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Cycloaddition Reaction of Zirconacyclopentadienes to Alkynes: Highly Selective Formation of Benzene Derivatives from Three Different Alkynes

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Abstract: Zirconacyclopentadienes reacted with acetylenecarboxylates in the presence of a stoichiometric amount (2 equiv) of copper chloride to give benzene derivatives in high yields along with the formation of a copper mirror on the wall of the reaction vessel. Reactions of unsymmetrical zirconacyclopentadienes prepared from two different alkynes with acetylenecarboxylates gave benzene derivatives from three different alkynes in high yields with high selectivities. Preparation of unsymmetrical zirconacyclopentadienes and benzene derivatives formation can be done in one-pot. The structure of the reaction product of the unsymmetrical zirconacyclopentadiene having a trimethylsilyl group and a methyl group in the α- and *β*-position, respectively, with acetylenedicarboxylate was determined by X-ray analysis. It indicated that the regiochemistry of those substituents was maintained during the reaction. When the coupling reaction of zirconacyclopentadienes with acetylenedicarboxylate in the presence of copper chloride was carried out at −78 °C, linear trienes were obtained as the intermediates in high yields after hydrolysis. Warming the mixture without hydrolysis gave the desired benzene derivatives in high yields. Use of an unsymmetrical zirconacyclopentadiene afforded a mixture of two isomers of the linear triene as intermediates after hydrolysis. When the mixture of the two isomers was warmed to room temperature without hydrolysis, both isomers gave the same benzene derivative. In the presence of a catalytic amount of copper chloride (10 mol %), this cycloaddition proceeded to give benzene derivatives in good yields without formation of the copper mirror. The reaction under the catalytic conditions at −78 °C also gave a linear triene after hydrolysis.

Introduction

Benzene derivatives have been very important compounds not only in synthetic chemistry but also in the history of organic chemistry. It is well-known that benzene derivatives have been prepared from three alkynes in the presence of a catalytic or a stoichiometric amount of transition metal compounds.[1−13] However, the control of the intermolecular coupling of the three alkynes remained to be studied. When two or three different alkynes were used, in most cases a mixture of several benzene derivatives was obtained.[3a−c] Therefore, there has been no selective intermolecular coupling of three different alkynes giving benzene derivatives in high yields.[14] One of the major problems is the difficulty in selective intermolecular coupling

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(1) (a) Schore, N. E. *Chem. Rev.* **1988,** *88*, 1081. (b) Schore, N. E. in *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Tokyo, 1991: Vol. 5, p 1144. (c) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry* II; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pargamon: 1995; Vol. 12, p 741.

(2) For Co review, see: (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984,** *23*, 539−556. (b) Hubert, A. J.; Dale, J. *J. Chem. Soc.* **1965**, 3160−3170. (c) Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 3800−3807. (d) Chalk, A. J.; Jerussi, R. A. *Tetrahedron Lett.* **1972**, 61−62. (e) Krüerke, U.; Hüberl, W. *Chem. Ber.* **1961**, *94*, 2829. (f) Hopff, H.; Gat, A. *Helv. Chim. Acta* **1965**, *48*, 509. (g) Krüerke, U.; Hoogzand, C.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2817. (h) Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 4729.

(3) For Ni: (a)Sauer, J. C.; Cairns, T. L. *J. Am. Chem. Soc.* **1957**, *79*, 2659−2660. (b) Meriwether, L. S.; Colthup, E. C.; Kennerly, G. W.; Reusch, R. N. *J. Org. Chem.* **1961**, *26*, 5155−5163. (c) Donda, A. F.; Moretti, G. *J. Org. Chem.* **1966**, *31*, 985−987. (d) Reference 2c−f.

(4) For Pd: (a) Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 161−176. (b) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93−99. (c) Reference 2c.

(5) For Rh: (a) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298−1303.

(6) For Ir: (a) Rappoli, B. J.; Churchill, M. R.; Janik, T. S.; Rees, W. M.; Atwood, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 5145−5149. (b) Reference 5a. (c) Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127−5129.

(7) For Ti: (a) Lutz, E. F. *J. Am. Chem. Soc.* **1961**, *83*, 2551−2554. (b) Meijer-Veldman, M. E. E.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1984**, *260*, 199−205. (c) Reference 2c. (d) Hoover, F. W.; Webster, O. W.; Handy, C. T. *J. Org. Chem.* **1961**, *26*, 2234. (e) Franzus, B.; Canterino, P. J.; Wicklifte, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 1514. (f) Hübel, W.; Hoogzand, C. *Chem. Ber.* **1960**, *93*, 3, l03.

(8) For Nb: (a) Masuda, T.; Deng, Y.; Higashimura, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2798−2801. (b) Williams, A. C.; Sheffels, P.; Sheehan, D.; Livinghouse, T. *Organometallics* **1989**, *8*, 1566.

(9) For Ta: (a) Reference 8 (b) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067−2069. (c) Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holms, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275.

(10) For Fe: (a) Reppe, W.; Vetter, H. *Liebigs, Ann. Chem.* **1953**, *585*, 133.

(11) For Cr: (a) Tsutsui, M.; Zeiss, H. *J. Am. Chem. Soc.* **1959**, *81*, 6090. (b) Herwig, W.; Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1959**, *81*, 6203. (c) Throndesen, H. P.; Metlesics, W.; Zeiss, H. *J. Organomet. Chem.* **1966**, *5*, 176.

(12) For Al: Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 2213.

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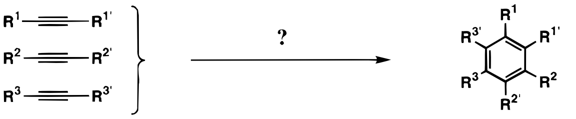
of two different alkynes to give unsymmetrical metallacyclopentadienes as intermediates to benzene derivatives. On the other hand, in the case of zirconium, several preparative methods of highly selective intermolecular coupling of two different alkynes have been reported.[15,16] Unfortunately, a further reaction of zirconacyclopentadienes with the third alkyne to give benzene derivatives has not been known.

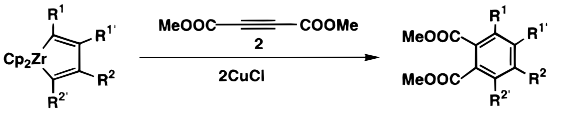


(1)

In this paper we would like to report the reaction of zirconacyclopentadienes with acetylenecarboxylates in the presence of copper chloride.[17] This reaction led to the highly selective one-pot formation of benzene derivatives by intermolecular coupling of three different alkynes in high yields. We would like to also report the mechanistic aspects of the cycloaddition reaction of zirconacyclopentadienes to the third alkyne.

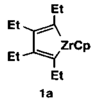
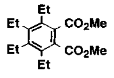
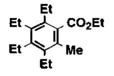
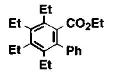
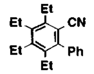
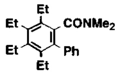
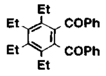
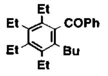
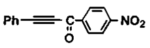
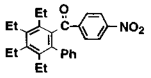
Results and Discussion

Cycloaddition Reaction of Zirconacyclopentadienes with Dimethyl Acetylenedicarboxylate. Zirconacyclopentadienes (**1**) do not react with the third alkyne such as 4-octyne and dimethyl acetylenedicarboxylate **2** to give benzene derivatives.[18] However, in the presence of copper chloride[19] they reacted with **2** at room temperature for 1 h to give benzene derivatives.[17] The best yield was achieved when 2 equiv of copper chloride was used. The results are shown in Table 1.



1 **3** (2)

Table 1. Reaction of Zirconacyclopentadienes with Acetylene Derivatives[a]

Zirconacyclopentadienes	Alkyne	Time/h	Product	Yield/%[b]
 **1a**	**2**	1	 **3a**	95(59)
1a	Me—≡—CO_2Et	48	 **3b**	84(58)
1a	Ph—≡—CO_2Et	36	 **3c**	92(57)
1a	Ph—≡—CN	3	 **3d**	97(70)
1a	Ph—≡—$CONMe_2$	12	 **3e**	82(55)
1a	PhCO—≡—COPh	3	 **3f**	57(48)
1a	Bu—≡—COPh	48	 **3g**	54(28)
1a		1	 **3h**	64(42)

[a] The reaction was carried out in the presence of 2 equiv of CuCl in THF at room temperature. Zirconacyclopentadienes were prepared in situ. [b] GC yields. Yields were based on alkynes. Isolated yields were given in parentheses.

The desired benzene derivatives were obtained in good to high yields. Zirconacyclopentadiene **1a** prepared in situ from Cp_2ZrBu_2 (Negishi reagent)[20] and 2 equiv of 3-hexyne reacted with **2** in the presence of 2 equiv of CuCl gave dimethyl 3,4,5,6-tetraethyl-1,2-benzenedicarboxylate **3a** in 95% yield for 1 h. After the reaction, the formation of a copper mirror on the wall of the reaction vessel was observed. In the presence of 2 equiv of CuCN, CuI, or CuBr instead of CuCl, **3a** was obtained in a similar yield. Use of $CuCl_2$ gave a low yield (28%) of **3a**. When other metal halides such as $SnCl_2$, $SnCl_4$, $CoBr_2$, and $BiCl_3$ were used instead of CuCl, **3a** was obtained in 15−35% yields.

Acetylene with a one electron-withdrawing group such as ethyl propiolate and ethyl phenylpropiolate could be used for the cycloaddition reaction. However, longer reaction time (38−48 h) was necessary to complete the reaction (yields: 84% and 92%, respectively). Other electron-withdrawing groups such as CN, $CONMe_2$, COPh also afforded satisfactory results as shown in Table 1. Unactivated acetylene such as 4-octyne did not give the desired benzene derivatives even at higher temperature. For this benzene formation from zirconacyclopentadienes, at least one electron-withdrawing group was requisite for the third alkyne.

This addition reaction similarly proceeded under the same conditions for bicyclic zirconacyclopentadienes **4a**−**4d** prepared

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(13) For heterogeneous catalysts, see: (a) Jhingan, A. K.; Maier, W. F. *J. Org. Chem.* **1987**, *52*, 1161−1165. (b) Bertolini, J. C.; Massardier, J.; Dalmai-Imelik, G. *J. Chem. Soc.* **1978**, *74*, 1720. (c) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M., *J. Chem. Soc., Chem. Commun.* **1983**, 623. (d) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *Surf. Sci.* **1983**, *135*, 128. (e) Sesselmann, W.; Waratsckeck, B.; Ertl, G.; Küppers, J.; Haberland, H. *Surf. Sci.* **1983**, *130*, 245.

(14) Yamazaki and Wakatsuki et al. reported the formation of a benzene derivative with three different alkynes via a cyclopentadienyl cobalt diphenylacetylene complex. However, the intermediate, cobaltocyclopentadiene, was obtained as a mixture of two isomers in a ratio of 1:8. After separation by column chromatography, the reaction with the third alkyne was carried out. In addition, the combined yield of the cobaltocyclopentadienes was 48%, and the yield of benzene derivatives from the cobaltocyclopentadiene was 36% yield. Therefore overall yield of the benzene derivatives with three different alkynes based on cobalt diphenylacetylene complex was only ca. 15%. See: Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549.

(15) For intermolecular cross-coupling reactions of alkynes with zirconocene, see: (a) Takahashi, T.; Swanson, R. D.; Negishi, E. *Chem. Lett.* **1987**, 623. (b) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870. (c) Wagenen, B. C. V.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495. (d) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687. (e) Hara, R.; Xi, Z.; Kotora, M.; Xi, C.; Takahashi, T. *Chem. Lett.* 1996, 1003.

(16) Xi, Z.; Hara, R.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444.

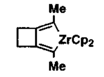
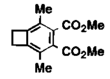
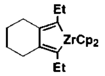
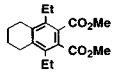
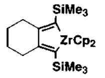
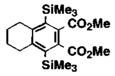
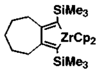
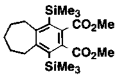
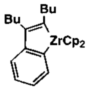
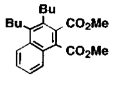
(17) Preliminary result has been reported, see: Takahashi, T.; Kotora, M.; Xi, Z. *J. Chem. Soc., Chem. Commun.* **1995**, 361−362.

(18) Insertion of an alkyne into a zirconacyclopentadiene has been reported, see: Famili, A.; Farona, M. F.; Thanedar, S. *J. Chem. Soc., Chem. Commun.* **1983**, 435−436. This result is different from our observation. However, the reaction of zirconacyclopentadienes with the third alkyne is quite dependent on the presence of salts. Therefore we assume that some salts such as mercury halides have a remarkable effect in Farona's case, but it is not clear.

(19) Cu(I)-catalyzed or mediated C−C bond formation of zirconacyclopentadienes has been recently developed. See: (a) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154. (b) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Organometallics* **1994**, *13*, 4183.

(20) (a)Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (b) Negishi, E.; Holms, S. J.; Tour, J.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336−3346.

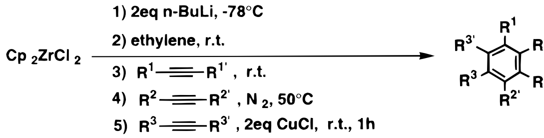
Table 2. Reaction of Bicyclic Zirconacyclopentadienes with 2 in the Presence of Copper Chloride[a]

Bicyclic Zirconacyclopentadienes	Products	Yield/%
 **4a**	 **5a**	73(57)
 **4b**	 **5b**	93(64)
 **4c**	 **5c**	85(70)
 **4d**	 **5d**	85(67)
 **4e**	 **5e**	80(54)

[a] Bicyclic zirconacyclopentadiene **4a**−**4d** were prepared in situ from Cp_2ZrBu_2 (Negishi reagent) and diynes.[20,21] Zirconaindene **4e** was prepared according to the literature.[22]

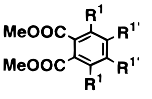
from diynes.[20,21] The benzene derivatives **5a**−**5d** were obtained in high yields. Zirconaindene complex **4e**[22] also reacted with **2** to give dibutylnaphthalene derivative **5e** in 80% yield. The results are shown in Table 2.

One-Pot Coupling of Three Different Alkynes. Recently we have reported a highly selective coupling of alkynes to prepare the unsymmetrical zirconacyclopentadienes via zirconacyclopentane[23] and zirconacyclopentenes.[15d,16,24] Combination of this addition reaction of zirconacyclopentadienes with the preparation of unsymmetrical zirconacyclopentadienes is very attractive and provides a convenient one-pot reaction from three different alkynes to benzene derivatives as shown in the following (eq 3).



(3)

Results of this one-pot reaction are shown in Table 3. In all cases the yields were very high. Other benzene derivatives **6** and **7** as byproducts are also shown in Table 3. In most cases, the total amount of these byproducts was less than 4%.


6

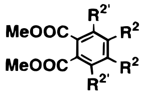

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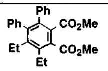
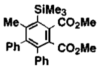
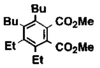
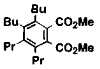
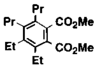
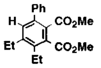
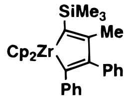
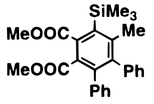
Table 3. Formation of Benzene Derivatives from Three Different Alkynes by One-Pot Reaction

1st Alkyne	2nd Alkyne	3rd Alkyne	Product		Yield/%	**6**/%	**7**/%
Et—≡—Et	Ph—≡—Ph	**2**		**3i**	95(63)	0	tr
Me₃Si—≡—Me	Ph—≡—Ph	**2**		**3j**	(56)	<2	<2
Bu—≡—Bu	Et—≡—Et	**2**		**3k**	90(71)	3	tr
Bu—≡—Bu	Pr—≡—Pr	**2**		**3l**	87(62)	tr	4
Pr—≡—Pr	Et—≡—Et	**2**		**3m**	91(60)	0	2
Et—≡—Et	Me₃Si—≡—Bu	**2**		**3n**	83(74)	0	tr
Et—≡—Et	Ph—≡—H	**2**		**3o**	85(66)	2	0

The scheme of this one-pot reaction is shown below (Scheme 1). The reaction of Cp_2ZrCl_2 with 2 equiv of *n*-BuLi gives Cp_2ZrBu_2 (Negishi reagent) quantitatively, that is converted into a zirconocene butene complex which behaves as a Cp_2Zr equivalent.[20] The Cp_2Zr equivalent reacts with 2 equiv of ethylene to provide zirconacyclopentane **8** quantitatively. In the presence of ethylene gas, zirconacyclopentane **8** reacts selectively only with one alkyne to give **9**. At 50 °C under nitrogen atmosphere, ethylene in the reaction mixture gradually disappears, and then **9** reacts with the second alkyne to give unsymmetrical zirconacyclopentadienes in high yields with high selectivities. To the reaction mixture of unsymmetrical zirconacyclopentadienes **1** was added 2 equiv of CuCl and **2**. As described above, benzene derivatives are formed in high yields with high selectivities.

Formation of zirconacyclopentadiene **1j** was observed in the reaction of diphenylacetylene and 1-trimethylsilylpropyne. A trimethylsilyl group and a methyl group are selectively in the α and *β* position of **1j**. To verify the order of the substituents of the product **3j**, we determined the molecular structure of **3j** by X-ray analysis. The structure of **3j** is shown in Figure 1. The regiochemistry of a trimethylsilyl group and a methyl group in **1j** was maintained during the reaction.


1j


3j

Mechanism of Cycloaddition Reaction of Zirconacyclopentadienes to Dimethyl Acetylenedicarboxylate. The mechanism of the benzene formation reaction from alkynes catalyzed or mediated by transition metal compounds has been intensively investigated.[14,25] One of the most acceptable intermediates is a metallacyclopentadiene. In the case of cobalt, the cobaltacyclopentadienes were isolated, and they reacted with the third alkyne to form benzene derivatives.[14,25d] However, the reaction mechanism from metallacyclopentadienes to benzene derivatives still remained unclear. Although two possible paths from metallacyclopentadienes to benzene derivatives have been suggested many times, experimental observation of the intermediates was very limited. As shown in Scheme 2, there are

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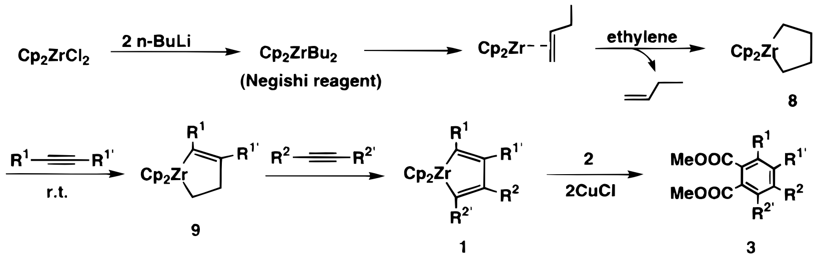
(21) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788−2796.

(22) (a)Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411−7413. See also (b) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (c) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (d) Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246.

(23) Takahashi, T.; Fischer, R.; Xi, Z.; Nakajima, K. *Chem. Lett.* **1996**, 357−358.

(24) Takahashi, T.; Xi, Z.; Rousset, C. J.; Suzuki, N. *Chem. Lett.* **1993**, 1001−1004.

Scheme 1



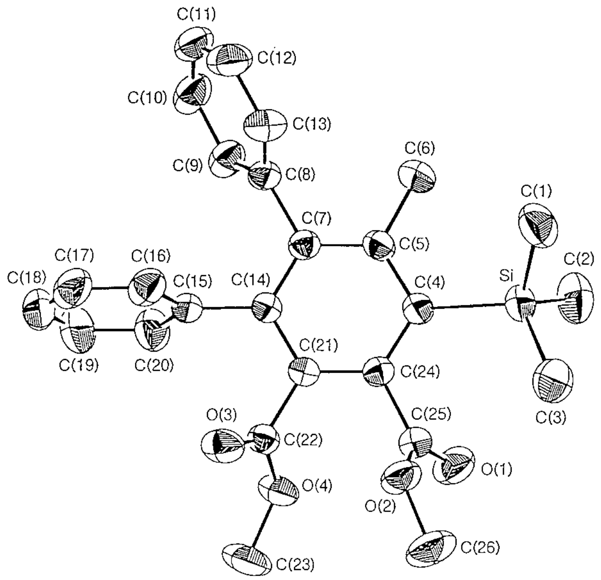
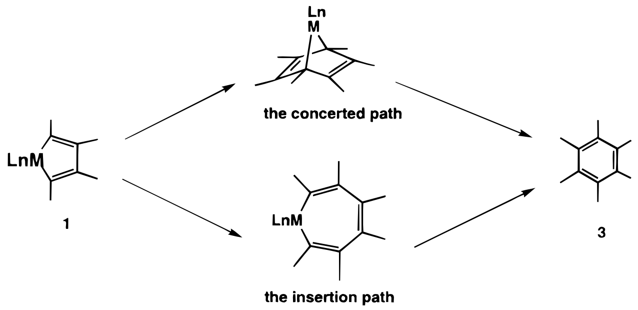


Figure 1.

Scheme 2



mainly two paths, one is the concerted path (Diels−Alder type) and the other is the stepwise insertion path.

In some cases strong evidence for the concerted path was observed.[26] However, there has been no report on the experimental observation of the insertion intermediate in conversion of metallacyclopentadienes into benzene derivatives, although the same type of compound has been prepared and characterized in different reactions. Interestingly, when the reaction of **1a** with **2** was carried out at −78 °C, the reaction proceeded, and the linear triene **10** was obtained in 78% yield after hydrolysis. When the mixture was warmed to room temperature, benzene derivative **3a** was formed as a single product.

This clearly indicated that the third alkyne **2** was inserted into the carbon−metal bond. Since **1a** does not react with **2** in the absence of CuCl, transmetalation of one or two sp^2 carbons in **1a** from zirconium to copper must occur first by the reaction with CuCl.[19,27−29] It is reasonable that the sp^2 carbon attached to the copper metal center reacts with **2** via Michael addition to give dimetallotriene derivatives **11** or **12**. Hydrolysis of the dimetallotriene derivative affords the triene **10**. Deuteriolysis instead of hydrolysis gave dideuterated product **10D**. Since only the syn-addition product **10** was formed under conditions used here, the intermediate **11** is more likely. At higher temperature **11** reacts further to give **3a**. As an intermediate, a monometalotriene shown in the parenthesis is also possible.

The triene formation was also observed for unsymmetrical zirconacyclopentadiene **1n**. At −78 °C **1n** reacted with **2** to give a mixture of two isomers **13** and **14** in a ratio of 4:1 in 64% combined yield after hydrolysis. Hydrolysis of the dimetallotriene intermediates **15** and **16** (or their corresponding enolates) gives trienes. After stirring of the mixture at 50 °C without hydrolysis, both isomers gave the same benzene derivative **3n**.

The ratio of 4:1 of two triene isomers can be explained by the different reactivity between the silyl-substituted carbon and the ethyl-substituted carbon attached to zirconium in **1n** toward the transmetalation reaction from zirconium to copper or addition reaction to **2** after the transmetalation.

From the results obtained here we would like to propose the following mechanism of the cycloaddition reaction of zirconacyclopentadienes to **2** giving benzene derivatives as shown in Scheme 3. Transmetalation reaction of the organic moiety of **1** to copper is reasonable as the first step.[19,27,28g] Since there are two zirconium-sp^2 carbon bonds, both intermediates **17** and **18** can be considered. From **17** or **18** there are mainly two reaction paths (i)−(ii). (i) Michael addition of **18** to dimethyl acetylenedicarboxylate forms **20**. Alternatively, **17** reacts with **2** to give **19** followed by transmetalation from zirconium to copper giving **20**. Ring-closure coupling reaction of two

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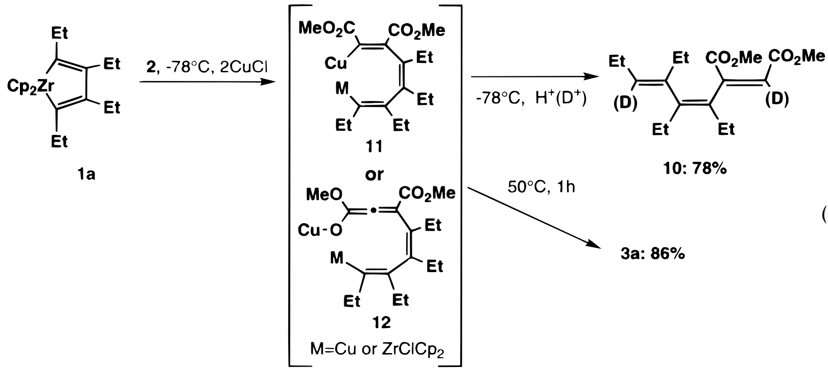
(25) (a) Reference 5. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (c) AmAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666. (d) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157. (e) Strickler, J. R.; Bruck, M. A.; Wigley, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 2814. (f) Reference 9b. (g) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 962. (h) Abdulla, K.; Booth, B. L.; Stacey, C. *J. Organomet. Chem.* **1988**, *293*, 103. (i) Arney, D. J.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 1282.

(26) (a) Reference 6c. (b) Reference 9c. See, also: (c) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211.

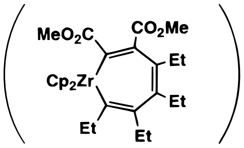
(27) Yoshifuji, M.; Loots, M.; Schwartz, J. *Tetrahedron Lett.* **1977**, 1303−1306.

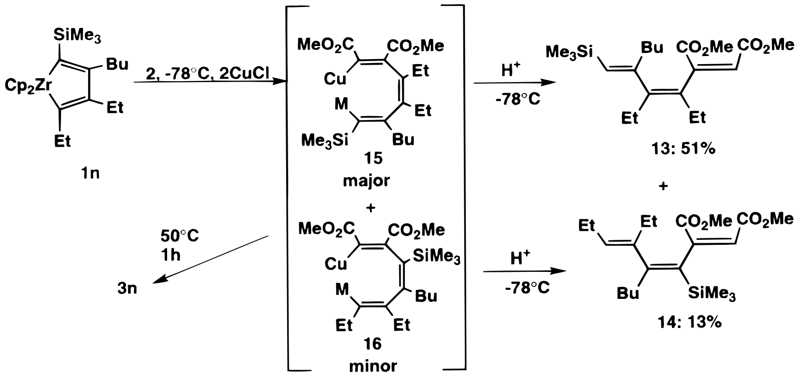
(28) (a) Lipshutz, B. H.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 7440−7441. (b) Babiak, K. A.; Behling, J. R.; Dygos, J. H.; McLanghlin, K. T.; Ng. J. S.; Kalish, V. J.; Kramer, S. W.; Shone, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 7441−7442. (c) Lipshutz, B. H.; Hato, K. *Tetrahedron Lett.* **1991**, *32*, 5647−5650. (d) Lipshutz, B. H.; Fatheree, P.; Hagan, W.; Stevens, K. L. *Tetrahedron Lett.* **1992**, *33*, 1041−1044. (e) Lipshutz, B. H.; Keil, R. *J. Am. Chem. Soc.* **1992**, *114*, 7919−7920. (f) Lipshutz, B. H.; Wood, M. R. *J. Am. Chem. Soc.* **1993**, *115*, 12625−12626. (g) Lipshutz, B. H.; Segi, M. *Tetrahedron* **1995**, *51*, 4407.

(29) (a) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Tetrahedron Lett.* **1994**, *35*, 5685−5688. (b) Takahashi, T.; Kotora, M.; Fischer, R.; Nishihara, Y.; Nakajima, K. *J. Am. Chem. Soc.* **1995**, *117*, 11039−11040. (c) Takahashi, T.; Kotora, M.; Xi, Z. *J. Chem. Soc., Chem. Commun.* **1995**, 1503. (d) Kasai, K.; Kotora, M.; Suzuki, N.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 109.



(4)

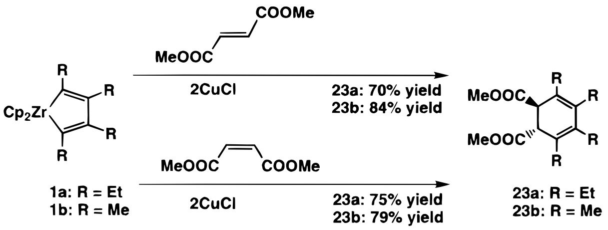




(5)

alkenylcopper moieties of **20** gives **3** along with formation of a copper mirror. (ii) Intramolecular Michael addition of **20** gives cyclohexadiene derivatives **21**. Reductive elimination of copper metal from **21** affords **3**. Although a third mechanism (iii) involving the Diels−Alder type of cyclization of **18** (the concerted path) with **2** cannot be ruled out, the major path for this reaction is the insertion path (Michael addition path), since triene compounds were obtained in good yields as intermediates. Even though the insertion path (Michael addition path) is the major path, other reaction paths might take place to some extent.

When alkenes such as dimethyl maleate and dimethyl fumarate were used instead of **2**, both dimethyl maleate and dimethyl fumarate gave the same cyclohexadiene **23a** and **23b** for **1a** (R = Et) and **1b** (R = Me), respectively. The trans configuration of **23b** was determined by X-ray analysis. When the reaction of **1a** with dimethyl maleate was carried out at −55 °C, only the cyclized compound **23a** was obtained in 15% yield along with the formation of free fumarate. No maleate remained. No formation of the intermediate compound was observed. This result indicates that dimethyl maleate isomerizes to dimethyl fumarate first as known for alkenes and then cyclization giving **23a** proceeds.



(6)

Copper-Catalyzed Cycloaddition Reaction of Zirconacyclopentadienes to Acetylenedicarboxylate. As described above, the yields were the best when 2 equiv of copper chloride was used. We observed the formation of a metallic copper mirror on the wall of the reaction vessel. Therefore, it was believed that a stoichiometric amount of copper chloride was required in the reaction of **1** with **2**. Actually, the yield of **3a** decreased with decrease of the amount of copper chloride. Surprisingly, in the presence of 0.1 equiv of copper chloride, **3a** was formed in 46% yield as shown in Table 4. It is noteworthy that after the catalytic reaction the formation of a metallic mirror on the wall was not observed.

Copper-catalyzed Michael addition of alkenylzirconocene or zirconacyclopentene has been reported by Lipshutz et al.[28f] However, our reaction suggested that there is a different reaction mechanism from (i)−(iii). At −78 °C this catalytic reaction also gave triene **10** in 36% yield after hydrolysis. Therefore, the catalytic reaction path involves the insertion path (Michael addition path). Our proposed mechanism for this catalytic reaction is shown in Scheme 4.

In the presence of a small amount of copper chloride, intermediate **17** might be the major active species. Reaction of **17** with **2** gives **19** (and/or **26**). Since the yield of **10** was more than 10%, a zirconium-containing species such as **24** (or **25**) without copper should be considered as intermediates. And then the desired compound **3a** was formed in 46% yield after 24 h. Unfortunately we could not clarify the final step of this catalytic reaction. According to Table 4, the catalytic reaction was not as fast as the stoichiometric reaction described above. It clearly indicates that at least two reaction mechanisms are involved in the cycloaddition reaction of **1** to **2** to form **3**.

Scheme 3

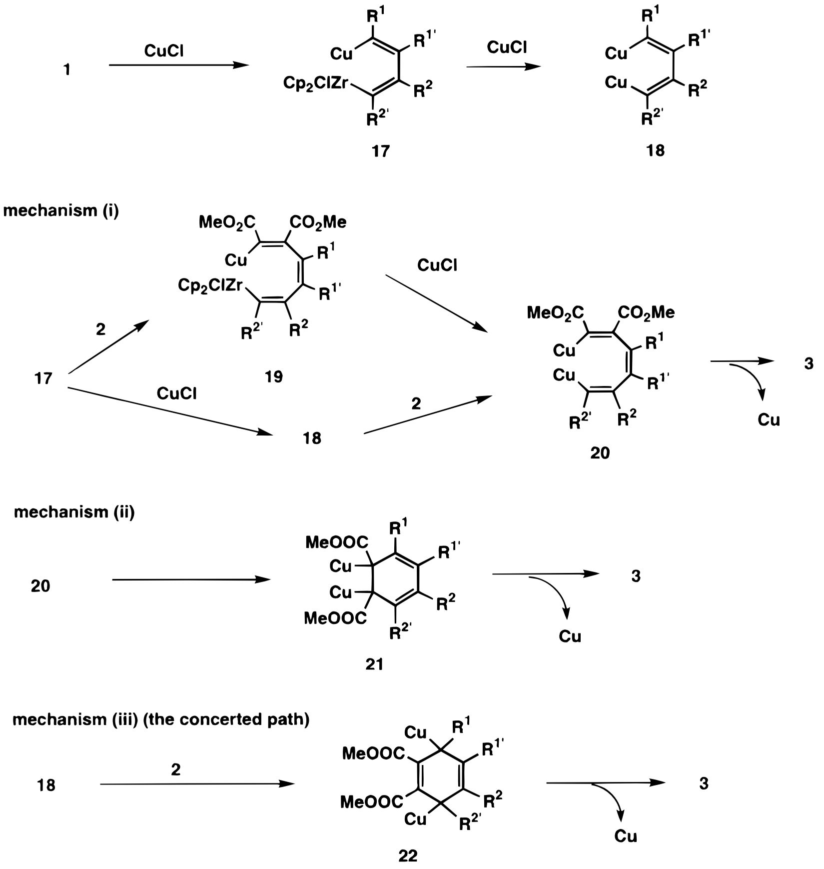
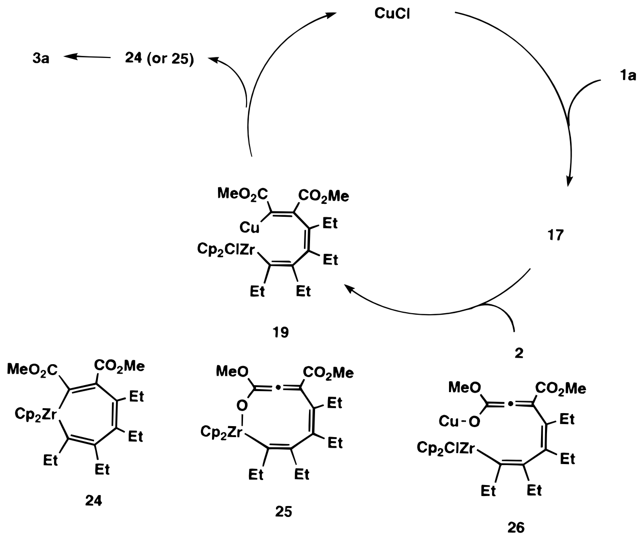


Table 4. Reaction of **1a** with **2** in the Presence of Various Amount of Copper Chloride

$$1a \xrightarrow[\text{CuCl}]{2} 3a \qquad (7)$$

CuCl/eq	time/h	yield/%	turnover no.
2	1	95	0.95
1.5	3	83	1.1
1	3	73	1.5
0.5	3	58	2.3
0.2	24	50	5.0
0.1	24	46	9.2

Scheme 4



Experimental Section

All reactions involving organometallic compounds were carried out under nitrogen. Tetrahydrofuran (THF) was dried over sodium and benzophenone. Zirconocene dichloride was purchased from Aldrich Chemical Co., Inc. Dimethyl fumarate and alkynes were purchased from TCI Co., Ltd. Dimethyl maleate and copper(I) chloride were purchased from Wako Pure Chemical Industries Ltd. Dimethyl acetylenedicarboxylate was purchased from Nacalai Tesque Inc. Zirconacyclopentadiene derivatives were prepared according to the literature.[16,20-22] ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL EX270 NMR spectrometer. IR spectra were recorded on SHIMADZU FTIR-4200 spectrometer. GC analysis was performed on SHIMADZU GC-14A equipped with fused silica capillary column SHIMADZU CBP1-M25-O25 and SHIMADZU C−R6A-Chromatopac integrator. Appropriate alkanes or mesitylene were used as internal standards.

A General Procedure for the Reaction of 1a with 2. Formation of Dimethyl 3,4,5,6-Tetraethylbenzene-1,2-dicarboxylate (3a). Dimethyl acetylenedicarboxylate **2** (284 mg, 2 mmol) and CuCl (198 mg, 2 mmol) were added at 0 °C to a THF solution of zirconacyclopentadiene **1a** (1 mmol) prepared in situ according to a known procedure.[20a] The reaction mixture was then warmed to room temperature and stirred for 1 h. After hydrolysis with 3 N HCl, the mixture was extracted wtih diethyl ether. The extract was washed with water, $NaHCO_3$, brine, and water and then dried over $MgSO_4$. Concentration in vacuo followed by flash-chromatography using a mixture of hexane and diethyl ether (10%) afforded **3a** as a colorless liquid. GC yield 95%. Isolated yield (181 mg) 59%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.15 (t, $J = 7.6$ Hz, 6H), 1.19 (t, $J = 7.6$ Hz, 6H), 2.64−2.75 (m, 8H), 3.84 (s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.49, 15.98, 22.07, 23.54, 52.16, 130.46, 138.13, 143.25, 169.74; IR ($CDCl_3$ solution) 2971, 1732, 1439, 1294, 1207, 1059 cm^{-1}; HRMS calcd for $C_{18}H_{26}O_4$ 306.1831, found 306.1829.

Ethyl 2-Methyl-3,4,5,6-tetraethylbenzene Carboxylate (3b). GC yield 84%. Isolated yield (320 mg) 58%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.10−1.22 (m, 12H), 1.37 (t, $J = 7.3$ Hz, 3H), 2.22 (s, 3H), 2.53−2.71 (m, 8H), 4.38 (q, $J = 7.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ

14.29, 14.50, 15.80, 15.87, 16.03, 16.39, 21.80, 22.25, 22.50, 24.10, 60.77, 129.43, 134.01, 135.43, 137.93, 138.79, 141.26, 171.53; HRMS calcd for $C_{18}H_{28}O_2$ 276.2089, found 276.2084.

Ethyl 2-Phenyl-3,4,5,6-tetraethylbenzene Carboxylate (3c). GC yield 92%. Isolated yield (193 mg) 57%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, $J = 7.3$ Hz, 3H), 0.91 (t, $J = 7.6$ Hz, 3H), 1.20 (t, $J = 7.6$ Hz, 3H), 1.21 (t, $J = 7.6$ Hz, 3H), 1.22 (t, $J = 7.3$ Hz, 3H), 2.44 (q, $J = 7.6$ Hz, 2H), 2.63 (q, $J = 7.6$ Hz, 2H), 2.72 (q, $J = 7.6$ Hz, 4H), 3.84 (q, $J = 7.3$ Hz, 2H), 7.20−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.68, 15.62, 15.76, 15.81, 16.01, 21.88, 22.23, 22.95, 23.92, 60.39, 126.84, 127.44 (2C), 130.11(2C), 133.62, 135.36, 136.98, 138.24, 139.71, 139.96, 141.44, 170.40; IR (neat) 2973, 2934, 1726, 1277, 1182 cm^{-1}; HRMS calcd for $C_{23}H_{30}O_2$ 338.2246, found 338.2250.

2,3,4,5-Tetraethyl-6-phenyl Benzonitrile (3d). GC yield 97%. Isolated yield 70%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.92 (t, $J = 7.5$ Hz, 3H), 1.20−1.31 (m, 9H), 2.46 (q, $J = 7.5$ Hz, 2H), 2.72−2.78 (m, 4H), 2.92 (q, $J = 7.5$ Hz, 2H), 7.26−7.46 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.38 (2x), 15.50, 15.57, 22.07, 22.51, 23.03, 25.11, 111.88, 117.99, 127.75, 128.19, 129.17, 139.09, 139.33, 140.17, 143.56, 144.05, 145.62. HRMS calcd for $C_{21}H_{25}N$ 291.1986, found, 291.1991.

2,3,4,5-Tetraethyl-6-phenyl *N,N*-Dimethyl Benzamide (3e). GC yield 82%. Isolated yield 55%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.88 (t, $J = 7.5$ Hz, 3H), 1.16−1.24 (m, 9H), 2.38−2.55 (m, 4H), 2.59 (s, 3H), 2.60 (s, 3H), 2.70−2.76 (m, 4H), 7.16−7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.35, 15.37, 15.62, 15.73, 21.71, 21.96, 22.65, 23.39, 33.39, 38.37, 126.48, 126.54, 127.70, 128.67, 130.57, 134.85, 135.07, 135.92, 138.05, 139.42, 139.87, 140.50, 170.96. HRMS calcd for $C_{23}H_{31}ON$ 337.2404, found 337.2405.

3,4,5,6-Tetraethyl-1,2-dibenzophenone (3f). GC yield 57%. Isolated yield 48%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.02 (t, $J = 7.5$ Hz, 6H), 1.25 (t, $J = 7.5$ Hz, 6H), 2.50 (q, $J = 7.4$ Hz, 4H), 2.78 (q, $J = 7.5$ Hz, 4H), 7.26−7.65 (m, 10H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.71, 15.86, 21.72, 23.36, 127.97, 129.81, 133.05, 136.23, 136.77, 137.85, 141.91, 199.13. HRMS calcd for $C_{28}H_{30}O_2$ 398.2244, found 398.2257.

2,3,4,5-Tetraethyl-6-butyl Benzophenone (3g). GC yield 54%. Isolated yield 28%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.75−1.27 (m, 21H), 2.22−2.75 (m, 8H), 7.39−7.81 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.57, 15.85, 15.90, 15.93, 15.97, 21.54, 21.62, 22.14, 23.23, 23.74, 30.63, 33.85, 128.35, 129.43, 133.12, 134.54, 135.63, 138.06, 138.13, 138.18, 138.31, 141.01, 201.12. HRMS calcd for $C_{25}H_{34}O$ 350.2608, found 350.2602.

2,3,4,5-Tetraethyl-6-phenyl 4′-Nitrobenzophenone (3h). NMR yield 64%. Isolated yield 42%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.92 (t, $J = 7.4$ Hz, 3H), 1.11 (t, $J = 7.5$ Hz, 3H), 1.26−1.31 (m, 6H), 2.77−2.83 (m, 8H), 7.02−7.06 (m, 5H), 7.59 (d, $J = 8.6$ Hz, 2H), 8.06 (d, $J = 8.6$ Hz, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.58, 15.78, 15.85, 16.19, 21.77, 22.33, 22.59, 23.58, 123.06, 126.76, 127.30, 129.72, 131.00, 136.13, 136.91, 137.25, 138.38, 138.71, 140.27, 142.19, 143.21, 149.68, 198.90. HRMS calcd for $C_{27}H_{29}O_3N$ 415.2146, found 415.2132.

Dimethyl 1,4-Dimethylbenzocyclobutene-2,3-dicarboxylate (5a). GC yield 73%. Isolated yield (283 mg) 57%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.20 (s, 6H), 3.05 (s, 4H), 3.84 (s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.32, 27.22, 52.16, 129.04, 131.14, 147.13, 169.13; HRMS calcd for $C_{14}H_{16}O_4$ 248.1049, found 248.1047.

Dimethyl 1,4-Diethyl-5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylate (5b). GC yield 93%. Isolated yield (390 mg) 64%. mp 109−110 °C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.15 (t, $J = 7.6$ Hz, 6H), 1.76−1.81 (m, 4H), 2.65 (q, $J = 7.2$ Hz, 4H), 2.76 (t, $J = 6.6$ Hz, 4H), 3.84 (s, 6H); ^{13}C NMR δ 14.61, 22.57, 23.20, 26.79, 52.15, 129.56, 138.15, 138.45, 169.63; IR ($CDCl_3$ solution) 2948, 1734, 1458, 1285, 1206, 1069 cm^{-1}; HRMS calcd for $C_{18}H_{24}O_4$ 304.1675, found 304.1662.

Dimethyl 1,4-Bis(trimethylsilyl)-5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylate (5c). GC yield 85%. Isolated yield (552 mg) 70%. Mp 146−147 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.32 (s, 18H), 1.65−1.75 (m, 4H), 2.75−2.80 (m, 4H), 3.81 (s, 6H); ^{13}C NMR δ 1.69, 20.70, 30.42, 52.24, 135.42, 136.15, 147.58, 170.80; IR($CDCl_3$) 2951, 1732, 1283, 1253, 1155 cm^{-1}; HRMS calcd for $C_{20}H_{32}Si_2O_4$ 392.1839, found 392.1843.

Dimethyl 6,7,8,9-Tetrahydro-1,4-bis(trimethylsilyl)-5*H*-benzocyclo-heptene-2,3-dicarboxylate (5d). GC yield 85%. Isolated yield (544 mg) 67%. Mp 137−138 °C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.30 (s, 18H), 1.55−1.65 (m, 4H), 1.75−1.85 (m, 2H), 2.95−3.05 (m, 4H), 3.80 (s, 6H); ^{13}C NMR δ 2.03(6C), 28.01(2C), 31.48, 35.06(2C), 52.24(2C), 135.74(2C), 136.91(2C), 151.50(2C), 170.80(2C). IR ($CDCl_3$) 1730, 1265, 1151, 848 cm^{-1}. Anal. Calcd for $C_{20}H_{32}Si_2O_4$: C, 62.02; H, 8.43. Found: C, 62.06; H, 8.47.

Dimethyl 3,4-Diethylnaphthalene-1,2-dicarboxylate (5e). GC yield 80%. Isolated yield (204 mg) 54%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.26 (t, $J = 7.6$ Hz, 3H), 1.28 (t, $J = 7.6$ Hz, 3H), 2.85 (q, $J = 7.6$ Hz, 2H), 3.15(q, $J = 7.6$ Hz, 2H), 3.92 (s, 3H), 3.97 (s, 3H), 7.45−760 (m, 2H), 8.05−8.10 (m, 1H), 8.13−8.18 (m, 1H); ^{13}C NMR δ 15.20, 15.79, 21.67, 24.04, 52.45, 52.58, 124.20, 126.45, 126.56, 127.40, 127.96, 128.61, 132.45, 132.61, 134.86, 141.77, 168.44, 169.68; IR ($CDCl_3$ solution) 2972, 1734, 1435, 1271, 1226, 1201, 1163 cm^{-1}. HRMS calcd for $C_{18}H_{20}O_4$ 300.1362, found: 300.1356.

Reaction of 1a with 2 in the Presence of Other Metal Halides Instead of CuCl. The reaction procedure was essentially the same as that described above when CuCl was used. Commercially available metal halides were used without further purification. When $CuCl_2$, $SnCl_2$, and $SnCl_4$ were used, **3a** was formed in 28%, 26%, and 30% yields, respectively, though GC analysis showed that hydrolysis compound of **1a** almost completely disappeared. Use of $CoBr_2$ and $BiCl_3$ afforded **3a** in 15% and 35% yields, respectively. In the case of $CoBr_2$, 47% of **1a** remained unreacted, while 36% of **1a** was recovered in the case of $BiCl_3$.

A Representative Procedure for One-Pot Preparation of Benzene Derivatives from Three Different Alkynes: Dimethyl 3,4-Dibutyl-5,6-diethylbenzene-1,2-dicarboxylate (3k). A 50 mL Schlenk tube under dried nitrogen was charged with Cp_2ZrCl_2 (2.5 mmol, 730 mg) and THF (20 mL). The mixture was cooled to −78 °C (dry ice/methanol bath), and then 1.7 M *n*-BuLi (5 mmol, 2.94 mL) was added dropwise via a syringe. The reaction mixture was stirred at −78 °C for 1 h under nitrogen, ethylene gas was introduced for 1 h, and the reaction mixture was gradually warmed to room temperature. The reaction mixture changed from light yellow to yellow-brown. 5-Decyne (2 mmol, 0.36 mL) was added, and the resulting mixture was stirred for 1 h at room temperature under a positive pressure of ethylene gas. After 3-hexyne (2 mmol, 0.23 mL) was added, the mixture was heated at 50 °C under an atmosphere of dry N_2 instead of ethylene gas and was stirred for 1 h. Then, to the above reaction solution containing zirconacyclopentadiene **1k** were added dimethyl acetylenedicarboxylate **2** (568 mg, 4 mmol) and copper(I) chloride (396 mg, 4 mmol) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was quenched with 3 N HCl and extracted with diethyl ether. The extract was then washed with water, $NaHCO_3$, brine, and water and then dried over $MgSO_4$. The solvent was evaporated in vacuo to give a light brown oil. Column chromatography on silica gel (4/1 hexane/Et_2O) afforded 510 mg of **3k** (71% isolated yield). GC yield 90%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90−1.00 (m, 6H), 1.12−1.22 (m, 6H), 1.33−1.56 (m, 8H), 2.59−2.73 (m, 8H), 3.83 (s, 3H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.84 (2C), 15.49, 15.98, 22.19, 23.32, 23.47, 23.52, 29.07, 30.26, 33.49, 33.94, 52.15 (2C), 130.42, 130.47, 137.14, 137.97, 142.15, 143.29, 169.75 (2C); IR (neat) 2959, 1730, 1458, 1294, 1204, 1177 cm^{-1}; HRMS calcd for $C_{22}H_{34}O_4$ 362.2460, found 362.2466.

Dimethyl 3,4-Diethyl-5,6-diphenylbenzene-1,2-dicarboxylate (3i). GC yield 95%. Isolated yield (507 mg) 63%. Mp 162−163 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.95 (t, $J = 7.3$ Hz, 3H), 1.28 (t, $J = 7.3$ Hz, 3H), 2.53 (q, $J = 7.3$ Hz, 2H), 2.85 (q, $J = 7.6$ Hz, 2H), 3.40 (s, 3H), 3.89 (s, 3H), 6.9−7.15 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.29, 15.94, 23.40, 23.49, 51.97, 52.45, 126.41, 126.56, 127.07(2C), 127.40(2C), 129.72(2C), 130.03(2C), 130.58, 131.71, 138.36, 139.10, 139.35, 139.60, 143.56, 143.99, 168.96, 169.38; IR ($CDCl_3$ solution) 2974, 1734, 1439, 1333, 1215 cm^{-1}. HRMS calcd for $C_{26}H_{26}O_4$ 402.1831, found 402.1841.

Dimethyl 1-Trimethylsilyl-4,5-diphenyl-6-methylbenzene-2,3-dicarboxylate (3j). Isolated yield (250 mg) 56%. Mp 160−161 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.39 (s, 9H), 2.21 (s, 3H), 3.41 (s, 3H), 3.85 (s, 3H), 6.88−7.16 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.63 (3C), 23.91, 51.99, 52.46, 126.58, 126.65, 127.19 (2C), 127.82 (2C), 129.46 (2C), 129.80 (2C), 130.72, 137.24, 137.71, 138.74, 139.65, 139.92, 143.54, 145.09, 169.38, 170.11; IR (neat) 2951, 1734, 1443, 1395 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{28}O_4Si$ 432.1757, found 432.1758.

Dimethyl 3,4-Dibutyl-5,6-dipropylbenzene-1,2-dicarboxylate (3l). GC yield 87%. Isolated yield (485 mg) 62%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.93−1.07 (m, 12H), 1.36−1.59 (m, 12H), 2.59−2.63 (m, 8H), 3.83 (s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.82 (2C), 14.77, 14.91, 23.31, 23.47, 24.71, 25.10, 29.20, 30.21, 31.75, 32.69, 33.42, 33.94, 52.13 (2C), 130.38, 130.49, 136.93, 137.00, 142.14, 142.26, 169.81 (2C); IR (neat) 2960, 1732, 1456, 1295, 1206, 1176 cm^{-1}. HRMS calcd for $C_{24}H_{38}O_4$ 390.2770, found 390.2775. Anal. Calcd for $C_{24}H_{38}O_4$: C, 73.81; H, 9.81. Found: C, 73.94; H, 9.84.

Dimethyl 3,4-Diethyl-5,6-dipropylbenzene-1,2-dicarboxylate (3m). GC yield 91%. Isolated yield (400 mg) 60%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.98 (t, $J = 7.3$ Hz, 3H), 1.05 (t, $J = 7.3$ Hz, 3H), 1.14 (t, $J = 7.6$ Hz, 3H), 1.19 (t, $J = 7.6$ Hz, 3H), 1.42−1.6 (m, 4H), 2.57−2.73 (m, 8H), 3.83 (s, 3H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.79, 14.91, 15.51, 15.98, 22.21, 23.52, 24.73, 25.09, 31.61, 32.72, 52.16 (2C), 130.40, 130.46, 137.09, 137.97, 142.08, 143.32, 169.74, 169.79; IR (neat) 2960, 1730, 1453, 1292, 1208, 1177 cm^{-1}. HRMS calcd for $C_{20}H_{30}O_4$ 334.2144, found 334.2119. Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.75; H, 9.13.

Dimethyl 1-Trimethylsilyl-4,5-diethyl-6-butylbenzene-2,3-dicarboxylate (3n). GC yield 83%. Isolated yield (560 mg) 74%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.32 (s, 9H), 0.96 (t, $J = 6.9$ Hz, 3H), 1.13−1.18 (m, 6H), 1.39−1.45 (m, 4H), 2.65−2.84 (m, 6H), 3.80 (s, 3H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 2.37 (3C), 13.77, 15.49, 15.65, 21.44, 23.24, 23.33, 33.71, 35.31, 52.06 (2C), 130.71, 135.56, 136.26, 140.22, 142.46, 150.30, 170.13, 170.28; HRMS calcd for $C_{21}H_{34}O_4Si$ 378.2226, found 378.2245.

Dimethyl 3,4-Diethyl-6-phenylbenzene-1,2-dicarboxylate (3o). GC yield 85%. Isolated yield (430 mg) 66%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.22 (t, $J = 7.6$ Hz, 3H), 1.25 (t, $J = 7.6$ Hz, 3H), 2.70−2.78 (m, 4H), 3.54 (s, 3H), 3.88 (s, 3H), 7.25−7.40 (m, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.33, 15.53, 23.05, 25.53, 52.08, 52.43, 127.40, 128.17 (2C), 128.25 (2C), 128.93, 131.93, 133.37, 138.79, 139.03, 140.52, 145.19, 169.04, 169.43; HRMS calcd for $C_{20}H_{22}O_4$ 326.1518, found 326.1513.

Reaction of 2,3,4,5-Tetraethylzirconacyclopentadiene (1a) with Dimethyl Fumarate or Dimethyl Maleate. Formation of Dimethyl 3,4,5,6-Tetraethylcyclohexa-3,5-diene-1,2-dicarboxylate (23a). Reaction of zirconacyclopentadiene **1a** (1 mmol) with dimethyl fumarate (4 mmol) in the presence of CuCl (2 mmol) at room temperature for 1 h gave the title compound **23a** after purification by flash-chromatography using a mixture of hexane and diethyl ether (5%). GC yield 70%. Isolated yield (147 mg) 48%. Mp 56−57 °C. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.87 (t, $J = 7.6$ Hz, 6H), 0.98 (t, $J = 7.6$ Hz, 6H), 1.95−2.10 (m, 4H), 2.30−2.50 (m, 4H), 3.46 (s, 2H), 3.60 (s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.06, 14.72, 20.50, 25.95, 45.41, 51.72, 129.38, 135.65, 173.31; IR ($CDCl_3$ solution) 2967, 1732, 1435, 1242, 1169 cm^{-1}; HRMS calcd for $C_{18}H_{28}O_4$ 308.1988, found 308.1987. Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H 9.15. Found: C, 69.95; H, 9.18. When dimethyl maleate (4 mmol) was used instead of dimethyl fumarate, the same compound **23a** was isolated. GC yield 75%. Isolated yield (185 mg) 60%.

Determination of the Stereochemistry of 23b. Although **23a** was a crystalline compound, it did not give good crystals suitable for X-ray analysis. To determine the stereochemistry of **23a**, **23b** was prepared in a similar way using 2-butyne and dimethyl maleate. This compound was obtained as colorless crystals suitable for X-ray analysis. The X-ray analysis of **23b** clearly indicated that **23b** had the trans configuration. GC yield 79%. Isolated 55%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.78 (s, 6H), 1.81 (s, 6H), 3.36 (s, 2H), 3.68 (s, 6H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.81, 19.94, 47.42, 51.94, 122.59, 129.07, 173.28. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.46; H, 7.99. When dimethyl fumarate was used instead of dimethyl maleate, the same compound **23b** was obtained. GC yield 84%. Isolated yield 60%.

Structure Determination of 3j. A colorless prismatic crystal measuring 0.3 × 0.5 × 0.5 mm was mounted onto a glass fiber and placed on an Enraf-Nonius CAD-4 diffractometer (Cu K_α, $\lambda = 1.5418$ Å) equipped with a graphite monochromator. The cell dimensions were obtained by least-squares refinement of the setting angles for 25 reflections. Crystallographic data: fw = 432.6, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 11.841(1)$ Å, $b = 10.370(1)$ Å, $c = 19.621(4)$ Å, $\beta = 100.56(1)°$, V = 2368(5) Å^3, $D_x = 1.21$ g cm^{-3}, and μ(Cu K_α) = 10.85. Diffraction data were collected in ω-2θ mode at room temperature. Three intensity control reflections were monitored every 2 h of data collection. No significant trend in these intensities was observed during the course of data acquisition. Intensity data of 4491 reflections were collected in the range $2° < 2\theta < 140°$, of which 4263 reflections were independent with $|F_o| > 3\sigma(|F_o|)$. The structure was solved by direct methods (SHELXS-86)[30] and refined by full-matrix least-squares techniques using Xtal3.2[31] software on a Fujitsu S-4/5 workstation. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from a difference Fourier synthesis and included with isotropic thermal parameters. Refinement of positional and thermal parameters led to convergence with $R = 0.044$, $R_w = 0.066$.

Cu(I)-Catalyzed Benzene Derivative (3a) Formation from 1a. To a THF solution (5 mL) containing **1a** prepared according to a known procedure [20] in situ from 3-hexyne (2 mmol, 0.23 mL) and Cp_2ZrBu_2 (1 mmol) were added dimethyl acetylenedicarboxylate **2** (284 mg, 2 mmol) and copper(I) chloride (10 mg, 0.1 mmol) at room temperature. The reaction was then monitored by GC after hydrolysis. After stirring for 24 h at room temperature, benzene derivative **3a** was formed in 46% yield and isolated.

Isolation of Triene (10) in the Reaction of 1a with 2 in the Presence of a Stoichiometric Amount of CuCl. The reaction of **1a** with **2** was carried out at −78 °C. After stirring for 1 h at −78 °C, the usual workup provided **10** in 78% yield as a pure compound after flash-chromatography using a mixture of hexane and diethyl ether (5:1). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90−1.05 (m, 12H), 1.96−2.27 (m, 8H), 3.70 (s, 3H), 3.76 (s, 3H), 5.25 (t, $J = 7.2$ Hz, 1H), 5.82 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.96, 13.30, 13.48, 13.78, 21.35, 23.09, 24.24, 24.47, 51.68, 52.13, 121.20, 131.73, 133.91, 139.03, 148.75, 150.01, 165.93, 168.50; HRMS calcd for $C_{18}H_{28}O_4$ 308.1986, found 308.1959.

10D was obtained in 78% yield (D > 98%) when the above reaction mixture was quenched with DCl/D_2O instead of 3 N HCl. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91−0.99 (m, 12H), 2.08−2.25 (m, 8H), 3.70 (s, 3H), 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.94, 13.28, 13.43, 13.75, 21.23, 23.05, 24.24, 24.47, 51.65, 52.11, 121.25 (coupled with D), 131.72, 133.90 (coupled with D), 138.94, 148.65, 149.95, 165.88, 168.48. HRMS calcd for $C_{18}D_2H_{26}O_4$ 310.2110, found 310.2118.

Isolation of Triene (10) in the Reaction of 1a with 2 in the Presence of a Catalytic Amount of CuCl. The reaction was performed in the same way as described above using 0.1 equiv of CuCl. The triene **10** was obtained in 36% GC yield. Isolated yield (77 mg) 25%.

Isolation of Trienes (13) and (14) in the Reaction of Unsymmetrical Zirconacyclopentadiene (1i) with 2 in the Presence of a Stoichiometric Amount of CuCl. Unsymmetrical zirconacyclopentadiene (**1n**) was prepared in situ according to the reported procedure.[15e,16] Then, dimethyl acetylenedicarboxylate (284 mg, 2 mmol) and copper(I) chloride (198 mg, 2 mmol) were added at −78 °C. After stirring for 1 h at the same temperature, the reaction mixture was quenched with 3 N HCl at −78 °C and extracted with ether. The extract was washed with water, $NaHCO_3$, brine, and water and dried over $MgSO_4$. The crude products of **13** and **14** were obtained as a 4:1 mixture. They were purified by flash-chromatography using a mixture of hexane and ethyl acetate (10%). Isolated yield was 64% as a mixture of **13** and **14**.

Methyl-3-methoxycarbonyl-4,5-diethyl-6-butyl-7-trimethylsilyl-(2*Z*,4*Z*,6*E*)-2,4,6-heptatrienoate (13). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.08 (s, 9H), 0.87−1.00 (m, 9H), 1.30−1.33 (m, 4H), 2.17−2.24 (m, 6H) 3.70 (s, 3H), 3.78 (s, 3H), 5.36 (s, 1H), 5.85 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −0.06 (3C), 13.14, 13.22, 13.90, 23.25, 23.70, 25.12, 31.55, 35.99, 51.58, 52.10, 122.42, 130.51, 131.16, 148.60, 149.45, 157.76, 165.61, 168.12. HRMS: $C_{21}H_{36}O_4Si$ calcd 380.2381, found 380.2389. Anal. Calcd for $C_{21}H_{36}O_4Si$: C, 66.27, H, 9.53; Found: C, 66.09, H, 9.47.

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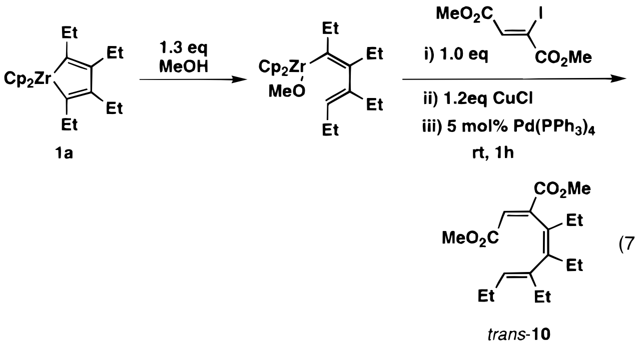
[30] Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Determination; University of Göttingen, Germany, 1986.

[31] Hall, S. R.; Flack, H. D.; Stewart, J. M. Xtal3.2, Program for X-Ray Crystal Structure Analysis; Universities of Western Australia, Geneva, and Maryland: 1992.

Methyl-3-methoxycarbonyl-4-trimethylsilyl-5-butyl-6-ethyl-(2*Z*,4*E*,6*E*)-2,4,6-nonatrienoate (14). ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 5.04 (t, J = 7.2 Hz, 1H), 5.55 (s, 1H), other peaks were covered with peaks of major isomer; ^{13}C NMR (CDCl$_3$, Me$_4$Si) 0.86 (3C), 12.71, 14.03, 20.98, 22.44, 22.74, 30.72, 34.83, 51.66, 122.28, 132.53, 133.01, 139.38, 149.39, 159.71, 165.93, 167.80, two peaks were covered with peaks of the major isomer.

Determination of the Stereochemistry of 10, 13, and 14. To determine the stereochemistry of **10**, **13** and **14**, two independent experiments were carried out for **10** as the representative. **Preparation of Authentic 10:** Stereocontrolled syn-addition of organocopper reagents to the triple bond of dimethyl acetylenedicarboxylate has been reported.[32] We have reported that alcoholysis of zirconacyclopentadienes affords monoprotonated dienylzirconium intermediates which undergo further C−C bond formation reaction with aryl or alkenyl iodides in the presence of CuCl.[33] Treatment of the above dienylzirconium intermediate formed in situ from methanolysis of **1a** with **2** in the presence of a stoichiometric amount of CuCl at room temperature afforded stereocontrolled syn-addition product **10**. GC yield 83%. Isolated yield 64%. The ^{1}H and ^{13}C NMR spectra of the product prepared by this method are exactly the same as that of **10** prepared by the low-temperature reaction of **1a** with **2**. **Preparation of *trans*-10:** Treatment of the dienylzirconium intermediate formed in situ from methanolysis of **1a** with dimethyl 2-iodofumarate in the presence of a stoichiometric amount of CuCl and a catalytic amount of Pd(PPh$_3$)$_4$ (5 mol %) at room temperature afforded stereodefined product ***trans*-10**.[33] The NMR spectrum of the methylcarboxylate groups of trans-**10** was different from **10** obtained in the text.



(7)

trans-**10**. Isolated yield 63%. ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.81−1.01 (m, 12H), 1.91−1.98 (m, 4H), 2.18−2.32 (m, 4H), 3.71 (s, 3H), 3.72 (s, 3H), 5.00 (t, J = 7.2 Hz, 1H), 6.61 (s, 1H). ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 12.74, 13.00, 13.65, 13.90, 21.26, 22.91, 23.68, 26.11, 51.53, 52.29, 126.05, 129.83, 132.52, 140.59, 144.21, 149.22, 165.89, 167.86. HRMS calcd for C$_{18}$H$_{28}$O$_4$ 308.1986, found 308.1978.

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Supporting Information Available: Crystallographic data, positional and thermal parameters, and lists of bond lengths and angles for **3j** and **23b** (11 pages). See any current masthead page for ordering and Web access instructions.

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[32] (a) Yamamoto, Y.; Yatagai, H.; Maruyama, H. *J. Org. Chem.* **1979**, *44*, 1744. (b) Nishiyama, H.; Sasaki, M.; Itoh, K. *Chem. Lett.* **1981**, 905.

[33] Hara, R.; Nishihara, Y.; Landre, P. D.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 447.