

# Reaction of Zirconocene Ethylene Complex with Diynes. Formation of Bridged Zirconacyclopentenes

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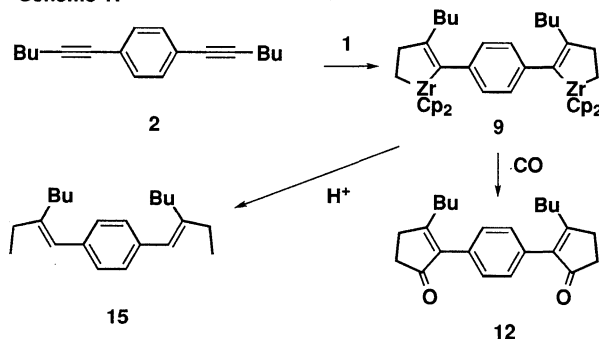
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Reactions of diynes  $\text{RCC-X-CCR}$  with zirconocene ethylene complex  $\text{Cp}_2\text{Zr}(\text{CH}_2=\text{CH}_2)$  were investigated. When X was  $\text{C}_6\text{H}_4$  or  $\text{C}_4\text{H}_2\text{S}$ , bridged zirconacyclopentenes were selectively formed. They were easily converted into bridged cyclopentenone derivatives. In the case of  $(\text{CH}_2)_n$  groups as X, the reaction products were strongly dependent on the R group.

Recently we have reported a selective and convenient intermolecular coupling reaction of ethylene with alkynes giving zirconacyclopentenes.<sup>1</sup> Zirconacyclopentenes could be converted into functionalized compounds such as cyclopentenones,<sup>1a,2</sup> heterocycles<sup>3</sup> and other zirconacycles.<sup>1a,c</sup> However, preparation of bridged compounds from the two functionalized products is rather difficult. For example,  $\alpha,\alpha'$ -bridged cyclopentenones are difficult to prepare from two cyclopentenones, since the substitution reaction method at the  $\alpha$ -carbon is limited.<sup>4</sup> In this sense bridged zirconacyclopentenes are very attractive, because these are easily converted into bridged functionalized compounds. However, formation of bridged zirconacyclopentenes has not been reported. One of the major reason is that the alkyne-alkyne coupling reaction is usually much faster than the intermolecular alkyne-alkene coupling on reduced zirconocene compounds. In this paper we would like to report the reaction of  $\text{Cp}_2\text{Zr}(\text{CH}_2=\text{CH}_2)$  **1** with diynes such as  $\text{RCC-X-CCR}$  (**2**: R = *n*-Bu, X = 1,4- $\text{C}_6\text{H}_4$ ; **3**: R = *n*-Bu, X = 1,3- $\text{C}_6\text{H}_4$ ; **4**: R = *n*-Bu, X = 2,5- $\text{C}_4\text{H}_2\text{S}$ ; **5a-d**: R = Me, X =  $(\text{CH}_2)_n$  (*n* = 3 - 6); **6a-d**: R = *t*-Bu, X =  $(\text{CH}_2)_n$  (*n* = 3 - 6); **7a-d**: R = Ph, X =  $(\text{CH}_2)_n$  (*n* = 3 - 6); **8a-d**: R =  $\text{Me}_3\text{Si}$ , X =  $(\text{CH}_2)_n$  (*n* = 3 - 6)). Bridged zirconacyclopentenes **9-11** were selectively formed by the reaction of **2-4** with **1**, respectively. They were easily converted into  $\alpha,\alpha'$ -bridged cyclopentenones **12-14** in high yields. We also report the reaction of non-conjugated diynes **5-8** with **1** where the reaction products were strongly dependent on the R group.

Scheme 1.



Typical procedure is as follows. To a mixture of  $\text{Cp}_2\text{ZrCl}_2$  (2.4 mmol, 0.70 g) and 2 equiv of  $\text{EtMgBr}$  (4.8 mmol, 1.0 mmol/dm<sup>3</sup>, 4.8 cm<sup>3</sup>) in 10 ml of THF at -78 °C was added 1.0

mmol of 1,4-bis(hexynyl)benzene (**2**, 0.24 g). The mixture was warmed up to 0 °C and was stirred for 3 h at 0 °C. A bridged zirconacyclopentene compound **9** was formed in 84% yield.

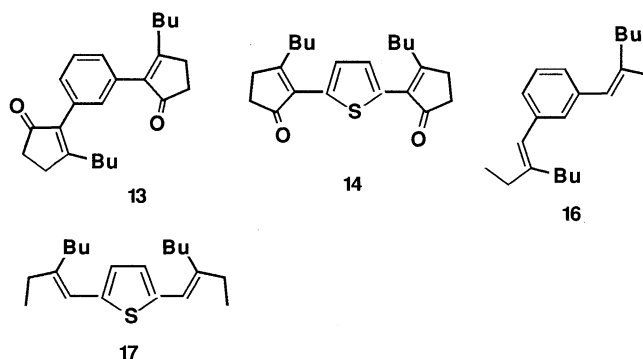
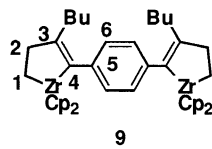
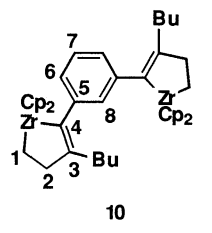
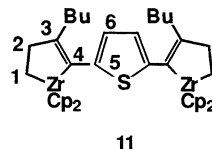
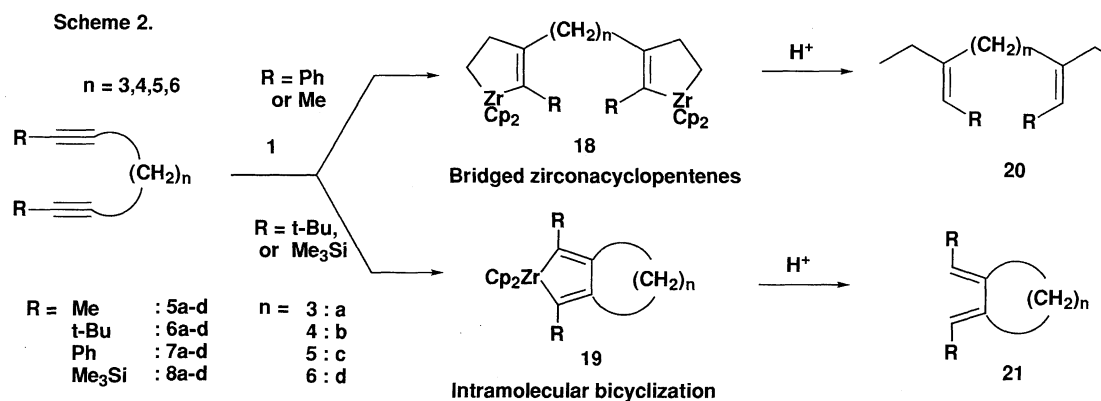


Table 1. Comparison of <sup>13</sup>C NMR data for bridged zirconacyclopentenes **9-11**, bridged cyclopentenones **12-14**, and hydrolysis products **15-17**

Bridged zirconacyclopentenes	Yield /% <sup>a</sup>	<sup>13</sup> C NMR data <sup>b</sup>			
		9 <sup>c</sup>	12 <sup>d</sup>	15	
	84	C1	41.32	34.73	12.92
		C2	30.86	29.11	30.17
		C3	144.57	176.24	145.08
		C4	185.38	131.25	123.57
		C=O	-	207.92	-
		C5	144.66	140.02	136.26
		C6	125.74	129.00	128.34
		10 <sup>c</sup>	13 <sup>d</sup>	16	
	81	C1	41.44	34.72	12.90
		C2	30.89	29.13	29.94
		C3	144.04	176.12	145.10
		C4	185.60	131.89	123.84
		C=O	-	207.80	-
		C5	149.90	140.14	138.49
		C6	120.47	128.34	126.13
		C7	127.81	128.16	127.69
		C8	123.11	130.06	129.16
		11 <sup>c</sup>	14 <sup>d</sup>	17	
	76	C1	40.92	34.56	12.94
		C2	32.24	29.89	31.03
		C3	149.13	174.64	143.99
		C4	172.99	132.67	117.23
		C=O	-	206.74	-
		C5	147.72	132.88	139.85
		C6	119.37	126.86	125.91

<sup>a</sup>NMR yields. <sup>b</sup>*n*-Butyl groups were omitted. <sup>c</sup>Assignment for C3 and C5 was not clear. <sup>d</sup>Assignment for C4 and C5 was not clear.



**Table 2.** Reaction of Diynes  $\text{RCC}(\text{CH}_2)_n\text{CCR}$  with  $\text{Cp}_2\text{ZrEt}_2^a$

n	R	Yield of <b>20</b> /%	Yield of <b>21</b> /%
3	Me	89 (65) <sup>b</sup>	0
4	Me	71 (68) <sup>b</sup>	0
5	Me	92 (74) <sup>b</sup>	0
6	Me	92 (71) <sup>b</sup>	0
3	<i>t</i> Bu	trace	77(58)
4	<i>t</i> Bu	0	95(62)
5	<i>t</i> Bu	0	90(68)
6	<i>t</i> Bu	25	10
3	Ph	90 (74)	3
4	Ph	95 (70)	trace
5	Ph	89 (71)	2
6	Ph	93 (73)	trace
3	Me <sub>3</sub> Si	0	81 (67)
4	Me <sub>3</sub> Si	0	87 (71)
5	Me <sub>3</sub> Si	5	83 (61)
6	Me <sub>3</sub> Si	10	20

<sup>a</sup>All reactions were carried out at 0°C. Yields were based on diynes. Isolated yields were given in the parentheses.

<sup>b</sup>Combined yield of three isomers.

Hydrolysis of the mixture gave **15** in 69% yield. Treatment of the reaction mixture containing **9** with CO gas at -78 °C followed by the treatment with iodine gave  $\alpha, \alpha'$ -bridged cyclopentenone **12** in 73% yield.

It is noteworthy that NMR spectrum of **9 - 11** showed the selective formation of bridged zirconacyclopentenes. Their <sup>13</sup>C NMR data are summarized in Table 1. Hydrolysis of **9 - 11** afforded **15 - 17** in 69%, 62%, and 76% yields respectively.

The bridging groups X (aromatic groups) were in the  $\alpha$ -position of both zirconacyclopentene rings of **9 - 11**, judging from the NMR spectra of hydrolysis products **15 - 17**. This regioselectivity is consistent with that observed before.<sup>1</sup> These zirconacyclopentenes **9 - 11** were converted into bridged cyclopentenones **12 - 14** in 73%, 80%, and 86% yields, respectively. Since the C-C bond formation method at  $\alpha$ -carbon of cyclopentenone is limited,<sup>4</sup> selective formation of  $\alpha, \alpha'$ -bridged cyclopentenones by this method is very attractive.

It is well known that the non-conjugated diynes **5a - c**, **6a - c**, **7a - c**, **8a - c** reacts with a low valent zirconocene species

prepared from  $\text{Cp}_2\text{ZrCl}_2$  and metal amalgam<sup>6</sup> or Negishi reagent ( $\text{Cp}_2\text{ZrCl}_2 + 2\text{BuLi}$ )<sup>7</sup> to give cleanly the intramolecular cyclization products. However, the reaction of non-conjugated diynes such as **5a - d** and **7a - d** with  $\text{Cp}_2\text{Zr}(\text{CH}_2=\text{CH}_2)$  **1** afforded bridged zirconacyclopentenes **18** selectively<sup>1</sup> because the ethylene on zirconocene was not so labile and therefore the intermolecular coupling between an ethylene and an alkyne of diynes overcomes the intramolecular cyclization of diynes **5a - d** and **7a - d**. In contrast, **6a - c** or **8a - c** gave **19** as shown in Scheme 2 and Table 2.

Thus the reaction products were strongly dependent on R group of diynes. Phenyl substituted diynes **7a - d** gave regioselectively bridged zirconacyclopentenes. In the case of methyl group, three regioisomers were formed as we expected.

## References and Notes

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