Pergamon

TETRAHEDRON

Tetrahedron 58 (2002) 1107–1117

Copper(I)-catalyzed tandem inter–intramolecular cyclization reactions of zirconacycles: formation of highly substituted styrenes, vinylcyclohexadienes, and related compounds

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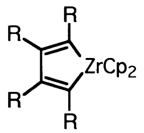
Received 28 May 2001; accepted 5 December 2001

Abstract—Copper(I)-catalyzed or mediated reactions of five-membered zirconacycles with propargyl or allyl halides afforded a variety of useful vinylated cyclic compounds, including highly substituted styrenes, vinylcyclohexadienes and methylenecycloheptadienes, via tandem inter–intramolecular allylation reactions. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Tandem reactions are very attractive and useful approaches for construction of cyclic compounds.[1] We have been interested in the development of novel methodologies for cyclic compounds using zirconacycles, including zirconacyclopentadienes **1**, zirconacyclopentenes **2** and zirconacyclopentanes **3**, as reactive organometallic intermediates.[2] One of the most interesting reactive properties of such metallacycles is that there exist two metal–carbon bonds in one molecule. Those two reactive sites enable tandem reactions with bifunctional compounds to give useful cyclic structures in a sequence. Recently, we have demonstrated that, in the presence of a catalytic amount or a stoichiometric amount of CuCl, tandem inter–intramolecular reactions of zirconacyclopentadienes **1** with difunctional allyl halides such as 3,4-dichlorobutene **6** and 3-chloro-2-(chloromethyl)propene **5** to give vinylcyclohexadienes and methylenecycloheptadienes, respectively.[3] These useful and interesting preliminary results prompted us to further investigate the scope of the novel transformation reaction. In this paper, we would like to present our results in detail.



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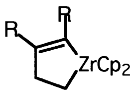

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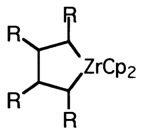

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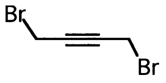

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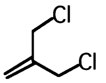

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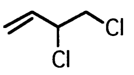

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2. Results and discussion

2.1. Generation of highly substituted styrenes from the reaction of zirconacyclopentadienes with 1,4-dibromo-2-butyne mediated by copper salts

Styrene derivatives are important compounds for polymer science, polymer industry,[4] and synthetic organic chemistry as well.[5] However, methodologies for the preparation of styrene derivatives using transition metal complexes have not been developed as such, although transition metal-mediated cyclotrimerization of alkynes are extremely important and useful reactions for the synthesis of various aromatic compounds.[6] Yamamoto and co-workers recently reported excellent methods for the formation of styrene derivatives via Pd-catalyzed [4+2] homodimerization of enynes.[7] 4,α-Disubstituted styrenes and 2,6-disubstituted styrenes were synthesized via homodimerization of 2- and 4-substituted enynes, respectively.[8]

Keywords: vinylated cyclic compounds; five-membered rings; six-membered rings; seven-membered rings; zirconacycles; organocopper compounds; transmetalation; tandem reactions; styrene derivatives.

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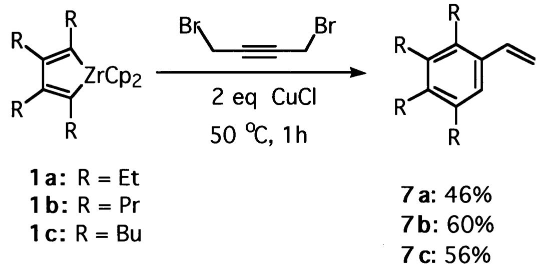
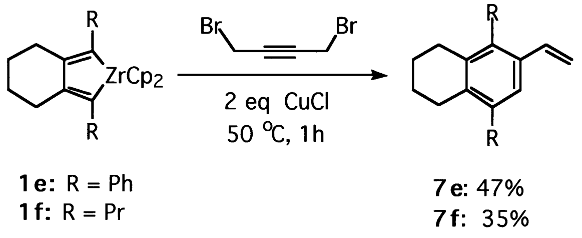


Scheme 1.



Scheme 3.

We have applied zirconacyclopentadienes which are prepared in situ from two different or the same alkynes for constructing highly substituted aromatic compounds.[9–13] Recently, we reported when zirconacyclopentadienes were treated with 2 equiv. of propargyl halides in the presence of CuCl, 2,3-butadien-1-yl benzenes are formed.[14] This reaction prompted us to use 1,4-dihalo-2-butynes which have two leaving groups and the corresponding reactive positions. Results showed that highly substituted styrenes were formed from the reaction of zirconacyclopentadienes with 1,4-dibromo-2-butyne **4** in the presence of CuCl via a tandem inter–intramolecular reaction sequence (Scheme 1).

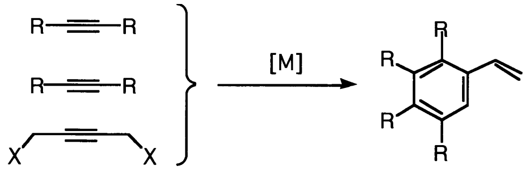
Firstly, we applied symmetrical zirconacyclopentadienes **1** for the reaction with **4**. Reaction of zirconacyclopentadiene **1b** (R=Pr) prepared in situ by dimerization of 4-octynes[15] with 1 equiv. of 1,4-dibromo-2-butyne **4** in the presence of 2 equiv. of CuCl at 50°C for 1 h afforded 2,3,4,5-tetrapropylstyrene **7b** in 60% yield. Similarly, styrene derivatives **7c** and **7a** were obtained in 56 and 46% yields, from **1c** and **1a**, respectively.

It is noteworthy that, besides 1,4-dibromo-2-butyne, 1,4-dichloro-2-butyne could also be used, affording styrene derivatives in similar yields. In the case of 1,4-dichloro-2-butyne, a catalytic amount of CuCl (10 mol%) was also effective for the styrene formation reaction, although the yields were relatively lower.

As shown in Scheme 2, when the unsymmetrical zirconacyclopentadiene **1d**[9] prepared in situ from 2-butyne and diphenylacetylene was treated in the presence of 2 equiv. of CuCl with 1 equiv. of 1,4-dibromo-2-butyne, styrene derivatives were formed as a mixture of two regioisomers (**7d** and **7d′**) in a ratio of 2:1 in 30% combined yield.

Styrene derivatives **7e** (R=Ph) and **7f** (R=Pr) were formed similarly in 47 and 35% yields, respectively, from the reaction of the corresponding bicyclic zirconacyclopentadienes with 1,4-dibromo-2-butyne in the presence of 2 equiv. of CuCl (Scheme 3).

Although the yields of styrenes are not satisfactory enough, to the best of our knowledge, the reaction represents the first example of intermolecular formation of highly substituted styrenes from three molecules of alkynes (Scheme 4).

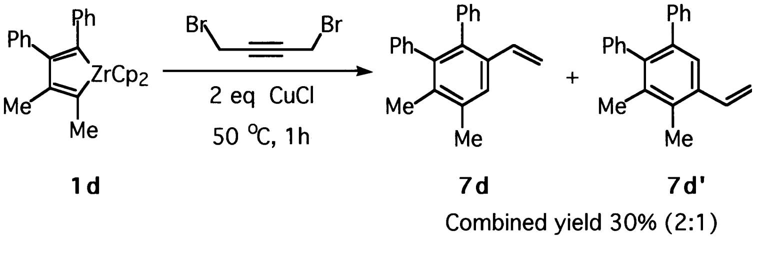


Scheme 4.

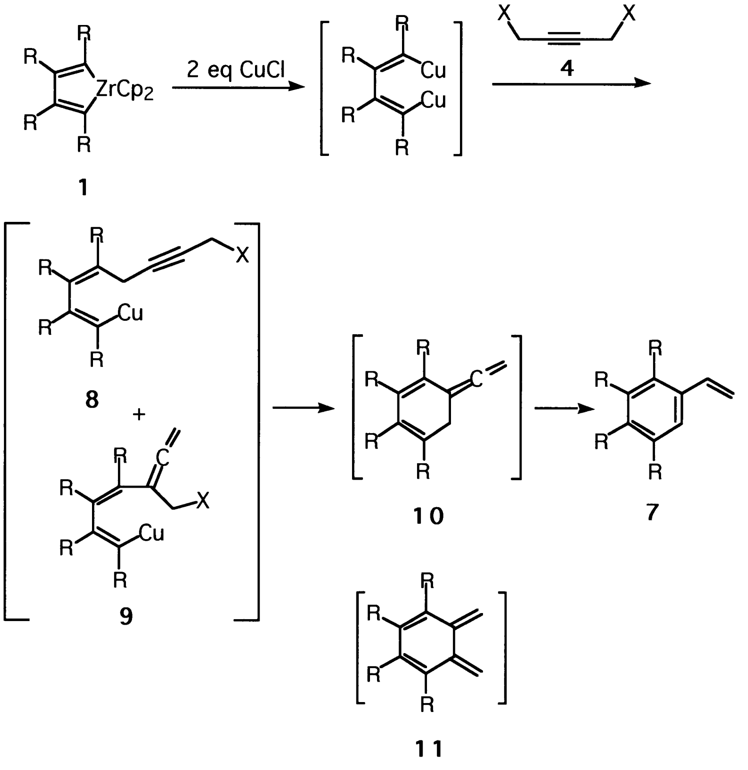
It is noteworthy that, under these reaction conditions, the starting materials were all consumed. This result indicates that an unclear reaction path is involved leading to unknown products. Shown in Scheme 5 is a proposed reaction mechanism for the formation of styrenes. We have reported the first example of transmetalation of zirconacyclopentadienes **1** with CuCl to dicopper compounds.[16] Reaction of the dicopper compounds with **4** may lead to two intermediates **8** and **9**, via intermolecular coupling and via intermolecular γ attack, respectively. Both **8** and **9** afford intermediate **10** via an intramolecular reaction pattern. Intermediate **10** finally transforms to the styrene derivatives **7**. No evidence was observed for the formation of quinodimethene **11**.

2.2. Generation of methylenecycloheptadienes and vinylcyclohexadienes from the reaction of zirconacyclopentadienes with 3-chloro-2-(chloromethyl)-propene and 3,4-dichlorobutene mediated by copper salts

Cyclic dienes are important compounds, for example, for



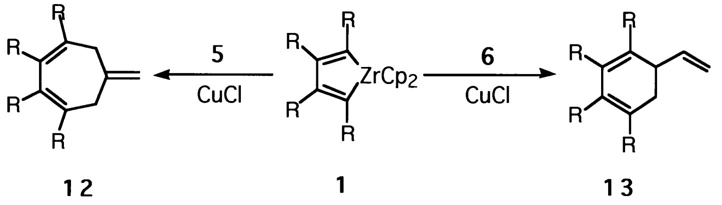
Scheme 2.



Scheme 5.

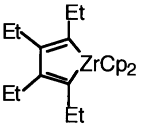
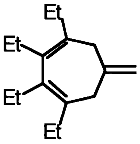
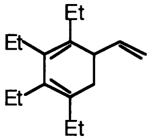
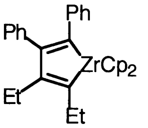
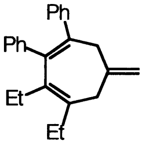
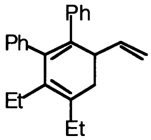
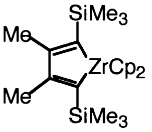
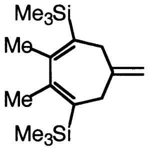
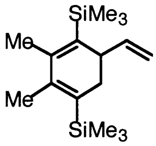
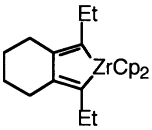
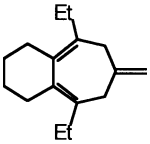
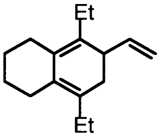
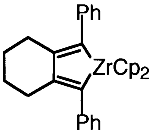
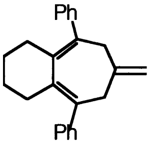
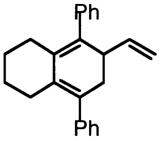
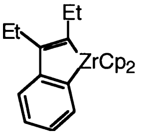
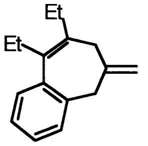
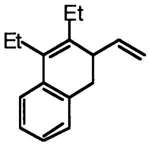
the construction of more complexed polycyclic molecules.[17] One possible and attractive approach to the synthesis of cyclic dienes is the utilization of reactions of five-membered zirconacycles. In order to prepare cyclopentadienes from five-membered zirconacycles, a one-carbon unit building block is required. For six- and seven-membered cyclic dienes, a two-carbon unit and a three-carbon unit building block are necessary, respectively. We have reported preparation of cyclopentadienes by copper-catalyzed reaction of zirconacyclopentenes with acyl chlorides,[18] by the copper-catalyzed reaction of zirconacyclopentadienes with ethyl propynoate,[19] and by $AlCl_3$-mediated deoxygenative cyclization of zirconacyclopentadienes with aldehydes.[20] In these reactions, acyl chlorides, ethyl propynoates and aldehydes acted as one-carbon unit building blocks. Ethyl maleate and fumarate have been used as two-carbon unit building blocks to react with zirconacyclopentadienes to afford cyclohexadiene derivatives.[11,21] Further investigation demonstrated that 3-chloro-2-(chloromethyl)propene **5** reacted with zirconacyclopentadienes **1** as a three-carbon unit building block to form methylenecycloheptadiene **12**, while 3,4-dichlorobutene **6** as a two-carbon unit building block to form vinylcyclohexadiene **13**, via tandem inter–intramolecular allylation (Scheme 6). Results are summarized in Table 1. Generally, various zirconacyclopentadienes (monocyclic, bicyclic, and indenyl) could react with **5** or **6** in the presence of a catalytic (10 mol%) or stoichiometric (2 equiv.) amount of CuCl. It is interesting to note that in the cases of trimethylsilyl substituted zirconacyclopentadienes, the desired product **13c** could be obtained in a high yield only when a stoichiometric amount of CuCl was used. Use of a catalytic amount (10 mol%) of CuCl either afforded very low yield of the product (<10%) or the reaction did not proceed at all. In the case of **13c**, the carbon having a sterically hindered TMS group has to attack the internal carbon. Therefore, the catalytic reaction gave only low yield of the product. As expected, the reaction of unsymmetrically substituted zirconacyclopentadienes afforded a mixture of two regioisomers. In addition to 3,4-dichlorobutene **6**, 1,4-dichloro-2-butene could react also with a zirconacyclopentadiene to afford the same product. For example, **13a** was obtained in 58% yield from the reaction of zirconacyclopentadiene **1a** with 1,4-dichloro-2-butene under similar reaction conditions.

The mechanism of two types of reactions described earlier is similar. As shown in Scheme 7, the essential step is



Scheme 6.

Table 1. Reaction of zirconacyclopentadienes with 3,4-dichlorobutene and 3-chloro-2-(chloromethyl)propene in the presence of a catalytic amount of CuCl

Zirconacyclopentadiene **1**	Product **12**	Yield (%)[a]	Product **13**	Yield (%)[a]
 **1a**		**12a**, 87 (62)		**13a**, 66 (59)
 **1g**		**12b**, 66 (47)		**13b**, 73 (61)[b]
 **1h**		**12c** (51)		**13c** (60)[c]
 **1i**		**12d** (50)		**13d**, 58 (37)[c]
 **1j**		**12e**, 71 (64)		**13e** (61)
 **1k**		**12f**, 79 (59)		**13f**, 57 (46)[d]

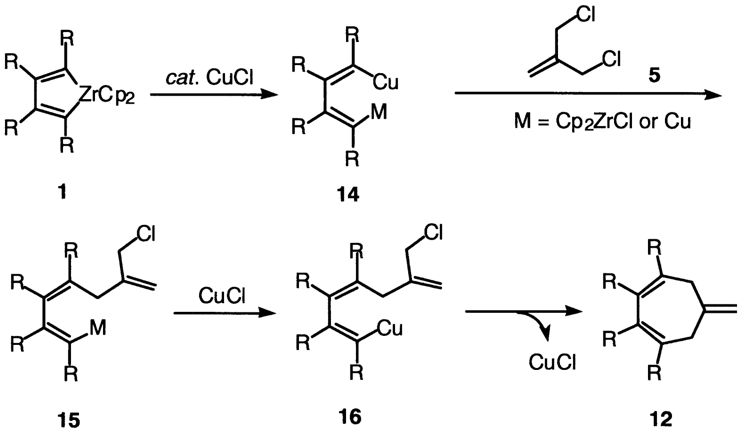
Otherwise noted, CuCl: 10 mol%, 3,4-dichlorobutene: 1 equiv. to zirconacylopentadiene; 3-chloro-2-(chloromethyl)propene: 1 equiv. to zirconacylopentadiene.

[a] GC yields. Isolated yields are given in parenthese.

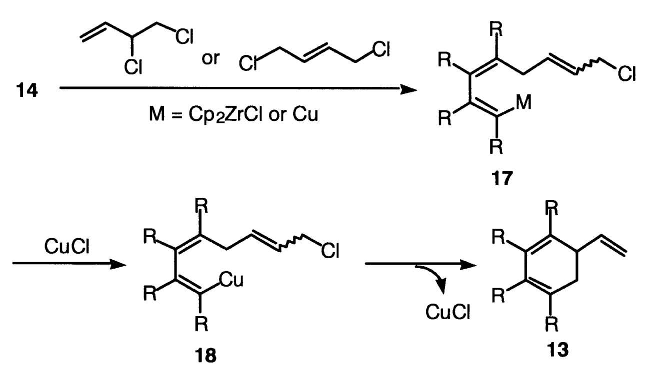
[b] A mixture of two regioisomers in a ratio of 3:2.

[c] 2 equiv. of CuCl were used.

[d] A mixture of two regioisomers in a ratio of 3:2.



Scheme 7.



Scheme 8.

transmetalation of Zr–C bonds of zirconacyclopentadienes to more reactive Cu–C bonds.[2,16] The reaction mechanism for the formation of vinylcyclohexadiene derivatives **13** is shown in Scheme 8.

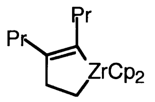
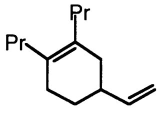
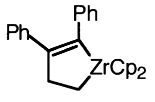
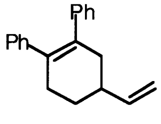
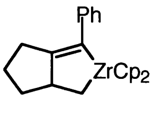
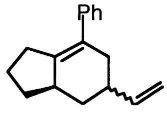
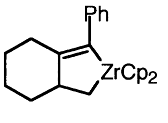
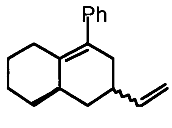
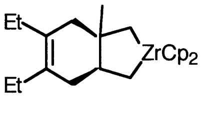
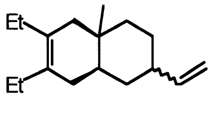
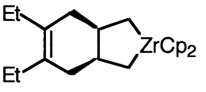
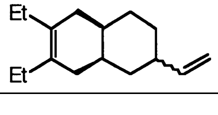
Lower yields in some cases may be attributed to the intermolecular side reactions which afford products with high molecular weights. Indeed, formation of small amount of polymeric materials was observed. Generally, this protocol offers a convenient and simple method for direct transformations of zirconacyclopentadienes to six- or seven-membered cyclic diene compounds.

2.3. Tandem reaction of zirconacyclopentenes and zirconacyclopentanes with 3,4-dichlorobutene and 3-chloro-2-(chloromethyl)propene

As we described earlier, tandem reactions of zirconacyclopentadienes **1** with **4–6** afforded highly substituted styrenes **7**, methylenecycloheptadiene derivatives **12** and vinylcyclohexadiene derivatives **13**, respectively. We then extended the above useful protocol to other five-membered zirconacycles, zirconacyclopentenes **2** and zirconacyclopentanes **3**, and found that the above reaction pattern works too. Results are summarized in Table 2.

Monocyclic zirconacyclopentenes **2** (run **1** and **2**, Table 2) prepared in situ by our ethylene gas procedure[9] reacted with 3,4-dichlorobutene **6** in the presence of a catalytic amount of CuCl (10 mol%) at 50°C for 1 h to afford 1,2-disubstituted-4-vinylcyclohexenes **19** in good yields as single products (Scheme 9). 1,2-Dipropyl-4-vinylcyclohexene **19a** and 1,2-diphenyl-4-vinylcyclohexene **19b** were obtained in 73 and 78% yields, respectively. Although the reason is not clear, when the above monocyclic zirconacyclopentenes **2** were prepared in situ from our Cp_2ZrCl_2/2EtMgBr/alkyne method,[22] products **19a** and **19b** were formed in low yields (~30%). In cases of bicyclic zirconacyclopentenes (run **3** and **4**, Table 2), similar reactions proceeded to form products **19c** and **19d** as mixtures of diastereoisomers in good combined yields.

Table 2. Reaction of zirconacyclopentenes and zirconacyclopentanes with 3,4-dichlorobutene in the presence of a catalytic amount of CuCl

Run	Zirconacycle **2**, **3**	*T* (°C)	*t* (h)	Product **19**, **21**	Yield (%)[a]
1	 **2a**	50	1	 **19a**	73 (55)
2	 **2b**	50	1	 **19b**	78 (55)
3	 **2c**	20	24	 **19c**	62 (56)[b]
4	 **2d**	20	24	 **19d**	71 (54)[c]
5	 **3a**	50	3	 **21a**	39 (35)[d]
6	 **3b**	50	3	 **21b**	41 (36)[d]

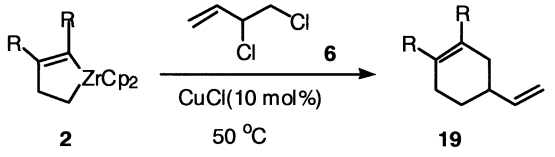
CuCl: 10 mol%, 3,4-dichlorobutene: 1 equiv. to zirconacycle.

[a] GC yields. Isolated yields are given in parentheses.

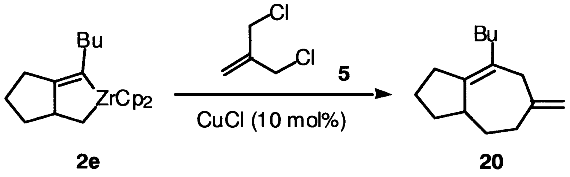
[b] A mixture of two stereoisomers in a ratio of 2:1.

[c] A mixture of two stereoisomers in a ratio of 1.2:1.

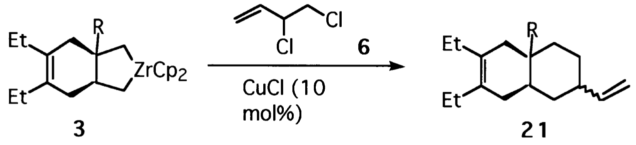
[d] A mixture of two isomers in a ratio of 2.5:1.



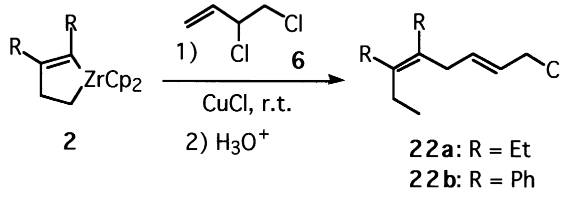
Scheme 9.



Scheme 10.



Scheme 11.



Scheme 12.

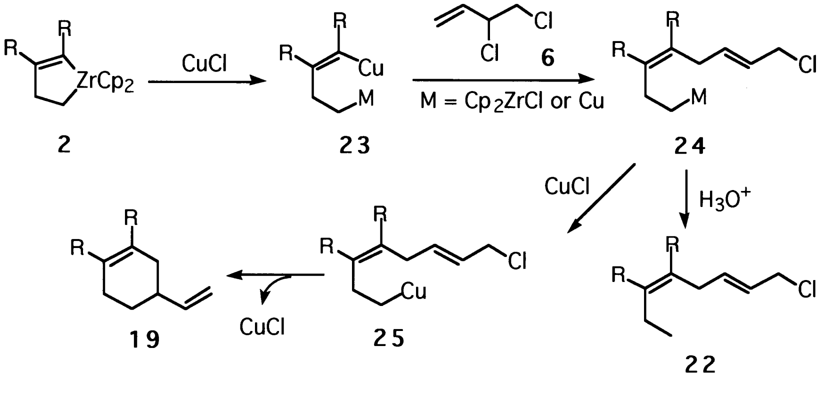
A reaction of zirconacyclopentene **2e** with 3-chloro-2-(chloromethyl)propene **5** was also carried out in the presence of a catalytic amount of CuCl (Scheme 10). The reaction afforded the desired product **20** in a low yield (38% by NMR). The low yield may be attributed to the preferential intermolecular allylation resulting in the formation of unknown compounds rather than the intramolecular allylation that affords a seven-membered ring compound.

Zirconacyclopentanes **3** reacted also in a similarly way with 3,4-dichlorobutene **6** to afford vinylated bicyclic products **21** as mixtures of diastereomers in good combined yields (Scheme 11).[2,23]

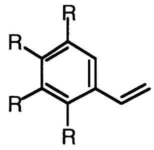
The reaction mechanism of zirconacyclopentenes and zirconacyclopentanes with 3,4-dichlorobutene is essentially the same as that of zirconacyclopentadienes with 3,4-dichlorobutene described previously. The only difference between a zirconacyclopentene and a zirconacyclopentadiene is that there exist one Zr–sp^{2}C bond and one Zr–sp^{3}C bond in a zirconacyclopentene, but two Zr–sp^{2}C bonds in a zirconacyclopentadiene. We have reported that the Zr–sp^{2}C bond, not the Zr–sp^{3}C bond, is preferentially transmetalated with CuCl.[2,24] In fact, when the reaction of monocyclic zirconacyclopentenes **2** with 3,4-dichlorobutene **6** was carried out at room temperature instead of 50°C, linear dienes **22** were obtained after hydrolysis (Scheme 12). These results show that the Zr–sp^{2}C bond of zirconacyclopentenes is allylated firstly at room temperature. Therefore, a plausible reaction path is given in Scheme 13.

3. Conclusion

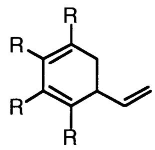
We developed a new method for the construction of vinylated cyclic compounds from five-membered zirconacycles and polyfunctional dihalo reagents via tandem inter–intramolecular reactions catalyzed or mediated by copper(I) salts. We demonstrated in this paper that a wide variety of vinylated cyclic compounds (including Types I–V) could be prepared by this useful protocol. 1,4-Dihalo-2-butyne behaved as a two-carbon unit building block to afford highly substituted styrene derivatives (Type I). In their CuCl-catalyzed or mediated reactions with five-membered zirconacycles, 3,4-dichloro-1-butene or 1,4-dichloro-2-butene, and 3-chloro-2-(chloromethyl)propene behaved as two-carbon unit building blocks and three-carbon unit building blocks, respectively, affording six-membered and seven-membered vinylated cyclic compounds (Types II–V).



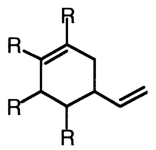
Scheme 13.



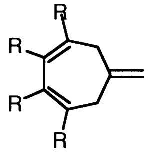
I



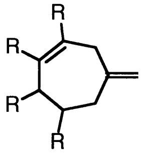
II



III



IV



V

4. Experimental

4.1. General

Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions involving organometallic compounds were carried out under a positive pressure of dry N_2 using standard Schlenk techniques. Tetrahydrofuran (THF) was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Zirconocene dichloride was purchased from Aldrich Chemical Company, Inc., or from Nichia Chemical Industries, Ltd. Japan. 3-Chloro-2-(chloromethyl)propene was purchased from Aldrich Chemical Company Inc. 3,4-Dichlorobutene was from TCI Company Ltd. *n*-BuLi and EtMgBr were obtained from Kanto Chemicals Company Ltd.

GC analysis was performed on a gas chromatograph (Shimadzu GC-14B) equipped with a flame ionization detector using a fused silica capillary column (CBP1-M25-025) and Shimadzu CR6A-Chromatopac integrator. GC yields were determined using suitable hydrocarbons as internal standards. NMR spectra were recorded on a Bruker-400 NMR spectrometer, or on a JEOL JNM-AL300 NMR spectrometer.

4.2. A general procedure for the formation of highly substituted styrenes 7 from the CuCl-mediated reaction of zirconacyclopentadienes 1 with 1,4-dibromo-2-butyne 4

To a THF (10 mL) solution of zirconacyclopentadiene **1** (2.0 mmol), prepared in situ from Cp_2ZrBu_2 (Negishi reagent) (2.0 mmol) and the corresponding alkyne (for mono-yne 4.0 mmol, for di-yne 2.0 mmol),[15] were added CuCl (4.0 mmol, 396 mg) and 1,4-dibromo-2-butyne (2.0 mmol, 0.22 mL) at −78°C. The reaction mixture was then warmed to 50°C and stirred at 50°C for 1 h. Hydrolysis with 3N HCl followed by normal work up afforded crude products, which were purified by column chromatography (silica gel, hexane).

4.2.1. 2,3,4,5-Tetraethyl-1-vinylbenzene (7a). Colorless liquid, GC yield 46%, isolated yield 37% (160 mg). ^1H NMR ($CDCl_3$, Me_4Si) δ 1.11–1.28 (m, 12H), 2.62–2.73 (m, 8H), 5.22 (dd, J=11.0, 1.8 Hz, 1H), 5.58 (dd, J=17.4, 1.8 Hz, 1H), 7.01 (dd, J=17.4, 11.0 Hz, 1H), 7.19 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.38, 15.54, 15.62, 15.88, 21.91, 21.98, 22.05, 25.76, 114.53, 124.23, 134.69, 135.90, 137.31, 139.70, 139.73, 139.78; HRMS calcd for $C_{16}H_{24}$ 216.1878, found 216.1891.

4.2.2. 2,3,4,5-Tetrapropyl-1-vinylbenzene (7b). Colorless liquid, GC yield 60%, isolated yield 45% (244 mg). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.97–1.08 (m, 12H), 1.45–1.64 (m, 8H), 2.63–2.51 (m, 8H), 5.19 (dd, J=11.0, 1.6 Hz, 1H), 5.55 (dd, J=17.0, 1.6 Hz, 1H), 6.97 (dd, J=17.0, 11.0 Hz, 1H), 7.15 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.51, 14.78, 15.00, 15.04, 24.50, 24.74, 24.75, 24.98, 31.60, 31.72, 31.87, 35.39, 114.32, 124.83, 134.56, 136.01, 136.09, 138.38, 138.74, 138.84; HRMS calcd for $C_{20}H_{32}$ 272.2504, found 272.2501.

4.2.3. 2,3,4,5-Tetrabutyl-1-vinylbenzene (7c). Colorless liquid, GC yield 56%, isolated yield 44% (286 mg). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.93–1.00 (m, 12H), 1.38–1.61 (m, 16H), 2.55–2.65 (m, 8H), 5.17 (dd, J=10.8, 1.8 Hz, 1H), 5.54 (dd, J=17.4, 1.8 Hz, 1H), 6.97 (dd, J=17.4, 10.8 Hz, 1H), 7.15 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.87 (2C), 14.03 (2C), 23.09, 23.38, 23.55 (2C), 29.01 (2C), 29.13, 32.96, 33.41, 33.63, 33.83, 34.01, 114.24, 124.86, 134.54, 135.97, 136.07, 138.46, 138.64, 138.71; HRMS calcd for $C_{24}H_{40}$ 328.3130, found 328.3132.

4.2.4. 2,3-Diphenyl-4,5-dimethyl-1-vinylbenzene (7d) and 2,3-dimethyl-4,5-diphenyl-1-vinylbenzene (7d′). Unsymmetrical zirconacyclopentadiene **1d** was prepared in situ according to a known procedure.[9] The product was obtained as a mixture of two regioisomers in a ratio of 2:1. Colorless solid, GC yield 30%, isolated yield 18% (101 mg). NMR data for the major: ^1H NMR ($CDCl_3$, Me_4Si) δ 2.01 (s, 3H), 2.40 (s, 3H), 5.04 (dd, J=11.1, 1.5 Hz, 1H), 5.63 (dd, J=17.4, 1.5 Hz, 1H), 6.39 (dd, J=17.7, 11.1 Hz, 1H), 6.90–6.94 (m, 2H), 7.02–7.15 (m, 8H), 7.50 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.52, 20.77, 113.45, 125.31, 125.87, 125.91, 127.14 (2C), 127.37 (2C), 130.19 (2C), 130.81 (2C), 133.48, 134.53, 135.98, 136.04, 138.27, 139.84, 140.97, 141.68; NMR data for the minor: ^1H NMR ($CDCl_3$, Me_4Si) δ 2.09 (s, 3H), 2.35 (s, 3H), 5.31 (dd, J=11.1, 1.5 Hz, 1H), 5.62 (dd, J=17.4, 1.5 Hz, 1H), 6.39 (dd, J=17.4, 11.1 Hz, 1H), 6.90–6.92 (m, 2H), 6.98–7.17 (m, 8H), 7.38 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 16.04, 18.18, 115.99, 125.25, 125.86, 126.16, 127.59 (2C), 127.79 (2C), 129.75 (2C), 130.58 (2C), 133.44, 135.17, 135.73, 135.97, 139.27, 140.18, 140.89, 142.15; HRMS calcd for $C_{22}H_{20}$ 284.1565, found 284.1578.

4.2.5. 1,4-Diphenyl-2-vinyl-5,6,7,8-tetrahydronaphthalene (7e). The molar ratio of zirconacyclopentadiene **1e** to 1,8-diphenyl-1,7-octdiyne is 2:2. Colorless solid, GC yield 47%, isolated yield 44% (230 mg). ^1H NMR ($CDCl_3$, Me_4Si) δ 1.62–1.66 (m, 4H), 2.40 (t, J=5.7 Hz, 2H), 2.63 (t, J=5.4 Hz, 2H), 4.98 (dd, J=10.8, 1.5 Hz, 1H), 5.55 (dd, J=17.4, 1.5 Hz, 1H), 6.35 (dd, J=17.1, 10.8 Hz, 1H), 7.17–7.19 (m, 2H), 7.33–7.42 (m, 8H), 7.44 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 22.84, 23.03, 28.84, 29.10, 113.51, 123.44, 126.74, 126.77 (2C), 128.03 (2C), 128.29 (2C), 129.27 (2C), 129.72, 133.26, 134.63, 135.59, 139.90, 140.02 (2C), 141.41, 142.05; HRMS calcd for $C_{24}H_{22}$ 310.1722, found 310.1746.

4.2.6. 1,4-Dipropyl-2-vinyl-5,6,7,8-tetrahydronaphthalene (7f). The molar ratio of zirconacyclopentadiene **1f** to 4,10-tetradecadiyne is 2:2. Colorless liquid, GC yield 35%, isolated yield 27% (132 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89–1.03 (m, 6H), 1.44–1.65 (m, 4H), 1.76–1.79 (m, 4H), 2.49–2.61 (m, 4H), 2.72 (t, J=4.4 Hz, 4H), 5.21 (dd, J=10.8, 1.8 Hz, 1H), 5.56 (dd, J=17.1, 1.5 Hz, 1H), 6.99 (dd, J=17.4, 10.8 Hz, 1H), 7.15 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.46, 14.75, 22.84, 23.22, 23.26, 23.36, 26.82, 27.06, 30.73, 35.06, 114.50, 123.89, 133.89, 135.02, 135.09, 135.75, 136.08, 138.39; HRMS calcd for $C_{18}H_{26}$ 242.2035, found 242.2045.

4.3. A general procedure for the formation of methylenecycloheptadiene derivatives 12 from the CuCl-catalyzed reaction of zirconacyclopentadienes 1 with 3-chloro-2-(chloromethyl)propene 5

To a zirconacyclopentadiene **1** in THF (5 mL), prepared in situ from Cp_2ZrBu_2 (Negishi reagent) (1.0 mmol) and the corresponding alkyne (for mono-yne 2.0 mmol, for di-yne 1.0 mmol),[15] were added CuCl (0.1 mmol) and 3-chloro-2-(chloromethyl)propene (1.0 mmol) at room temperature. After being stirred at room temperature for 1–6 h till the starting material was consumed, the reaction mixture was hydrolyzed with 3N HCl followed by normal work up. Evaporation in vacuo afforded crude products, which were purified by column chromatography or Kugelrohr distillation.

4.3.1. 6-Methylene-1,2,3,4-tetraethyl-1,3-cycloheptadiene (12a). Kugelrohr distillation afforded 135 mg (62%) of the title compound as a colorless liquid, GC yield 87%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.88 (t, J=7.5 Hz, 6H), 1.01 (t, J=7.5 Hz, 6H), 2.10–2.20 (m, 8H), 2.66 (br, 4H), 4.55–4.60 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.92, 14.19, 21.86, 27.01, 40.81, 104.94, 135.92, 136.85, 160.43; HRMS calcd for $C_{16}H_{26}$ 218.2035, found 218.2032.

4.3.2. 1,2-Diphenyl-6-methylene-3,4-diethyl-1,3-cycloheptadiene (12b). Column chromatography on silica gel (hexane/diethyl ether=99:1) afforded 147 mg (47%) of the title compound as a colorless liquid, GC yield 66%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.85 (t, J=7.6 Hz, 3H), 1.14 (t, J=7.6 Hz, 3H), 1.90–2.05 (m, 2H), 2.32 (q, J=7.6 Hz, 2H), 2.99 (br, 2H), 3.22 (br, 2H), 4.52–4.58 (m, 1H), 4.65–4.70 (m, 1H), 6.85–7.15 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.82, 14.18, 22.70, 27.19, 40.88, 43.65, 106.99, 125.84, 125.93, 127.44, 127.55, 130.28, 129.56, 136.53, 139.19, 139.32, 140.03, 140.50, 143.20, 158.58; HRMS calcd for $C_{24}H_{26}$ 314.2035, found 314.2024.

4.3.3. 1,4-Bis(trimethylsilyl)-6-methylene-2,3-dimethyl-1,3-cycloheptadiene (12c). Kugelrohr distillation afforded 142 mg (51%) of the title compound as a colorless liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.25 (s, 18H), 1.84 (s, 6H), 2.78 (br, 4H), 4.70–4.73 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.92, 20.16, 39.39, 105.91, 134.86, 149.13, 159.91; HRMS calcd for $C_{16}H_{30}Si_2$ 278.1886, found 278.1894.

4.3.4. 3-Methylene-1,5-diethyl-bicyclo-[5.4.0]-5,11-dodecadiene (12d). Kugelrohr distillation afforded 108 mg (50%) of the title compound as a colorless liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.98 (t, J=7.5 Hz, 6H), 1.55–1.65 (m, 4H), 2.16 (q, J=7.5 Hz, 4H), 2.18–2.30 (m, 4H), 2.67 (m, 4H), 4.50–4.60 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.02, 26.75, 27.11, 29.04, 40.96, 104.70, 133.69, 134.59, 160.62; HRMS calcd for $C_{16}H_{24}$ 216.1877, found 216.1876.

4.3.5. 1,5-Diphenyl-3-methylene-bicyclo-[5.4.0]-5,11-dodecadiene (12e). White solid, GC yield 71%, isolated yield 64% (201 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.55–1.65 (m, 4H), 2.25–2.35 (m, 4H), 3.17 (s, 4H), 4.55–4.65 (m, 2H), 7.15–7.35 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 27.30, 31.20, 42.73, 106.86, 126.18, 127.95, 128.56, 134.67, 137.01, 143.37, 157.97; HRMS calcd for $C_{24}H_{24}$ 312.1877, found 312.1884.

4.3.6. 5,7-Dihydro-6-methylene-8,9-diethylbenzocycloheptene (12f). The indenyl zirconacyclopentadiene **1j** was prepared according to a known method.[25] Colorless liquid, GC yield 79%, isolated yield 59% (157 mg). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J=7.6 Hz, 3H), 1.09 (t, J=7.6 Hz, 3H), 2.29 (q, J=7.6 Hz, 2H), 2.55 (q, J=7.6 Hz, 2H), 2.57 (s, 2H), 3.31 (s, 2H), 4.65 (dt, J=1.6, 1.3 Hz, 1H), 4.71 (dt, J=1.6, 1.3 Hz, 1H), 7.10–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.82, 14.18, 25.35, 27.24, 40.20, 41.80, 106.05, 126.13, 126.18, 126.57, 128.23, 134.66, 136.55, 139.26, 141.65, 156.13; HRMS calcd for $C_{16}H_{20}$ 212.1565, found 212.1563.

4.4. A general procedure for the formation of vinylcyclohexadiene derivatives 13 from the CuCl-catalyzed reaction of zirconacyclopentadienes 1 with 3,4-dichlorobutene 6 and 1,4-dichloro-2-butene

To a THF solution (5 mL) of zirconacyclopentadiene **1** (1.0 mmol) were added 3,4-dichlorobutene (1.0 mmol) and CuCl (10 mg, 0.1 mmol). The reaction mixture was stirred at room temperature or 0°C till the starting material was consumed. The reaction was then quenched with 3N HCl, and extracted with hexane. Organic layers were collected, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Products were isolated by Kugelrohr distillation or column chromatography.

4.4.1. 6-Ethenyl-1,2,3,4-tetraethyl-1,3-cyclohexadiene (13a). Kugelrohr distillation afforded 128 mg (59%) of the title compound as a colorless liquid, GC yield 66%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.92 (t, J=7.6 Hz, 3H), 0.95 (t, J=7.6 Hz, 3H), 0.97 (t, J=7.6 Hz, 3H), 1.02 (t, J=7.6 Hz, 3H), 1.75–2.40 (m, 10H), 2.45–2.55 (m, 1H), 4.83 (dd, J=10.5, 2.2 Hz, 1H), 4.95 (ddd, J=17.3, 2.0, 0.9 Hz, 1H), 5.72 (ddd, J=17.2, 9.9, 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.00, 14.82, 15.35, 15.42, 20.32, 20.72, 24.95, 26.48, 34.10, 41.62, 113.16, 130.29, 131.95, 133.16, 134.91, 139.79; HRMS calcd for $C_{16}H_{26}$ 218.2033, found 218.2034.

4.4.2. 6-Ethenyl-1,2-diphenyl-3,4-diethyl-1,3-cyclohexadiene and 5-ethenyl-1,2-diphenyl-3,4-diethyl-1,3-cyclohexadiene (13b). Column chromatography on silica gel (hexane) afforded 191 mg (61%) of a mixture of the title compounds (3:2) as colorless liquid, GC yield 73%. Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.70 (t, *J*=7.4 Hz, 3H), 1.06 (t, *J*=7.5 Hz, 3H), 1.80–2.50 (m, 5H), 2.65–2.85 (m, 1H), 2.95–3.05 (m, 1H), 5.00–5.30 (m, 2H), 6.05 (ddd, *J*=17.4, 10.0, 7.5 Hz, 1H), 6.80–7.50 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.76, 14.73, 21.30, 26.55, 34.34, 44.56, 114.76, 125.37, 125.87, 127.18 (2C), 127.37 (4C), 128.76 (2C), 132.52, 133.07, 134.70, 137.93, 140.02, 140.66, 142.96. Minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.72 (t, *J*=7.4 Hz, 3H), 1.13 (t, *J*=7.5 Hz, 3H), 1.80–2.50 (m, 5H), 2.65–2.85 (m, 1H), 2.95–3.05 (m, 1H), 4.95–5.51 (m, 2H), 5.96 (ddd, *J*=17.4, 10.0, 7.5 Hz, 1H), 6.80–7.50 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.73, 14.89, 21.58, 25.06, 36.76, 41.24, 114.01, 125.34, 125.90, 127.18 (2C), 128.36 (2C), 128.76 (2C), 131.17, 134.01, 136.67, 136.88, 138.78, 140.43, 143.52; HRMS calcd for $C_{24}H_{26}$ 314.2033, found 314.2034.

4.4.3. 2-Ethenyl-1,4-bis(trimethylsilyl)cyclohexadiene (13c). Column chromatography on silica gel (hexane) afforded 167 mg (60%) of the title compound as a colorless liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.14 (s, 9H), 0.17 (s, 9H), 1.88 (d, *J*=2.5 Hz, 3H), 1.92 (s, 3H), 2.08–2.17 (m, 1H), 2.24 (dd, *J*=16.3, 0.9 Hz, 1H), 2.70–2.78 (m, 1H), 4.82 (d, *J*=10.2 Hz, 1H), 4.88 (d, *J*=17.2 Hz, 1H), 5.64 (ddd, *J*=17.2, 10.2, 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −0.22, 0.47, 19.57, 19.90, 32.94, 39.06, 113.22, 130.32, 134.27, 139.71, 142.71, 143.37; HRMS calcd for $C_{16}H_{30}Si_2$ 278.1884, found 278.1888.

4.4.4. 2-Ethenyl-1,4-diethyl-2,3,5,6,7,8-hexahydronaphthalene (13d). 2 equiv. of CuCl were used. Kugelrohr distillation afforded 80 mg (37%) of the title compound as a colorless liquid, GC yield 58%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.94 (t, *J*=7.6 Hz, 3H), 0.98 (t, *J*=7.6 Hz, 3H), 1.40–2.60 (m, 15H), 4.80–5.01 (m, 2H), 5.74 (ddd, *J*=17.5, 9.7, 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.15, 13.73, 24.11 (2C), 24.39, 25.87, 25.92, 26.15, 34.18, 41.98, 113.04, 127.32, 128.49, 128.88, 133.09, 140.04; HRMS calcd for $C_{16}H_{24}$ 216.1877, found 216.1871.

4.4.5. 2-Ethenyl-1,4-diphenyl-2,3,5,6,7,8-hexahydronaphthalene (13e). Column chromatography on silica gel (hexane) afforded 190 mg (61%) of the title compound as a yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.40–1.75 (m, 4H), 2.10–2.30 (m, 2H), 2.35–2.65 (m, 3H), 3.85–4.10 (m, 2H), 4.90–5.10 (m, 2H), 5.94 (ddd, *J*=17.4, 10.2, 7.2 Hz, 1H), 7.10–7.50 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.76, 23.86, 27.53, 27.86, 36.56, 43.97, 114.36, 126.13, 127.86 (2C), 127.97 (2C), 128.38 (2C), 128.88 (2C), 129.15, 131.52, 132.40, 133.35, 139.07, 142.29, 143.02; HRMS calcd for $C_{24}H_{24}$ 312.1877, found 312.1878.

4.4.6. 2-Ethenyl-3,4-diethyl-1,2-dihydronaphthalene and 1-ethenyl-3,4-diethyl-1,2-dihydronaphthalene (13f). The indenyl zirconacyclopentadiene **1j** was prepared according to a known method.[24] Column chromatography on silica gel (hexane) afforded 98 mg (46%) of a mixture of the title compounds (3:2) as a colorless liquid. Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.09 (t, *J*=7.6 Hz, 3H), 1.11 (t, *J*=7.5 Hz, 3H), 2.15–2.30 (m, 3H), 2.41 (dd, *J*=16.0, 6.4 Hz, 1H), 2.57 (q, *J*=7.5 Hz, 2H), 3.35–3.45 (m, 1H), 5.00–5.10 (m, 2H), 5.98 (ddd, *J*=16.8, 10.2, 8.0 Hz, 1H), 7.10–7.41 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.84, 14.31, 20.58, 26.91, 34.23, 43.10, 115.00, 122.86, 125.81, 126.62, 126.92, 130.71, 135.38, 135.60, 137.53, 140.86. Minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.14 (t, *J*=7.3 Hz, 3H), 1.15 (t, *J*=7.5 Hz, 3H), 2.22–2.30 (m, 2H), 2.50–2.60 (m, 2H), 2.72 (dd, *J*=14.9, 2.7 Hz, 1H), 2.80–2.90 (m, 1H), 3.03 (dd, *J*=14.9, 6.5 Hz, 1H), 4.85–5.00 (m, 2H), 5.65 (ddd, *J*=17.3, 9.8, 7.7 Hz, 1H), 7.10–7.41 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.08, 14.34, 20.84, 25.24, 35.08, 41.89, 114.12, 122.51, 125.73, 127.97, 128.75, 131.64, 134.11, 135.29, 138.95, 139.07; HRMS calcd for $C_{16}H_{20}$ 212.1564, found 212.1567.

4.5. Preparation of 1,2-disubstituted-4-vinylcyclohexene 19a,b from CuCl-catalyzed monocyclic zirconacyclopentenes 2 and 3,4-dichloro-1-butene 6

Zirconacyclopentenes were prepared in situ by our procedure.[9] To the THF (5 mL) solution of thus prepared zirconacyclopentene (1.0 mmol) were added 3,4-dichlorobutene (1.0 mmol) and CuCl (0.1 mmol) at room temperature. After being stirred at 50°C for 1 h, the reaction mixture was hydrolyzed with 3N HCl, followed by normal work up.

4.5.1. 1,2-Dipropyl-4-vinylcyclohexene (19a). Column chromatography on silica gel (hexane) afforded 210 mg (55%) of the title compound as a colorless liquid, GC yield 73%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, *J*=7.1 Hz, 3H), 0.91 (t, *J*=7.2 Hz, 3H), 1.29–1.43 (m, 6H), 1.74–1.87 (m, 2H), 1.96–2.26 (m, 7H), 4.94 (ddd, *J*=10.0, 1.1, 1.1 Hz, 1H), 5.02 (ddd, *J*=17.0, 1.6, 1.6 Hz, 1H), 5.85 (ddd, *J*=17.1, 10.2, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.23 (2C), 21.64, 21.70, 29.12 (2C), 34.98, 35.16, 35.39, 38.44, 112.10, 129.21, 129.98, 144.11; HRMS calcd for $C_{14}H_{24}$ 192.1878, found 192.1880.

4.5.2. 1,2-Diphenyl-4-vinylcyclohexene (19b). Column chromatography on silica gel (hexane) afforded 286 mg (55%) of the title compound as a colorless liquid, GC yield 78%. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.58–1.68 (m, 2H), 1.95–2.02 (m, 2H), 2.29–2.36 (m, 2H), 2.58–2.60 (m, 1H), 5.01 (ddd, *J*=10.0, 1.4, 1.4 Hz, 1H), 5.11 (ddd, *J*=17.3, 1.5, 1.5 Hz, 1H), 5.94 (ddd, *J*=17.1, 10.7, 6.7 Hz, 1H), 6.96–6.99 (m, 5H), 7.01–7.11 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 28.87, 31.58, 37.59, 38.09, 112.90, 125.77 (2C), 127.58 (2C), 127.62 (2C), 128.96 (2C), 128.99 (2C), 133.91, 134.63, 143.05, 143.34, 143.39; HRMS calcd for $C_{20}H_{20}$ 260.1565, found 260.1561.

4.6. Preparation of bicyclic compounds 19c,d from the CuCl-catalyzed reaction of bicyclic zirconacyclopentenes 2 with 3,4-dichlorobutene 6

To a THF (5 mL) solution of bicyclic zirconacyclopentene (1.0 mmol) prepared in situ from the reaction of Cp_2ZrBu_2 (1.0 mmol) and the corresponding enyne (1.0 mmol), were added 3,4-dichlorobutene (1.1 mmol) and CuCl (0.1 mmol) at 0°C. The reaction mixture was stirred at room temperature for 24 h. Normal work up followed by column chromatography on silica gel (hexane) afforded the products.

4.6.1. 2-Phenyl-4-ethenylbibyblo[4.3.0]non-1-ene (19c). A 2:1 mixture of diasteroisomers, colorless liquid, GC yield 62%, isolated yield 56% (125 mg). Major isomer: ^{1}H

NMR ($CDCl_3$, Me_4Si) δ 1.00–1.15 (m, 2H), 1.50–1.75 (m, 2H), 1.90–2.35 (m, 5H), 2.40–2.55 (m, 1H), 2.65–2.75 (m, 2H), 4.90–5.10 (m, 2H), 5.99 (ddd, J=17.0, 10.4, 6.2 Hz, 1H), 7.2–7.4 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.26, 29.42, 33.09, 33.38, 34.10, 36.12, 37.60, 113.11, 125.91, 126.80, 127.51, 127.58, 140.73, 142.43, 143.42. Minor isomer: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.35–1.45 (m, 2H), 1.50–1.75 (m, 2H), 1.90–2.25 (m, 5H), 2.40–2.55 (m, 3H), 4.90–5.10 (m, 2H), 5.91 (ddd, J=17.0, 10.3, 6.5 Hz, 1H), 7.20–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.54, 29.52, 33.14, 35.03, 36.73, 39.10, 42.82, 112.41, 125.96, 127.51, 127.58, 127.66, 141.00, 143.10, 143.85; HRMS calcd for $C_{17}H_{20}$ 224.1565, found 224.1565.

4.6.2. 2,3,4,4a,5,6,7,8-Octahydro-1-phenyl-3-ethenyl-naphthalene (19d). A 1.2:1 mixture of diasteroisomers, colorless liquid, GC yield 71%, isolated yield 54% (130 mg). Major isomer: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.00–1.25 (m, 2H), 1.30–1.80 (m, 6H), 1.85–1.95 (m, 1H), 2.05–2.50 (m, 5H), 4.90–5.11 (m, 2H), 5.88 (ddd, J=17.2, 10.4, 6.6 Hz, 1H), 7.10–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 27.01, 28.56, 31.50, 35.22, 35.80, 35.88, 37.56, 37.80, 112.65, 125.88, 127.95, 128.44, 130.42, 136.54, 143.38, 143.93. Minor isomer: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.00–1.25 (m, 2H), 1.30–1.80 (m, 6H), 1.85–1.95 (m, 1H), 2.05–2.50 (m, 5H), 4.89–5.10 (m, 2H), 5.83 (ddd, J=17.1, 10.4, 6.5 Hz, 1H), 7.08–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 26.37, 27.78, 30.48, 35.98, 37.92, 37.98, 38.57, 38.70, 112.30, 125.93, 127.95, 128.49, 128.93, 135.74, 143.69; HRMS calcd for $C_{18}H_{22}$ 238.1721, found 238.1718.

4.6.3. Formation of 2-phenyl-4-methylene-bicyclo[5.3.2]-dodec-1-ene (20) by the reaction of zirconacyclopentene 2e with 3-chloro-2-(chloromethyl)propene 5. The reaction procedure and conditions are essentially the same as those described earlier. Colorless liquid, NMR yield 38%, isolated yield 14% (28 mg). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J=7.1 Hz, 3H), 1.02–1.45 (m, 7H), 1.60–2.08 (m, 6H), 2.15–2.60 (m, 4H), 2.66 (d, J=14.0 Hz, 1H), 2.86 (d, J=14.0 Hz, 1H), 4.60 (s, 1H), 4.62 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.13, 22.61, 25.18, 30.01, 31.58, 34.46, 35.74, 36.03, 39.34, 41.83, 42.85, 109.06, 130.02, 141.50, 148.41; HRMS calcd for $C_{15}H_{24}$ 204.1878, found 204.1878.

4.7. Preparation of bicyclic compounds 21a,b from bicyclic zirconacyclopentanes 3 with 3,4-dichlorobutene 6

Bicyclic zirconacyclopentanes (2.0 mmol) were prepared in situ following the reported procedure.[26] To the reaction solution were added 3,4-dichlorobutene (2.0 mmol) and copper chloride (0.2 mmol). The reaction mixture was stirred at 50°C for 3 h, then was quenched with 3N HCl and extracted with hexane. The extract was washed with water and brine, dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel.

4.7.1. 3,4-Diethyl-1-methyl-8-vinylbicyclo[4.4.0]deca-3-ene (21a). Column chromatography on silica gel (hexane) afforded 160 mg (35%) of a 2.5:1 mixture of isomers as a colorless liquid, GC yield 39%. Major isomer: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.87 (s, 3H), 0.92–0.98 (m, 6H), 1.06–1.69 (m, 8H), 1.80–2.12 (m, 7H), 2.33–2.42 (m, 1H), 4.88 (ddd, J=10.2, 1.5, 1.5 Hz, 1H), 4.96 (ddd, J=17.2, 1.6, 1.6 Hz, 1H), 5.79 (ddd, J=17.1, 10.6, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.29, 13.36 (2C), 25.44, 25.51, 28.22, 28.27, 33.55, 34.29, 35.39, 39.07, 39.94, 42.15, 111.54, 127.88, 128.55, 144.67. Minor isomer: ^1H NMR ($CDCl_3$, Me_4Si) δ 2.19–2.25 (m, 1H), 4.97 (ddd, J=10.6, 1.6, 1.6 Hz, 1H), 5.02 (ddd, J=17.2, 1.8, 1.8 Hz, 1H), 5.90 (ddd, J=17.1, 10.6, 6.1 Hz, 1H), other peaks are covered by the major isomer; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.27, 13.42 (2C), 25.67, 25.79, 26.90, 27.47, 31.50, 31.54, 32.36, 32.88, 35.88, 35.96, 112.50, 127.48, 128.22, 143.94; HRMS calcd for $C_{17}H_{28}$ 232.2191, found 232.2186.

4.7.2. 3,4-Diethyl-8-vinylbicyclo[4.4.0]deca-3-ene (21b). Column chromatography on silica gel (hexane) afforded 155 mg (36%) of a 2.5:1 mixture of isomers as a colorless liquid, GC yield 41%. Major isomer: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J=7.5 Hz, 3H), 0.96 (t, J=7.5 Hz, 3H), 1.11–1.21 (m, 1H), 1.27–1.38 (m, 3H), 1.49–1.81 (m, 6H), 1.86–2.10 (m, 6H), 2.23–2.37 (m, 1H), 4.88 (ddd, J=10.3, 1.5, 1.5 Hz, 1H), 4.96 (ddd, J=17.3, 1.6, 1.6 Hz, 1H), 5.79 (ddd, J=17.1, 10.7, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.27, 13.35, 25.66, 25.76, 26.37, 28.54, 30.44, 31.47, 33.03, 34.58, 36.11, 42.15, 111.45, 128.64, 128.82, 144.82. Minor isomer: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.94 (t, J=7.5 Hz, 3H), 0.97 (t, J=7.5 Hz, 3H), 4.98 (ddd, J=17.3, 1.7, 1.7 Hz, 1H), other peaks are covered by the major isomer; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.21, 13.28, 25.68, 25.76, 26.67, 29.71, 32.04, 32.29, 34.50, 35.53, 35.61, 36.88, 111.77, 128.74, 128.81, 144.85; HRMS calcd for $C_{16}H_{26}$ 218.2035, found 218.2035.

4.8. Formation of dienes 22a,b from the CuCl-catalyzed reaction of zirconacyclopentenes 2 with 3,4-dichloro-butene 6 at room temperature

The reaction procedure was essentially the same as that for the preparation of **19a**,**b**, except that the reaction temperature was not 50°C, but room temperature. The reaction was stirred at room temperature for 6 h before hydrolysis. Dienes **22a**,**b** were obtained as pure compounds by column chromatography on silica gel (hexane).

4.8.1. 1-Chloro-5,6-diethyl-octa-2(*E*),5(*Z*)-diene (22a). Colorless liquid, isolated yield 33%. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J=7.5 Hz, 3H), 0.94 (t, J=7.5 Hz, 3H), 0.97 (t, J=7.5 Hz, 3H), 1.98–2.05 (m, 6H), 2.77 (d, J=6.1 Hz, 2H), 4.04 (dd, J=7.2, 0.7 Hz, 2H), 5.59 (ddd, J=15.0, 7.1, 7.1 Hz, 1H), 5.71 (ddd, J=15.1, 6.1, 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.59, 13.61, 13.84, 24.12, 24.30, 24.52, 33.87, 45.56, 125.91, 130.43, 134.88, 138.17; HRMS calcd for $C_{12}H_{21}Cl$ 200.1332, found 200.1341.

4.8.2. 1-Chloro-5,6-diphenyl-octa-2(*E*),5(*Z*)-diene (22b). White solid, isolated yield 54%. ^1H NMR ($CDCl_3$, Me_4Si) δ 1.05 (t, J=7.5 Hz, 3H), 2.65 (q, J=7.5 Hz, 2H), 3.40 (d, J=6.0 Hz, 2H), 4.07 (d, J=6.8 Hz, 2H), 5.77 (ddd, J=15.2, 6.7, 6.7 Hz, 1H), 5.85 (ddd, J=15.2, 6.0, 6.0 Hz, 1H), 6.99–7.12 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.07, 27.59, 37.11, 45.28, 125.73, 125.79, 126.66, 127.48 (2C), 127.50

(2C), 129.64 (4C), 133.09, 133.81, 141.82, 142.55, 142.90; HRMS calcd for $C_{20}H_{21}Cl$ 296.1332, found 296.1358.

Acknowledgements

This work was partially supported by National Science Fund for Distinguished Young Scholars (29825105), the Major State Basic Research Development Program (G2000077502), and National Natural Science Foundation of China (29702001). Qiu Shi Science and Technologies Foundation is gratefully acknowledged. This work was also partially supported by the Ministry of Education, Science, Sports and Culture, Japan.

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