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Zirconocene-Mediated and/or Catalyzed Unprecedented Coupling Reactions of Alkoxymethyl-Substituted Styrene Derivatives

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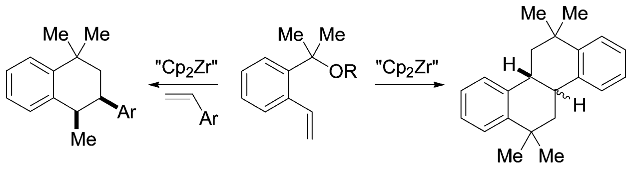
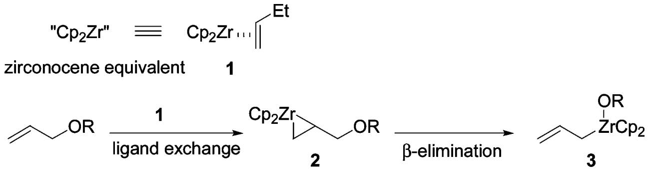
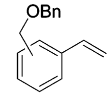


Reactions of *o*-(alkoxymethyl)styrene derivatives with a stoichiometric amount of zirconocene−butene complex (zirconocene equivalent, “Cp_2Zr”) brought about an insertion of the zirconocene species into a benzylic carbon−oxygen bond. The oxidative insertion of Cp_2Zr to the benzylic carbon−oxygen bond is a result of sequential reactions: (i) formation of zirconacyclopropane by the ligand exchange with *o*-(alkoxymethyl)styrene, (ii) elimination of the alkoxy group through an aromatic conjugate system giving metalated *o*-quinodimethane species, and (iii) transfer of zirconium metal to the benzylic position. Through use of a catalytic amount of “Cp_2Zr”, however, unprecedented homo-coupling reactions (dimerization) of *o*-(alkoxymethyl)styrene derivatives occurred to give a tetracyclic compound. On the other hand, reactions of *o*-(1-alkoxyisopropyl)styrene derivatives gave rise to the analogous tetracyclic compounds regardless of the amount of “Cp_2Zr” (stoichiometric or catalytic). Heterocoupling product between *o*-(1-alkoxyisopropyl)styrene and styrene congeners was obtained in high cis stereo- and regioselectivity by treating *o*-(1-alkoxyisopropyl)styrene derivatives with “Cp_2Zr” in the presence of an excess amount of styrene derivatives.

Introduction

Easy preparation and versatile reactivity of zirconocene−butene complex **1** (“Cp_2Zr”, Cp = cyclopentadienyl)[1] attracted synthetic organic chemists to the use of “Cp_2Zr” as a zirconocene equivalent for the study of new carbon−carbon bond formation.[2] During the course of our studies of “Cp_2Zr”-mediated carbon−carbon bond formation reactions, we reported an efficient generation of allylic zirconocene **3** species from allylic ethers through β-alkoxy elimination of the zirconacyclopropane intermediate **2**.[3] On the basis of the formation of allylic zirconocene **3**, we were tempted to examine “Cp_2Zr”-catalyzed or -mediated reactions of alkoxymethyl-substituted styrene derivatives **4**, which possess a reactive olefin site to “Cp_2Zr” and a leaving alkoxy group through the aromatic π-conjugated system. Preliminary examination of the reactions of *o*-, *m*-, or *p*-alkoxymethyl-substituted styrene derivatives **4** toward “Cp_2Zr” showed a remarkable difference in reactivity.[4]





4 (*o*-, *m*- and *p*-isomers)

In this paper, we disclose a full account of the “Cp_2Zr”-mediated or -catalyzed reactions of *o*-, *m*-, and

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

(2) For recent reviews, see: (a) Marek, I., Ed. *Titanium and Zirconium in Organic Synthesis*, Wiley-VCH: Weinheim, Germany, 2002. (b) Suzuki, K.; Wipf, P., Eds.; Recent advances in the chemistry of zirconocenes. In Symposium-in print *Tetrahedron* **2004**, *60*, 1267.

(3) For review, see: Hanzawa, Y.; Ito, H.; Taguchi, T. *Synlett* **1995**, 299.

(4) Hanzawa, Y.; Ikeuchi, Y.; Nakamura, T.; Taguchi, T. *Tetrahedron Lett.* **1995**, *36*, 6503.

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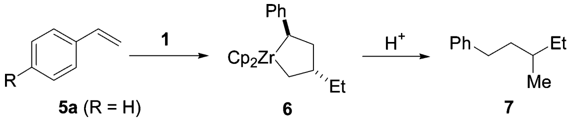


FIGURE 1. Regio- and stereoselective formation of **6**.[5]

p-alkoxymethyl-substituted styrene derivatives **4** and the unprecedented formation of homo- and heterocoupling products.

The reaction of styrene (**5a**) with “Cp_2Zr” has been reported to give regio- and stereoselectivily zirconacyclopentane intermediate **6**, which is converted to styrene−butene coupled product **7** in good yields by acid treatment (Figure 1).[5,6] In this coupling reaction, it is worth noting that the formation of the styrene−styrene homocoupling (dimerization) products has been reported to be less than 10% under thermodynamically equilibrated conditions.

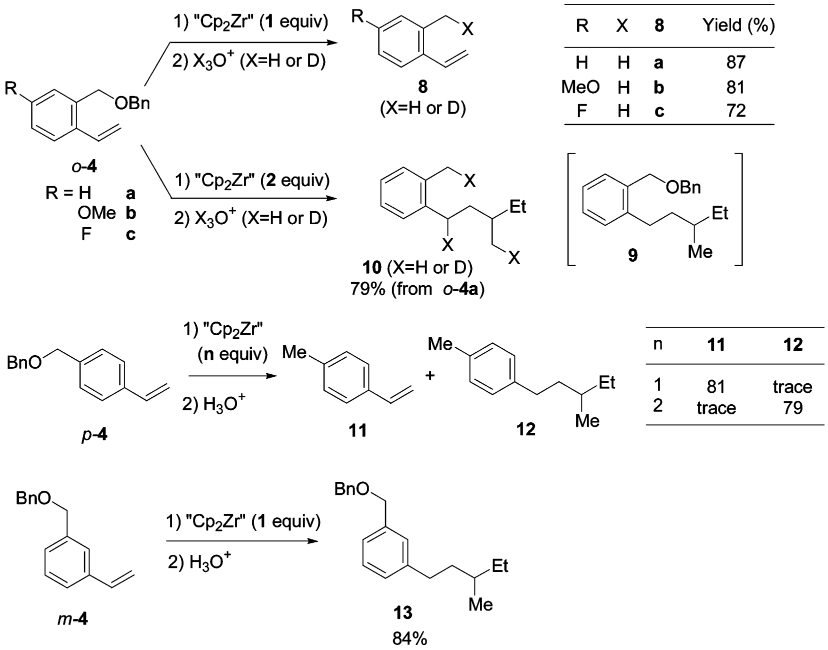
Results and Discussion

Generation of Benzylzirconocene Intermediates. The reactions of *o*-(benzyloxymethyl)styrene derivatives (*o*-**4a**−**c**) with a stoichiometric amount of “Cp_2Zr” in THF at room temperature gave *o*-methylstyrene compounds **8a**−**c** or the monodeuteriomethyl congener of **8a** after acidic workup ($HCl-H_2O$ or $DCl-D_2O$) in good yields (Scheme 1). To our surprise, butene-coupling product **9** could not be detected in the reaction media. The double bond of *o*-**4a** is indispensable because the reaction of dibenzyl ether with “Cp_2Zr” under the same conditions did not afford any products except the recovered starting material. Through use of 2 equiv of “Cp_2Zr”, *o*-**4a** afforded butene-coupling compound **10a** (X = H) in a 79% yield, and three deuterium atoms were incorporated into **10a** (X = D) by $DCl-D_2O$ workup. The reaction of *p*-(benzyloxymethyl)styrene (*p*-**4**) with “Cp_2Zr” indicated similar reactivity to that of *o*-**4a**. Thus, the formation of *p*-methylstyrene (**11**) or butene-coupling product **12** depended on the amount of “Cp_2Zr” employed. In the reaction of meta-substituted isomer *m*-**4** with an equivalent amount of “Cp_2Zr”, however, butene-coupling product **13** was obtained as the sole product as in the case of the styrene−“Cp_2Zr” reaction.

These results indicate that the insertion of zirconocene into the benzylic carbon−oxygen bond took place in the reactions of *o*- and *p*-**4** and not in the reaction of *m*-**4**, and thus, the importance of the π-conjugation is obvious. It is also obvious that benzylic zirconocene species is formed prior to the addition of the second “Cp_2Zr” in the reactions of *o*- and *p*-**4**. Thus, benzylzirconocene species **16**, for example, would be formed through (i) the ligand exchange of the first equivalent of “Cp_2Zr” with a double bond of *o*-**4a** giving a zirconacyclopropane derivative **14**, (ii) the elimination of the alkoxy group in **14** through the aromatic π-system to generate *o*-quinodimethane intermediate **15**,[7] and (iii) the transfer of the Cp_2Zr moiety to a benzylic position (Figure 2). The described processes (i−iii) explain the formation of **10** (X = H or D) in the reaction of *o*-**4a** with 2 equiv of “Cp_2Zr” or the formation of **13**.

Formation of Homocoupling Products (Dimerization). The reaction of *o*-(1-alkoxyisopropyl)styrene **17a**, which is a dimethyl-substituted analogue of *o*-**4a**, with an equivalent amount of “Cp_2Zr” afforded an unexpected homocoupling product **19a** as a mixture of trans/cis isomers[8] (ratio = 3.0/1). In addition, reduced product **18** was not detected (Scheme 2 and Table 1).[9] No deuterium was incorporated into **19a** by $DCl-D_2O$ workup. The homocoupling reactions were affected by the substituent, and thus *p*-methoxy-substituted styrene derivative **17c** gave a complex mixture (entry 3). It is worth mentioning that the reaction of the fluorine-substituted isomer **17d** with “Cp_2Zr” (1 equiv) gave a corresponding homocoupling product **19c** in a 29% yield (trans/cis = 2.5) together with **20** (X = H) in a 50% yield as a single cis-stereoisomer (entry 4).[8] The incorporation of one deuterium atom into **20** (X = D) by $DCl-D_2O$ workup indicates that the coupled product **20** is gener-

SCHEME 1



R	X	8	Yield (%)
H	H	a	87
MeO	H	b	81
F	H	c	72

n	11	12
1	81	trace
2	trace	79

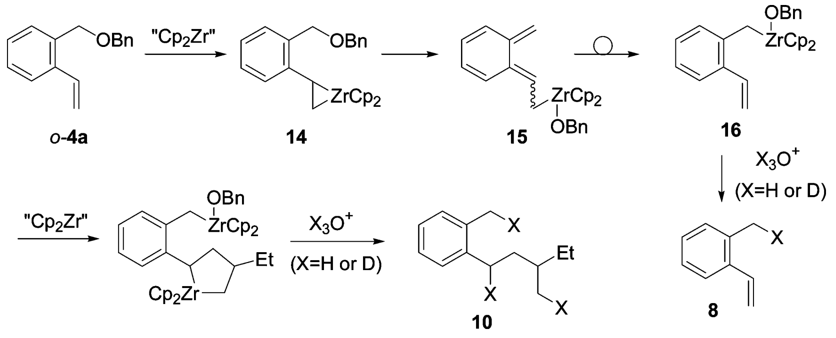


FIGURE 2. “Cp_2Zr”-mediated reaction pathway.

SCHEME 2

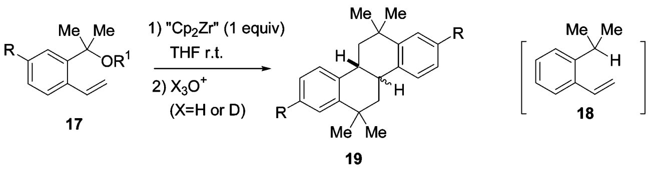
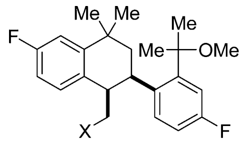


TABLE 1. Formation of 19^a



20 (*cis only*)
X = H, D, or $ZrCp_2(OMe)$

entry	**17**	% yield^b of **19** (trans/cis)	% yield^b of **20**
1	**17a**: R = H;	**19a**: 83 (3.0)	–
2	**17b**: R = H; $R^1 = CH_3$	**19a**: 78	–
3	**17c**: R = CH_3O; $R^1 = CH_3$	complex mixture	
4^c	**17d**: R = F; $R^1 = CH_3$	**19c**: 29 (2.5)	50
5^d	**17d**: R = F; $R^1 = CH_3$	**19c**: 53	28

^{a} Reaction conditions: **17** (0.5 mmol), “Cp_2Zr” (1.05 equiv), THF, rt. ^{b} Isolated yields. ^{c} 6.5 h of reaction time. ^{d} 97 h of reaction time.

ated as a zirconocene species in the reaction media. The prolonged reaction of **17d** (97 h) with an equivalent amount of “Cp_2Zr” increased the ratio of **19c** (53%) compared to **20** (28%) (entry 5), and thus the homocoupling reaction could be suggested to proceed with **20** (X = $ZrCp_2(OMe)$) as a key intermediate.

SCHEME 3

$$\textbf{17a} \xrightarrow[\text{room temp.}\ \text{THF}]{\text{"}Cp_2Zr\text{"}\ (n\ \text{equiv})} \textbf{19a} + \textbf{17a}$$

	Yield (%)^a	
n	**19a**	**17a**
1	83	-
1/2	84	-
1/3	62	31
1/3^b	75	-

^{a} Isolated yields. ^{b}*n*-BuLi (1/3 equiv) was added before hydrolytic workup.

The lack of deuterium introduction into **19** by the acidic workup with DCl−D_2O suggests that dimeric product **19** was not generated as an organometallic compound in the reaction media. A half equivalent of “Cp_2Zr” to **17a** was sufficient (84% yield) for the formation of **19a** (Scheme 3). The use of ⅓ equiv of “Cp_2Zr”, however, indicated a formation of **19a** in a lower yield (62%) with considerable recovery of **17a** (31%), and the addition of *n*-BuLi (⅓ equiv) to the reaction mixture prior to the hydrolytic workup increased the yield of **19a** (75%). Thus, the homocoupling process is a catalytic process with respect to “Cp_2Zr”.

The reactions of *o*-(alkoxymethyl)styrene derivatives with a catalytic amount of Cp_2ZrCl_2 (10 mol %) in the presence of 3 equiv of *n*-BuMgCl in THF at refluxing temperature[10] are summarized in Table 2. Under the catalytic conditions, improved yields of dimers **19** were observed in comparison to those under the stoichiometric conditions (entries 4−7). It is interesting to note that the styrene derivatives *o*-**4**, which did not give dimerization products under the stoichiometric conditions, gave dimerization products **19** under the catalytic conditions (entries 1 and 3). In contrast to the result of the reaction of *o*-**4**, *p*-(benzyloxymethyl)styrene (*p*-**4**) resulted in polymerization under catalytic conditions.

The catalytic process for the formation of **19** consisted of the prior formation of zirconacyclopropane **14′** and the formation of dialkoxyzirconocene, which regenerated “Cp_2Zr” through the reaction with Grignard reagent, and the dimerization product **19** was expelled from the catalytic cycle as shown in Figure 3.

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(5) Swanson, D. R.; Rousset, C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521.

(6) Besides the reactivity of styrene with a stoichiometric amount of **1**, the efficient alkylation reaction of the styrene double bond has been reported by treatment with a catalytic amount of Cp_2ZrCl_2 in the presence of Grignard reagent (3 equiv) and alkyl halides or tosylates. (a) Cesati, R. C., III; Armas, J.; Hoveyda, A. H. *Org. Lett.* **2002**, *4*, 395. (b) Armas, J.; Hoveyda, A. H. *Org. Lett.* **2001**, *3*, 2097. (c) Armas, J.; Kolis, S. P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 5977. (d) Terao, J.; Torii, K.; Saito, K.; Kambe, N.; Baba, A.; Sonoda, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 2653. (e) Terao, J.; Watanabe, T.; Saito, K.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1998**, *39*, 9201. (f) Swanson, D. R.; Rousset, C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521.

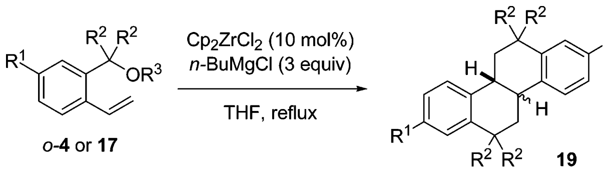
(7) The generation of *o*-quinodimethane intermediates from *o*-alkoxymethylstyrene and its related compounds through the elimination of an alkoxyl group has been reported. (a) Hirao, A.; Negishi, Y.; Hayashi, M.; Sako, K.; Ryu, W.; Loykulnant, S.; Matsuo, A.; Sugiyama, K. *Macromol. Chem. Phys.* **2001**, *202*, 3590. (b) Hirao, A.; Kitamura, K.; Takenaka, K.; Nakahama, S. *Macromolecules* **1993**, *26*, 4995. (c) Ishizone, T.; Kato, R.; Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1991**, *24*, 1449. See also: (d) Moss, R. J.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 1992. (e) Moss, R. J.; White, R.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 5132. (f) Moss, R. J.; Rickborn, B. *J. Org. Chem.* **1984**, *49*, 3694. (g) Tuschka, T.; Naito, K.; Rickborn, B. *J. Org. Chem.* **1983**, *48*, 70.

(8) Structure was determined by X-ray analysis.

(9) Although dimer **19a** was obtained in a lower yield, using methyl ether **17b**, than benzyl ether **17a**, for easy preparation of substrates, methyl ether derivatives were prepared for the other substrates. See the Supporting Information.

(10) It was essential to heat the reaction mixture to reflux to bring about an efficient formation of **19**.

TABLE 2. Formation of 19 from *o*-4 or 17 under Catalytic Conditions[a]



entry	*o*-4 or 17	% yield[b] of 19 (trans/cis)
1	***o*-4a**	**19d**: 57 (1.3)
2	***o*-4b**	**19e**: nd
3	***o*-4c**	**19f**: 52 (2.1)
4	**17a**	**19a**: 89 (2.8)
5	**17b**	**19a**: 81 (3.0)
6	**17c**	**19b**: 55 (2.4)
7	**17d**	**19c**: 44[c] (1.4)

[a] Reaction conditions: *o*-4 or **17** (0.5 mmol), Cp_2ZrCl_2 (10 mol %), *n*-BuMgCl (3 equiv), THF, reflux. [b] Isolated yields. [c] Coupled product **20** was also obtained in a 34% yield.

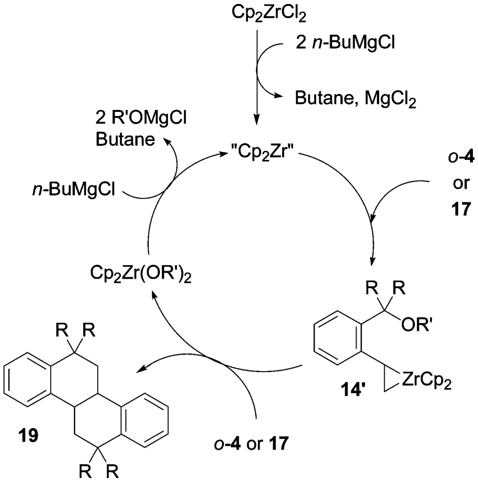
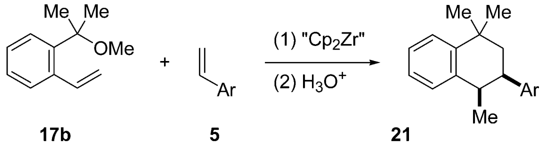
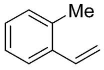


FIGURE 3. Catalytic cycle for the formation of **19**.

Formation of Heterocoupling Products. Although the mechanism for the Cp_2ZrCl_2-catalyzed or "Cp_2Zr"-mediated homocoupling formation of **19**, which will be discussed later, is still unclear, it may be of interest to investigate the possibility for the heterocoupling reaction of **17** with other olefins. Attempts to obtain such heterocoupling products would contribute to the understanding of the reaction mechanisms for the formation of **19**. The results of the reaction of **17** with styrene (**5a**) as a heterocoupling partner are shown in Table 3. Thus, in the "Cp_2Zr"-mediated reaction of **17b** with 1 equiv of styrene (**5a**), heterointermolecular coupling product **21a** was obtained in a 56% yield as a single cis-stereoisomer[8] along with homodimer **19a** (21% yield), and neither styrene (**5a**)−butene nor styrene−styrene coupling product (see, Figure 1) was obtained. Use of 3 equiv of styrene (**5a**) increased the yield of **21a** to 85% (entry 2). Treatment of the reaction mixture with DCl/D_2O afforded the monodeuteriomethyl compound of **21a** in an excellent deuterium content (>95% D, 79% yield). The intermolecular heterocoupling reaction of **17** was restricted to a styrene double bond, without a substituent on the double bond, as a coupling partner (Table 3). All other examined unsaturated compounds, such as maleic anhydride, 3,4-dihydrofuran, phenylacetylene, diphenylacetylene, *cis*- or *trans*-stilbene, and α- or *β*-methylstyrene, did not give a heterocoupling product but gave the homocoupling product **19**. It should be noted that the "Cp_2Zr"-mediated reaction of *o*-benzyloxymethystyrene (*o*-**4a**) with styrene (**5a**) gave a reduced product **8a** as the sole product (entry 8). The heterointermolecular coupling reaction of **17b** with styrene (**5a**) was also carried out under the same catalytic conditions with a similar efficiency to the stoichiometric conditions (entry 3).

TABLE 3. Heterocoupling Reactions of 17b with Styrene Derivatives[a]



entry	5 Ar		21 yield (%)[b]	
1	C_6H_5-	**5a**	56 (21)	**21a**
2[c]	C_6H_5-	**5a**	85 (5)	**21a**
3[d]	C_6H_5-	**5a**	85 (5)	**21a**
4	4-F-C_6H_4-	**5b**	81 (5)	**21b**
5	3,5-$(CF_3)_2$-C_6H_3-	**5c**	11 (-)	**21c**
6	4-CH_3O-C_6H_4-	**5d**	35 (60)	**21d**
7	2-CH_3O-C_6H_4-	**5e**	59 (29)	**21e**
8	***o*-4a + 5a**		 Me **8a**	

[a] Reaction conditions: **17b** (0.5 mmol), **5** (3 equiv), "Cp_2Zr" (1.2 equiv), THF, rt. [b] Isolated yields. The yields of **19** are shown in parentheses. [c] 1 equiv of **5a** was used. [d] Reaction conditions: Cp_2ZrCl_2 (10 mol %), *n*-BuMgCl (3 equiv), THF, reflux.

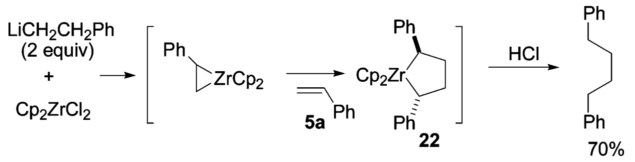
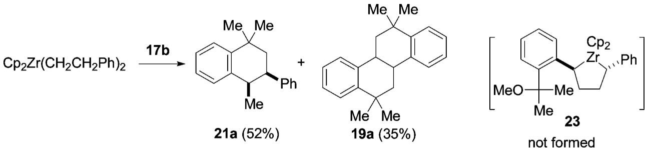


FIGURE 4. Regio- and stereoselective formation of **22** by Negishi et al.

SCHEME 4



Mechanistic Consideration of Coupling Reactions. Concerning the "Cp_2Zr"-mediated styrene−styrene homocoupling reaction, the reaction of $Cp_2Zr(CH_2CH_2Ph)_2$ with styrene has been reported to give *trans*-2,5-diphenylzirconacyclopenatane intermediate **22**.[5] The stereo- and regioselective formation of **22** was ex-

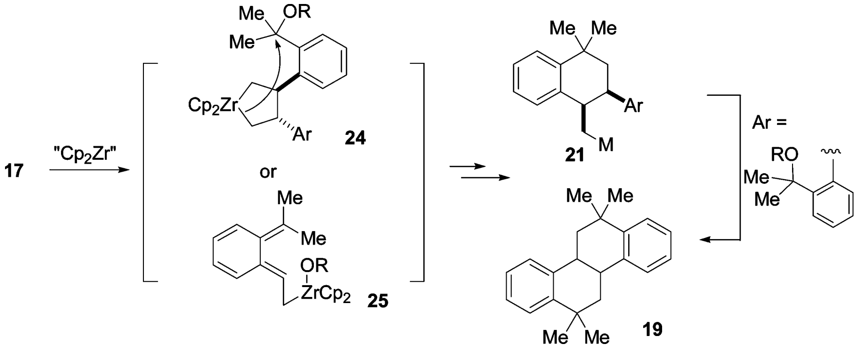
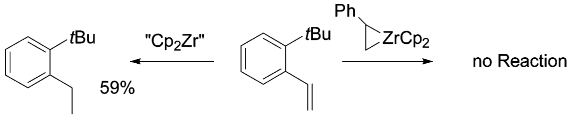


FIGURE 5. Supposed intermediates.

SCHEME 5



plained to be a result of the favorable thermodynamic effect of benzylic and/or agostic interaction of the α-phenyl group to Zr (Figure 4). Treatment of **17b** with $Cp_2Zr(CH_2CH_2Ph)_2$ under identical conditions afforded **19a** and **21a**, and a product derived from 2-[2-(methoxyisopropyl)phenyl]-5-phenylzirconacyclopentane **23**, which corresponds to **22** could not be obtained (Scheme 4). At this point in time, either one of the intermediates, zirconacyclopentane **24** or *o*-quinodimethane intermediate **25**, could be involved as a key intermediate for the formation of **19** or **21** (Figure 5). It is interesting to note that the reaction of *o*-*tert*-butylstyrene (**26**) with an equivalent amount of "Cp$_2$Zr" gave *o*-*tert*-butylethylbenzene (59%) along with the recovered **26** (35%) (Scheme 5). Furthermore, the reaction of $Cp_2Zr(CH_2CH_2Ph)_2$ with *o*-*tert*-butylstyrene (**26**) ended with a recovery of **26**. These observations imply that a ligand exchange would be possible in the reaction of *o*-*tert*-butylstyrene (**26**) with "Cp$_2$Zr" giving **26**−zirconocene complex, which did not react with butene. It is also obvious that **26** did not couple with styrene−zirconocene complex, and thus, the participation of the alkoxy group in *o*-**4** or **17** plays a significant role in the reaction with "Cp$_2$Zr". It should also be noted that the stereochemistry of heterocoupling products **21** or the supposed intermediate **20d** (R = F) for homocoupling (see, Scheme 2) is cis while the stereochemistry of homodimer **19** itself is a mixture of cis and trans isomers. Thus, the stereochemical outcome of homodimer **19** would suggest that once formed cis stereochemistry in **20** does not last through the reaction.[11]

Conclusions

In conclusion, we found unexpected and unprecedented reactions of "Cp$_2$Zr" with (alkoxymethyl)styrene derivatives. Reactions of *o*- or *p*-(alkoxymethyl)styrene derivatives with a stoichiometric amount of "Cp$_2$Zr" resulted in the insertion of zirconocene into a benzylic carbon−oxygen bond. Reactions of *o*-(1-alkoxyisopropyl)styrene derivatives with a stiochiometric and/or a catalytic amount of "Cp$_2$Zr" (Cp_2ZrCl_2 (10 mol %)) in the presence of 3 equiv of *n*-BuMgBr cause dimerization reactions as a major product. The catalytic process turned out to be efficient also for the dimerization of *o*-(alkoxymethyl)-styrene, which yields benzylzirconocene species under the stoichiometric conditions. Heterocoupling reactions of *o*-(1-alkoxyisopropyl)styrene derivatives with styrene have been brought about in high cis-stereoselectivity. Although the precise reaction mechanism for the described formation of homo- and heterocoupling products has yet to be elucidated, the intramolecular Diels−Alder reaction is supposed to be involved at this point in time.

Experimental Section

Typical Procedure for Generation and Butene-Coupling Reactions of Benzylzirconocene Intermediates. To a solution of Cp_2ZrCl_2 (153 mg, 0.53 mmol) in THF (5 mL) was added *n*-BuLi (1.6 M solution in *n*-hexane, 0.66 mL, 1.05 mmol) at −78 °C and the mixture was stirred for 1 h at the same temperature. To this solution was added a solution of *o*-**4a** (112 mg, 0.50 mmol) in THF (2 mL) with gradual warming to room temperature, and the solution was stirred for 3 h. To this reaction mixture was added 1 M HCl (aq), extracting with ether. The organic layer was washed with brine and dried over anhydrous $MgSO_4$, and the filtrate was concentrated to dryness. The residue was purified by flash chromatography (*n*-hexane) to give **8a** (52 mg, 88%).

1-Methy-2-vinylbenzene (8a): The structure was confirmed by comparison of spectral data from a commercially available sample.

1-Methyl-2-(3-methylpentyl)benzene (10): This product was prepared from *o*-**4a** (112 mg, 0.50 mmol), Cp_2ZrCl_2 (307 mg, 1.05 mmol), and *n*-BuLi (1.6 M, 1.31 mL, 2.10 mmol) according to the typical procedure. Colorless oil. IR (neat) 2961, 2928, 2873, 1906, 1605, 1493, 739 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.25−7.13 (4H, m), 2.78−2.56 (2H, m), 2.37 (3H, s), 1.66−1.25 (5H, m), 1.02 (3H, d, J = 6.1 Hz), 0.96 (3H, t, J = 7.2 Hz). ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 141.4, 135.7, 130.1, 128.7, 125.9, 125.7, 37.3, 34.7, 30.9, 29.4, 19.23, 19.19, 11.4. EI-MS (*m/z*) 176 (M$^+$).

Typical Procedure for Homocoupling Reactions under Catalytic Conditions. To a solution of **17b** (88 mg, 0.50 mmol) and Cp_2ZrCl_2 (14.6 mg, 0.05 mmol) in THF (5.2 mL) was added *n*-BuMgCl (0.84 M solution in THF, 1.79 mL, 1.50 mmol) at room temperature and the mixture was refluxed for 5 h. To this reaction mixture was added by 1 M HCl (aq) at 0 °C, extracting with ether. The organic layer was washed with brine and dried over anhydrous $MgSO_4$, and the filtrate was concentrated to dryness. The residue was purified by flash chromatography (*n*-hexane) to give **19a** (59 mg, 81%) as a

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[11] It is known that the formation of **19d** by intramolecular Diels−Alder reaction of *o*-quinodimethane intermediate is generated from a sulfone derivative. Thus, the formation of **19** from **21** might have occurred via a similar pathway. See: Levy, L. A.; Sashikumar, V. P. *J. Org. Chem.* **1985**, *50*, 1760.

mixture of trans/cis = 3.0. Recrystallization from EtOH gave *trans*-**19a** as a single isomer.

***trans*-6,6,12,12-Tetramethyl-4b,5,6,10b,11,12-hexahydrochrysene (*trans*-19a):** Colorless crystalline solid. Mp (EtOH) 169.5−172.0 °C. IR (KBr) 2955, 2905, 2854, 1485, 1344, 755, 743 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.46−7.18 (8H, m), 2.88 (2H, dd, *J* = 11.0, 1.0 Hz), 2.44 (2H, dd, *J* = 12.5, 1.0 Hz), 1.71 (2H, dd, *J* = 12.5, 11.1 Hz), 1.44 (12H, s). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 145.8, 138.9, 127.0, 126.1, 125.6, 125.4, 44.0, 38.6, 35.3, 33.1, 32.6. EI-MS (*m/z*) 290 (M$^+$). Anal. Calcd for $C_{22}H_{26}$: C, 90.73; H, 9.27. Found: C, 91.03; H, 9.23.

***cis*-6,6,12,12-Tetramethyl-4b,5,6,10b,11,12-hexahydrochrysene (*cis*-19a)**: Colorless crystalline solid. Mp (ether) 161.4−163.4 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.43−7.15 (8H, m), 3.25 (2H, dd, *J* = 13.1, 4.2 Hz), 1.99 (2H, br t, *J* = 13.1 Hz), 1.69 (2H, dd, *J* = 14.2, 4.2 Hz), 1.40 (6H, s), 1.35 (6H, s). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 145.0, 140.0, 129.5, 126.4, 125.7, 125.3, 43.4, 35.3, 34.8, 31.3, 30.3.

Typical Procedure for Heterocoupling Reactions. To a solution of Cp_2ZrCl_2 (175 mg, 0.60 mmol) in THF (5 mL) was added *n*-BuLi (1.6 M solution in *n*-hexane, 0.75 mL, 1.20 mmol) at −78 °C with 1 h of stirring at the same temperature. To this solution was added a solution of **17b** (112 mg, 0.50 mmol) and **5a** (156 mg, 1.50 mmol) in THF (2 mL), which was gradually warmed to room temperature and stirred for 3 h. To this reaction mixture was added 1 M HCl (aq), extracting with ether. The organic layer was washed with brine and dried over anhydrous $MgSO_4$, and the filtrate was concentrated to dryness. The residue was purified by flash chromatography (*n*-hexane), and further purification was carried out by MPLC (*n*-hexane) to give **21a** (106 mg, 85%).

1,1,4-Trimethyl-3-phenyl-1,2,3,4-tetrahydronaphthalene (21a): Colorless crystalline solid. Mp (ether) 75.4−76.4 °C. IR (KBr) 2962, 2931, 1487, 1452, 1040, 763, 751, 699 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.37−7.31 (3H, m), 7.26−6.97 (6H, m), 3.38 (1H, ddd, *J* = 13.6, 4.8, 1.9 Hz), 3.09 (1H, dq, *J* = 7.2, 4.8 Hz), 2.25 (1H, dd, 13.6, 13.0 Hz), 1.73 (1H, dd, *J* = 13.0, 1.9 Hz), 1.44 (3H, s), 1.31 (3H, s), 0.87 (3H, d, *J* = 7.2 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 144.8, 144.4, 142.1, 129.2, 128.2, 127.8, 126.9, 126.2, 126.0, 125.6, 40.4, 39.4, 37.2, 35.2, 32.7, 32.3, 18.1. EI-MS (*m/z*) 250 (M$^+$). Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.25; H, 8.46.

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Supporting Information Available: Experimental procedures and characterization data for products and starting materials, and X-ray data of **19a**−**c**,**f**, **20**, and **21a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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