzed coupling reaction[18] and copper-catalyzed allylation[19] 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 β-bromostyrene and 1-bromooctene also afforded oxidative addition products **3** and **4** in 63% and 65% yields, respectively.[20] However, phenyl halides such as



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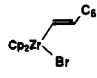

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phenyl iodide, bromide, and chloride did not give oxidative addition products.

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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[15] **2f**: ^1H NMR (C_6D_6, Me_4Si) δ 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); ^{13}C NMR (C_6D_6, Me_4Si) δ 31.0, 31.3, 33.3, 105.1, 109.0, 112.8, 115.5, 119.3, 142.9, 197.7. Anal. Calcd for $C_{21}H_{31}ClZr$: C, 61.50; H, 7.62; Cl, 8.64. Found: C, 61.35; H, 7.65; Cl, 8.58.

[16] Structures of alkenylzirconium complexes have been characterized and discussed. See: (a) Hyla-Kryspin, I.; Gleiter, R.; Krüger, C.; Zwettler, R.; Erker, G. *Organometallics* **1990**, *9*, 517. (b) Erker, G.; Zwettler, R.; Krüger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics* **1990**, *9*, 524. (c) Erker, G.; Frömberg, W.; Angermund, K.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372. (d) Erker, G.; Zwettler, R.; Krüger, C.; Schlund, R.; Hyla-Kryspin, I.; Gleiter, R. *J. Organomet. Chem.* **1988**, *346*, C15. (e) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281. (f) Rosenthal, U.; A. Ohff, A.; Michalik, M.; Görls, H.; Brlakov, V. V.; Shur, V. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193–1195. (g) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Organometallics* **1993**, *12*, 5016.

[17] Even in the presence of Cp_2ZrHCl, the isomerization of **2f** was not observed.

[18] Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254.

[19] (a) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N.*Tetrahedron Lett.* **1994**, *35*, 5685. (b)Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Organometallics* **1994**, *13*, 4183.

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