4444 *J. Org. Chem.* **1995,** *60,* 4444–4448

Highly Selective and Practical Alkyne–Alkyne Cross-Coupling Using Cp_2ZrBu_2 and Ethylene

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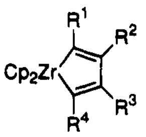
Received September 21, 1994®

Highly selective alkyne–alkyne cross coupling reactions were achieved using Cp_2ZrBu_2 and ethylene gas. First, alkynes were treated with 1.2 equiv of Cp_2ZrBu_2 (Negishi reagent) under ethylene gas to give zirconacyclopentenes with high selectivities. Subsequent addition of a second alkyne to the solution of zirconacyclopentenes at 50 °C gave unsymmetrical zirconacyclopentadienes selectively. After hydrolysis unsymmetrical dienes were obtained in high yields.

Introduction

Zirconacyclopentadienes **1**, which are alkyne–alkyne coupling products of zirconocene,[1,2] have attracted much attention since they have been shown to be useful for preparation of various heterocyclic compounds.[3] Very recently we have reported a copper catalyzed diallylation reaction of zirconacyclopentadienes and its application for syntheses of eight-five-fused ring compounds.[4] For these reactions the unsymmetrically substituted zirconacyclopentadienes are especially useful. From this view point, we have developed a flexible new method for preparing zirconacyclopentadienes.



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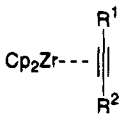

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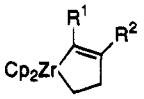
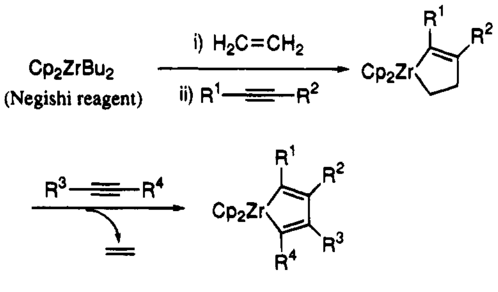


3

Several methods have been reported to prepare unsymmetrical zirconacyclopentadienes[2] in which the key step is the addition of a second alkyne to zirconocene–alkyne complexes **2**. The alkyne complexes **2** could be prepared either by addition of an alkyne to Cp_2ZrBu_2[2a,c] or hydrozirconation of an alkyne with Cp_2ZrHCl followed by methylation with MeLi and elimination of methane from the alkenyl(methyl)zirconocene.[1j,2b] The first method has severe limitations. When diphenylacetylene was used as the first alkyne, a cross coupling product was cleanly formed. However, when alkyl-substituted alkynes such as 4-octyne were used as a first alkyne, yields and selectivities were unsatisfactory. Although the second method is more general, it requires the use of Cp_2ZrHCl which is light-sensitive, insoluble in organic solvents, and more expensive than Cp_2ZrCl_2.

In order to circumvent these problems, we recently used Cp_2ZrEt_2 which gave zirconacyclopentenes **3** by reaction with the first alkyne.[2d] Addition of a second alkyne to the zirconacyclopentene **3** afforded the unsymmetrical zirconacyclopentadiene **1**.[2d] This method still has some limitations: (i) Small amounts of homo coupling products of both alkynes were formed (4–10%). (ii) When silyl-substituted alkynes were used, the yields of cross coupling products were not high. For example, the cross coupling reactions of 1-(trimethylsilyl)propyne with 4-octyne and with diphenylacetylene afforded the desired products in only 45% and 48% yields, respectively. In this paper we report a highly selective and practical method using Cp_2ZrBu_2 and ethylene gas to overcome the shortcomings described above (eq 1).



(eq 1)

Results and Discussion

Reaction of Alkynes with Cp_2ZrBu_2 under Ethylene. It is well known that an alkyne quantitatively dimerizes when treated with Cp_2ZrBu_2 prepared *in situ* by the reaction of Cp_2ZrCl_2 with 2 equiv of n-BuLi. Very interestingly, however, in the presence of ethylene gas, a cross-coupling reaction took place between an ethylene molecule and an alkyne on zirconocene to form a zirconacyclopentene in high yield with an excellent selectivity. No homo-coupling product of the alkyne was detected.[5]

® Abstract published in *Advance ACS Abstracts,* June 15, 1995.

[1] Dimerization reaction of alkynes with zirconocene, see (a) Watt, G. W.; Drummond, F. O., Jr. *J. Am. Chem. Soc.* **1970,** *92,* 826. (b) Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974,** *96,* 5936. (c) Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1977,** *141,* 299. (d) Yoshifuji, M.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978,** *153,* C15. (e) Lau, C. P.; Chang, B. H.; Grubbs, R. H.; Brubaker, C. H. *J. Organomet. Chem.* **1981,** *214,* 325. (f) Thanedar, D.; Farona, M. F. *J. Organomet. Chem.* **1982,** *235,* 65. (g) Skibbe, V.; Erker, G. *J. Organomet. Chem.* **1983,** *241,* 15. (h) Famili, A.; Farona, M. F.; Thanedar, S. *J. Chem. Soc., Chem. Commun.* **1983,** 435. (i) Parshall, G. W.; Nugent, W. A.; Chan, D. M. T.; Tam, W. *Pure Appl. Chem.* **1985,** *57,* 1809. (j) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987,** *109,* 2544.

[2] Intermolecular cross coupling reaction of alkynes on zirconcene, see (a) Takahashi, T.; Swanson, D. R.; 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.

[3] (a) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994,** *116,* 1880; (b) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988,** *110,* 2310.

[4] Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Organometallics* **1994,** *13,* 4183; see also, Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. Presented at The 67th Annual Meeting of Japan Chemical Society, 2K125, March, Tokyo, 1994.

[5] A preliminary report of this work has appeared: Takahashi, T.; Xi, Z.; Rousset, C. J.; Suzuki, N. *Chem. Lett.* **1993,** 1001.

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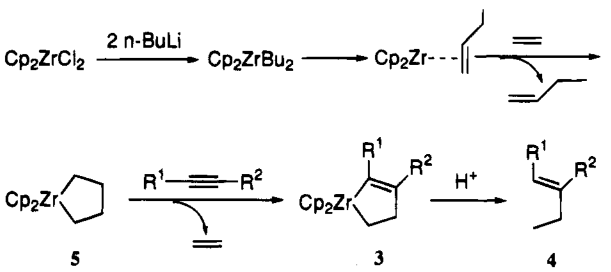
Table 1. Formation of Zirconacyclopentenes by the Reaction of Alkynes with Cp_2ZrBu_2/Ethylene Gas

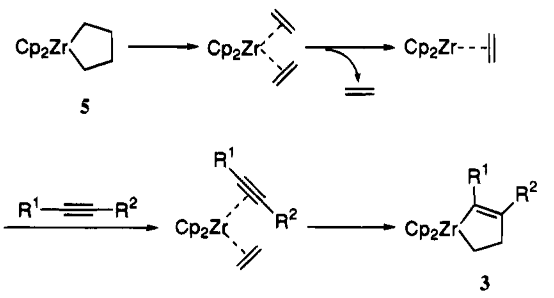
run	alkyne	product	yield, %[a]	dimer of alkyne, %
1	$BuC{\equiv}CBu$	**4a**	96	0
2	$PhC{\equiv}CPh$	**4b**	86	0
3	$PhC{\equiv}CMe$	**4c**	94	0
4	$PhC{\equiv}CBu$	**4d**	98	0
5	$Me_3SiC{\equiv}CMe$	**4e**	95[b]	0
6	$Me_3SiC{\equiv}CBu$	**4f**	92	0
7	$PhC{\equiv}CH$	**4g**	61[c]	0

[a] Yields were determined by GC after hydrolysis. [b] Two regioisomers, (*E*)-2-methyl-1-(trimethylsilyl)-1-butene and (*E*)-1-ethyl-1-(trimethylsilyl)-1-propene, were obtained in a ratio of 20:1. [c] Two regioisomers, (*E*)-1-phenyl-1-butene and 2-phenyl-1-butene, were obtained in a ratio of 1.4:1.

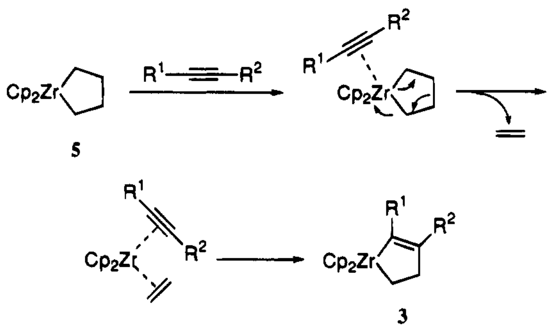
Scheme 1



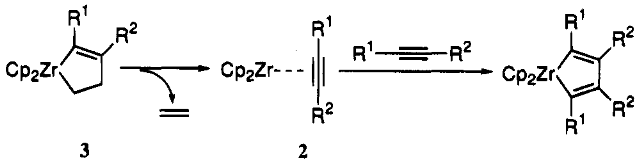
Scheme 2



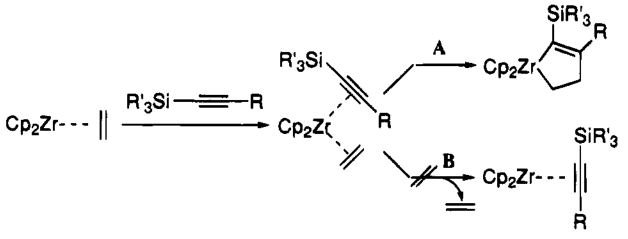
Scheme 3



Scheme 4



Scheme 5



Yields of **4** and alkyne dimers formed by this method are shown in Table 1. We have recently reported the formation of zirconacyclopentenes by the reaction of Cp_2ZrEt_2 with alkynes.[2d] However, (trimethylsilyl)alkynes did not give high yields of zirconacyclopentenes when they reacted with Cp_2ZrEt_2. The method reported here using Cp_2ZrBu_2 and ethylene gave 2-methyl-1-(trimethylsilyl)-1-butene in high yield (95%).

A plausible mechanism for this coupling reaction involves the formation of zirconacyclopentane **5** and a substitution reaction of one ethylene moiety of **5** by an alkyne (Scheme 1). In fact, when ethylene gas was introduced in a solution of Negishi reagent (Cp_2ZrBu_2), formation of **5** was observed by NMR (89% yield). Monitoring the reaction of **5** with 5-decyne at rt by NMR indicated a clean formation of **3** ($R^1 = R^2 =$ Bu) in >98% yield based on 5-decyne.

There are two possible paths from **5** to **3**, namely, dissociative path (Scheme 2) and associative path (Scheme 3). Both paths involve the elimination of one ethylene molecule. There are many reports for the dissociation of zirconacycles,[6] and it is also known that zirconacycles interact with unsaturated compounds such as aldehyde and alkyne.[7]

The complex **5** reacted with alkynes to give **3** and one ethylene molecule even under ethylene gas. The reverse reaction from **3** to **5** was not observed. Zirconacyclopentenes **3** slowly decomposed to give alkyne dimers via a zirconocene−alkyne intermediate without ethylene gas (Scheme 4). Under ethylene gas the decomposition of **3** was not observed even at 50 °C for 6 h. The complex **3** was so stable under ethylene gas that it did not react with the second alkyne. Therefore complex **3** was formed in high yield and no alkyne dimer was formed by this procedure.

Another advantage of this procedure using ethylene gas was a remarkable improvement in the case of trimethylsilylated alkynes compared with that using Cp_2ZrEt_2. Yields of zirconacyclopentenes by the reaction of silylated alkynes with Cp_2ZrEt_2 were less than 50%. This is because there is a path B (Scheme 5) where an silylated alkyne kicks out the ethylene molecule of the zirconocene−ethylene complex, in addition to the desired path A. However, under ethylene gas path B was completely suppressed. Thus (trimethylsilyl)alkynes gave high yields of zirconacyclopentenes by this method.

Several procedures have been reported so far for preparation of zirconacyclopentenes by the coupling reaction of alkenes and alkynes on zirconocenes.[2d,8,9] However, most of them involved intramolecular reaction,[9]

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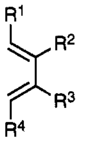
(6) For zirconacyclopentane, see: (a) Takahashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1989**, 852. (b) Takahashi, T.; Suzuki, N.; Hasegawa, M.; Nitto, Y.; Aoyagi, K.; Saburi, M. *Chem. Lett.* **1992**, 331. (c) Suzuki, N.; Aoyogi, K.; Kotora, M.; Hasegawa, M.; Nitto, Y.; Saburi, M.; Takahashi, T. *J. Organomet. Chem.* **1994**, *473*, 117.

(7) (a) Coperet, C.; Negishi, E.; Xi, Z.; Takahashi, T. *Tetrahedron Lett.* **1994**, *35*, 695. (b) Famili, A.; Farona, M. F.; Thanedar, S. *J. Chem. Soc., Chem. Commun.* **1983**, 435.

(8) (a) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281. (b) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (c) Reference 1j (d) Alt, H. G.; Denner, C. E. *J. Organomet. Chem.* **1989**, *368*, C15; **1990**, *390*, 53. (e) Fisher, R. A.; Buchwald, S. L. *Organometallics* **1990**, *9*, 871.

Table 2. Cross-Coupling Reaction of Alkynes on Zirconocene

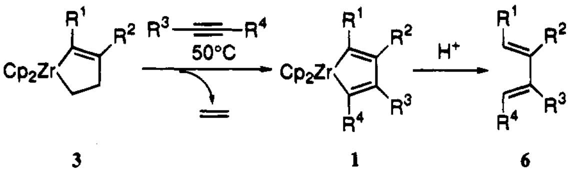


6a-g

run	1st alkyne $R^1C{\equiv}CR^2$	2nd alkyne $R^4C{\equiv}CR^3$	product	yield, %[a]	dimer of 1st alkyne, %[b]	dimer of 2nd alkyne, %[b]
1	PrC≡CPr	EtC≡CEt	**6a**	97	0	<1
2	PrC≡CPr	BuC≡CBu	**6b**	94	<1	0
3	PrC≡CPr	PhC≡CPh	**6c**	83[c]	2	0
4	PhC≡CPh	PrC≡CPr	**6c**	90	0	1
5	PrC≡CPr	PhC≡CH	**6d**	77[d]	0	0
6	$Me_3SiC{\equiv}CBu$	PhC≡CPh	**6e**	88	3	0
7	PhC≡CPh	$Me_3SiC{\equiv}CBu$	**6e**	92	1	0
8	$Me_3SiC{\equiv}CMe$	PhC≡CPh	**6f**	96	<1	0
9	PhC≡CPh	$Me_3SiC{\equiv}CMe$	**6f**	95	trace	0
10	PhC≡CPh	PhC≡CH	**6g**	93[e]	0	trace
11	PhC≡CH	PhC≡CPh	**6g**	71[f]	0	0

[a] Unless otherwise stated, yields were determined by GC after hydrolysis of the reaction mixtures. [b] Maximum yield of alkyne dimer is 50%. [c] Unreacted 2nd alkyne 5%. [d] Two isomers, (1*E*,3*E*)-3-propyl-1-phenyl-1,3-heptadiene and (3*E*)-3-propyl-2-phenyl-1,3-heptadiene were obtained in a ratio of 20:1. [e] Two isomers, (1*Z*,3*E*)-1,2,4-triphenyl-1,3-butadiene and (1*Z*)-1,2,3-triphenyl-1,3-butadiene were obtained in a ratio of 18:1. [f] Unreacted 2nd alkyne 8%, two isomers were obtained as those in run 10.

Scheme 6

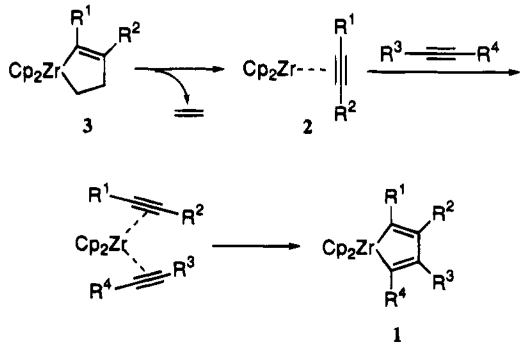


stabilization of alkene or alkyne complexes,[8] or a reaction of alkenes or alkynes prepared in situ from organozirconocenes.[2d,8b,e] The procedure we reported here involves the reaction of an alkyne with zirconacyclopentane.

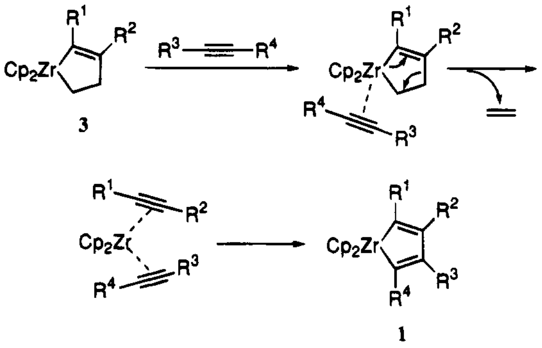
Reaction of Zirconacyclopentene with Second Alkynes to Produce Unsymmetrical Zirconacyclopentadienes. Zirconacyclopentene **3** was very stable under ethylene gas as described above. It did not react with the second alkyne even at 50 °C. However, introduction of nitrogen gas in the reaction vessel was very effective. The reaction with the second alkyne proceeded to give the cross-coupling product via the cleavage of the $C_\beta{-}C_{\beta'}$ bond with elimination of ethylene (Scheme 6).[10] The results are shown in Table 2.

We have reported the formation of zirconacyclopentadienes from zirconacyclopentenes which were prepared by the reaction of alkynes with Cp_2ZrEt_2. Yields obtained here were higher (about 10%) than those obtained from the reaction using Cp_2ZrEt_2. Yields were remarkably improved especially when a silyl-substituted alkyne was used as a first alkyne, since the zirconacyclopentene **3** was prepared in a high yield as described above. When terminal alkynes were employed, two regioisomers were obtained as generally observed for other methods.[11]

Scheme 7



Scheme 8



From **3** to **1**, there are two plausible paths, Schemes 7 and 8, although it is not clear yet which mechanism is more favorable.

Experimental Section

General. Unless otherwise noted, all starting materials were commercially available and were used without further

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(9) (a) Negishi, E.; Holms, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (c) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917. (d) Negishi, E.; Holms, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (e) Lund, E. C.; Livinghouse, T. *J. Org. Chem.* **1989**, *54*, 4487. (f) Wender, P. A.; Mcdonald, F. E. *Tetrahedron Lett.* **1990**, *31*, 3691. (g) Mori, M.; Uesaka, N.; Shibasaki, M. *J. Org. Chem.* **1992**, *57*, 3519.

(10) (a) Takahashi, T.; Suzuki, N.; Kageyama, M.; Kondakov, D. Y.; Hara, R. *Tetrahedron Lett.* **1993**, *34*, 4811. (b) Takahashi, T.; Kondakov, D. Y.; Suzuki, N. *Tetrahedron Lett.* **1993**, *34*, 6571. (c) Takahashi, T.; Kondakov, D. Y.; Suzuki, N. *Chem. Lett.* **1994**, 259. For cleavage of hafnacyclopentenes, see (d) Erker, G.; Dorf, U.; Rheingold, A. L. *Organometallics* **1988**, *7*, 138.

(11) When a terminal alkyne was used as a first alkyne, ref 2b showed a selective coupling reaction.

purification. All reactions were run under a positive pressure of dry N_2. THF was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. GLC analysis was performed on a gas chromatograph equipped with a flame ionization detector using a capillary column (CBP1-M25-025). GLC yields were determined using suitable hydrocarbons as internal standards.

A Representative Procedure for the Preparation of Zirconacyclopentenes: Synthesis of (*Z*)-5-Ethyl-5-decene (4a). A 50 mL Schlenk tube under dried nitrogen was charged with Cp_2ZrCl_2 (6 mmol, 1.75 g) and THF (30 mL). The mixture was cooled to −78 °C (dry-ice/methanol bath), and then 1.7 M *n*-BuLi (12 mmol, 7.1 mL) was added dropwise via 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 rt. The reaction mixture changed from light yellow to yellow brown. 5-Decyne (5.0 mmol, 0.90 mL) was added, and the resulting mixture was stirred for 1 h at rt under a positive pressure of ethylene gas. The cross-coupling intermediate, zirconacyclopentene (**3**: $R^1 = R^2 = Bu$) was formed in 98% yield (by NMR). The above reaction mixture was quenched with 3 N HCl and extracted with ether (3 × 70 mL). The extract was washed with water, $NaHCO_3$, brine, and water and dried over $MgSO_4$. The solvent was evaporated *in vacuo* to give a light-yellow liquid. Distillation provided the product **4a** as a colorless liquid, 0.71 g (isolated yield 85%, purity > 97%, GC yield 96%). ^1H-NMR ($CDCl_3$, Me_4Si) δ 5.09 (t, J = 7.3 Hz, 1H), 1.95−2.02 (m, 6H), 1.28−1.35 (m, 8H), 0.87−1.00 (m, 9H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 141.1 (C), 123.5 (CH), 32.5 (CH_2), 30.9 (CH_2), 30.0 (CH_2), 29.6 (CH_2), 27.4 (CH_2), 22.9 (CH_2), 22.5 (CH_2), 14.1 ($2CH_3$), 13.0 (CH_3). HRMS calcd for $C_{12}H_{24}$ 168.1878, found 168.1880.

(*Z*)-1,2-Diphenyl-1-butene (4b). Yield 86%. ^1H-NMR ($CDCl_3$, Me_4Si) δ 6.90−7.25 (m, 10H), 6.42 (s, 1H), 2.55−2.46 (dq, J = 1.3 Hz, 6.2 Hz, 2H), 1.09−1.05 (t, J = 7.3 Hz, 3H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 144.9 (C), 141.5 (C), 137.5 (C), 128.5 (2CH), 129.0 (2CH), 128.5 (2CH), 127.8 (2CH), 126.8 (CH), 126.0 (CH), 125.1 (CH), 33.5 (CH_2), 12.9 (CH_3). HRMS calcd for $C_{16}H_{16}$ 208.1252, found 208.1243. Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.54; H, 7.73.

(*E*)-2-Methyl-1-phenyl-1-butene (4c).[12] Yield 94%. ^1H-NMR ($CDCl_3$, Me_4Si) δ 7.32−7.13 (m, 5H), 6.26 (s, 1H), 2.22−2.15 (q, J = 7.3 Hz, 2H), 1.85 (s, 3H), 1.13−1.09 (t, J = 7.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 140.8 (C), 138.8 (C), 128.8 (2CH), 128.0 (2CH), 125.8 (CH), 123.6 (CH), 33.4 (CH_2), 17.7 (CH_3), 12.8 (CH_3). HRMS calcd for $C_{11}H_{14}$ 146.1096, found 146.1090.

1-Phenyl-2-ethyl-1-hexene (4d).[13] Yield 98%. ^1H-NMR ($CDCl_3$, Me_4Si) δ 7.33−7.13 (m, 5H), 6.25 (s, 1H), 2.26−2.14 (m, 4H), 1.51−1.23 (m, 4H), 1.12−1.08 (t, J = 7.3 Hz, 3H), 0.91−0.87 (t, J = 7.3 Hz, 3H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 145.3 (C), 138.8 (C), 128.7 (2CH), 128.0 (2CH), 125.8 (CH), 123.7 (CH), 30.6 (CH_2), 30.6 (CH_2), 30.0 (CH_2), 22.9 (CH_2), 14.0 (CH_3), 12.9 (CH_3). HRMS calcd for $C_{14}H_{20}$ 188.1565, found 188.1565. Anal. Calcd for $C_{14}H_{20}$: C, 89.30; H, 10.70. Found: C, 88.84; H, 10.54.

(*E*)-2-Methyl-1-(trimethylsilyl)-1-butene (4e). Yield 95%. ^1H-NMR ($CDCl_3$, Me_4Si) δ 5.18 (s, 1H), 2.13−2.10 (q, J = 6.3 Hz, 2H), 1.78 (s, 3H), 1.04−0.99 (t, J = 7.3 Hz, 3H), 0.10 (s, 9H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 157.0 (C), 121.1 (CH), 34.9 (CH_2), 21.6 (CH_3), 12.4 (CH_3), 0.1 ($3CH_3$). HRMS calcd for $C_8H_{18}Si$ 142.1178, found 142.1181.

(*E*)-2-Butyl-1-(trimethylsilyl)-1-butene (4f). Yield 92%. ^1H-NMR ($CDCl_3$, Me_4Si) δ 5.17 (s, 1H), 2.16−2.05 (m, 4H), 1.36−1.33 (m, 4H), 1.04−0.98 (t, J = 7.3 Hz, 3H), 0.95−0.90 (t, J = 6.9 Hz, 3H), 0.10 (s, 9H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 161.7 (C), 121.0 (CH), 36.2 (CH_2), 31.5 (CH_2), 31.3 (CH_2), 23.0 (CH_2), 14.1 (CH_3), 12.6 (CH_3), 0.5 ($3CH_3$). HRMS calcd for $C_{11}H_{24}Si$ 184.1647, found 184.1651.

(*E*)-1-Phenyl-1-butene/2-Phenyl-1-butene (4g).[14] Two regioisomers, (*E*)-1-phenyl-1-butene and 2-phenyl-1-butene were obtained in a ratio of 1.4:1. Yield (combined) 61%. ^1H-NMR ($CDCl_3$, Me_4Si) δ 7.42−7.13 (m, 10H), 6.40−6.20 (m, 2H), 5.27 (s, 1H), 5.05 (s, 1H), 2.55−2.46 (m, 2H), 2.26−2.16 (m, 2H), 1.12−1.07 (m, 6H). ^{13}C-NMR ($CDCl_3$, Me_4Si) for (*E*)-1-phenyl-1-butene: δ 138.0 (C), 132.6 (CH), 128.5 (2CH), 128.2 (CH), 126.8 (CH), 125.9 (2CH), 26.1 (CH_2), 13.7 (CH_3); for 2-phenyl-1-butene: δ 150.1 (C), 141.6 (C), 128.8 (2CH), 127.3 (CH), 126.0 (2CH), 110.9 (CH_2), 28.1 (CH_2), 13.0 (CH_3). HRMS calcd for $C_{10}H_{12}$ 132.0939, found 132.0934.

Observation of Formation of 5 by NMR. When the ethylene gas was introduced in the reaction mixture of Cp_2ZrCl_2 and 2 equiv of n-BuLi as described in a representative procedure for the preparation of **4a**, the mixture was checked by NMR at rt. Compound **5** was formed in 89% yield. ^{13}C NMR (C_6D_6−THF, Me_4Si) δ 111.4 (2Cp), 40.3 ($2CH_2$), 29.3 ($2CH_2$).

Observation of Formation of 3 from 5 by NMR. Compound **5** was prepared as described above using 1.2 mmol of Cp_2ZrCl_2 and 2.4 mmol of n-BuLi. To this solution was added 1.0 mmol of 5-decyne at rt. Compound **3** ($R^1 = R^2 = Bu$) was formed in >98% yield based on 5-decyne. ^{13}C NMR (C_6D_6−THF, Me_4Si) δ 184.4 (C), 140.1 (C), 110.9 (2Cp), 40.1 (CH_2), 36.9 (CH_2), 35.1 (CH_2), 34.0 (CH_2), 31.1 (CH_2), 28.3 (CH_2), 24.0 (CH_2), 23.4 (CH_2), 14.3 (CH_3), 14.2 (CH_3).

A Representative Procedure for Preparation of Zirconacyclopentadienes: Synthesis of (3*E*,5*E*)-4-Ethyl-5-propyl-3,5-nonene (6a). A yellow-brown homogeneous THF solution of zirconacyclopentene (**3**: $R^1 = R^2 = Pr$) was prepared *in situ* as described above using 5.0 mmol of 4-octyne. After 3-hexyne (5.0 mmol, 0.57 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. The cross-coupling intermediate, zirconacyclopentadiene (**1**: $R^1 = R^2 = Pr$, $R^3 = R^4 = Et$) was formed in 98% yield (by NMR). The above reaction mixture was quenched with 3 N HCl and extracted with ether (3 × 70 mL). The extract was washed with water, $NaHCO_3$, brine, and water and was dried over $MgSO_4$. The solvent was evaporated *in vacuo* to give a light brown liquid. Distillation provided the product **6a** as a colorless liquid (0.80 g; isolated yield 82%, purity > 97%, GC yield 94%). ^1H-NMR ($CDCl_3$, Me_4Si) δ 5.30−5.40 (m, 2H), 2.02−2.23 (m, 8H), 1.27−1.45 (m, 4H), 0.85−1.05 (m, 12H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 142.2 (C), 140.7 (C), 127.0 (CH), 126.1 (CH), 30.4 (CH_2), 30.1 (CH_2), 23.3 (CH_2), 22.2 (CH_2), 21.4 (CH_2), 21.1 (CH_2), 14.7 (CH_3), 14.2 (CH_3), 14.0 (CH_3), 13.8 (CH_3). HRMS calcd for $C_{14}H_{26}$ 194.2035, found 194.2036.

(4*E*,6*E*)-5-Propyl-6-butyl-4,6-undecene (6b). Yield 94%. ^1H-NMR ($CDCl_3$, Me_4Si) δ 5.30−5.38 (m, 2H), 2.00−2.18 (m, 8H), 1.20−1.44 (m, 12H), 0.85−0.95 (m, 12H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 141.4 (2C), 126.0 (2CH), 32.4 (CH_2), 31.2 (CH_2), 30.4 (CH_2), 30.1 (CH_2), 28.0 (CH_2), 27.8 (CH_2), 23.3 (CH_2), 22.8 (CH_2), 22.6 (CH_2), 22.1 (CH_2), 14.1 ($2CH_3$), 13.9 ($2CH_3$). HRMS calcd for $C_{18}H_{34}$ 250.2661, found 250.2657.

(1*Z*,3*E*)-1,2-Diphenyl-3-propyl-1,3-heptadiene (6c). First alkyne: diphenylacetylene, second alkyne: 4-octyne; yield 90%. However, when the first alkyne was 4-octyne (1.0 mmol, 0.15 mL) and the second alkyne was diphenylacetylene (1.0 mmol, 0.18 g), the title compound was obtained in 83% yield, along with 5% of the unreacted second alkyne. ^1H-NMR ($CDCl_3$, Me_4Si) δ 6.84−7.25 (m, 10H), 6.62 (s, 1H), 5.39−5.35 (t, J = 7.3 Hz, 1H), 2.28−2.24 (t, J = 7.3 Hz, 2H), 2.12−2.09 (m, 2H), 1.49−1.47 (m, 2H), 1.37−1.34 (m, 2H), 0.96−0.91 (t, J = 7.3 Hz, 3H), 0.90−0.87 (t, J = 7.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 144.9 (C), 142.7 (C), 140.3 (C), 137.8 (C), 132.2 (CH), 130.0 (2CH), 129.4 (2CH), 128.3 (2CH), 127.7 (2CH), 126.9 (CH), 126.1 (CH), 125.4 (CH), 30.7 (CH_2), 30.1 (CH_2), 22.9 (CH_2), 22.1 (CH_2), 14.1 (CH_3), 13.9 (CH_3). HRMS calcd for $C_{22}H_{26}$ 290.2035, found 290.2037.

(1*E*,3*E*)-3-Propyl-1-phenyl-1,3-heptadiene (6d). Two regioisomers, (1*E*,3*E*)-3-Propyl-1-phenyl-1,3-heptadiene and (3*E*)-

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[12] Mitchell, T. N.; Amamria, A. *J. Organomet. Chem.* **1983**, *252*, 47.

[13] Commercon, A.; Normant, J. F.; Villieras, J. *J. Organomet. Chem.* **1977**, *128*, 1.

[14] (a) Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915. (b) Angeletti, E.; Tundo, P.; Venturello, J. *Chem. Soc., Chem. Commun.* **1983**, *6*, 269.

3-propyl-2-phenyl-1,3-heptadiene, were obtained in a ratio of 20:1. Yield (combined) 77%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 7.20–7.39 (m, 5H), 6.70 (d, J = 16.5 Hz, 1H), 6.43 (d, J = 16.5 Hz, 1H), 5.62–5.58 (t, J = 7.3 Hz, 1H), 2.29–2.30 (t, J = 7.6 Hz, 2H), 2.17–2.23 (q, J = 7.3 Hz, 2H), 1.26–1.56 (m, 4H), 0.91–0.99 (m, 6H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 138.4 (C), 138.1 (C), 134.4 (CH), 133.1 (CH), 128.5 (2CH), 126.6 (CH), 126.1 (2CH), 125.2 (CH), 30.6 (CH_2), 28.8 (CH_2), 23.0 (CH_2), 22.3 (CH_2), 14.3 (CH_3), 14.0 (CH_3). HRMS calcd for $C_{16}H_{22}$ 214.1722, found 214.1727.

(1*E*,3*Z*)-2-Butyl–3,4-diphenyl-1-(trimethylsilyl)-1,3-butadiene (6e). Diphenylacetylene (5 mmol, 0.89 g) as the first alkyne and 1-(trimethylsilyl)-1-hexyne as the second alkyne (5 mmol, 1.01 mL). Yield 92%. However, when 1-(trimethylsilyl)-1-hexyne (1 mmol, 0.20 mL) was used as the first alkyne and diphenylacetylene (1 mmol, 0.18 g) as the second alkyne, the title compound was obtained in 88% yield. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 7.33–6.91 (m, 10H), 6.76 (s, 1H), 5.50 (s, 1H), 2.45–2.39 (t, J = 7.6 Hz, 2H), 1.58–1.36 (m, 4H), 0.98–0.94 (t, J = 7.3 Hz, 3H), 0.18 (s, 9H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 159.9 (C), 145.8 (C), 140.0 (C), 137.5 (C), 130.3 (CH), 130.0 (2CH), 129.6 (2CH), 128.4 (2CH), 127.8 (2CH), 127.0 (CH), 126.8 (CH), 126.4 (CH), 33.6 (CH_2), 32.0 (CH_2), 23.0 (CH_2), 14.1 (CH_3), 0.3 ($3CH_3$). HRMS calcd for $C_{23}H_{30}Si$ 334.2117, found 334.2124. Anal. Calcd for $C_{23}H_{30}Si$: C, 82.57; H. 9.04. Found: C, 82.72; H, 8.95.

(1*E*,3*Z*)-2-Methyl-3,4-diphenyl-1-(trimethylsilyl)-1,3-butadiene (6f). Diphenylacetylene (5 mmol, 0.89 g) as the first alkyne and 1-(trimethylsilyl)propyne as the second alkyne (5 mmol, 0.74 mL). Yield 95%. However, when 1-(trimethylsilyl)propyne (1 mmol, 0.15 mL) was used as the first alkyne and diphenylacetylene (1 mmol, 0.18 g) as the second alkyne, the title compound was obtained in 96% yield. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 7.00–7.52 (m, 11H), 5.64 (s, 1H), 2.37 (s, 3H), 0.35 (s, 9H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 153.2 (C), 146.2 (C), 139.9 (C), 137.4 (C), 131.6 (CH), 130.1 (2CH), 129.6 (2CH), 128.4 (2CH), 127.8 (2CH), 127.0 (CH), 126.8 (CH), 126.5 (CH), 20.2 (CH_3), 0.1 ($3CH_3$). HRMS calcd for $C_{20}H_{24}Si$ 292.1647, found 292.1652.

(1*Z*,3*E*)-1,2,4-Triphenyl-1,3-butadiene (6g).[15] Diphenylacetylene (5 mmol, 0.89 g) as the first alkyne, and phenylacetylene as the second alkyne (5 mmol, 0.55 mL). Two regioisomers, (1*Z*,3*E*)-1,2,4-Triphenyl-1,3-butadiene and (1*Z*)-1,2,3-Triphenyl-1,3-butadiene were obtained in a ratio of 18:1. Yield (combined) 93%. However, when phenylacetylene (1 mmol, 0.11 mL) was used as the first alkyne and diphenylacetylene (1 mmol, 0.18 g) as the second, the title compound was obtained in 71% yield. Major product. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 6.85–7.40 (m, 16H), 6.68 (s, 1H), 6.15 (d, J = 15.8 Hz, 1H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 141.6 (C), 138.3 (C), 137.3 (C), 136.8 (C), 134.2 (CH), 131.9 (CH), 131.2 (CH), 129.5 (2CH), 129.3 (2CH), 128.9 (2CH), 128.5 (2CH), 127.9 (2CH), 127.4 (CH), 127.4 (CH), 126.8 (CH), 126.4 (2CH). HRMS calcd for $C_{22}H_{18}$ 282.1409, found 282.1396.

Acknowledgment. We thank the Japanese Ministry of Education, Science and Culture for support of this study. We also thank Prof. Negishi for his useful information and discussion.

Supporting Information Available: Copies of ^{13}C NMR spectra of **4a–g** and **6a–g** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9416168

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[15] Shur, V. B.; Burlakov, V. V.; Vol'in, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, *8*, 1929; *Chem. Abstr.* **1984**, *100*, 6742y.