

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

Tamotsu Takahashi,* Kayoko Kasai, Zhenfeng Xi, and Victor Denisov

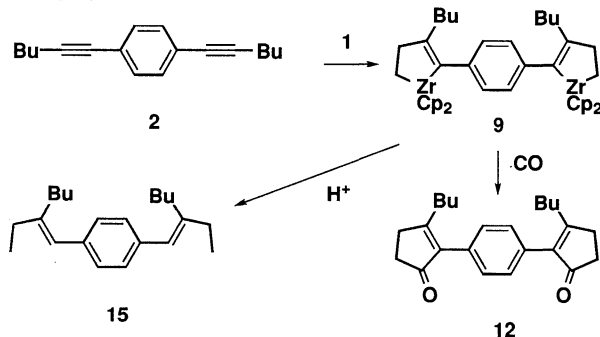
Coordination Chemistry Laboratories, Institute for Molecular Science and the Graduate University for Advanced Studies, Myodaiji, Okazaki 444

(Received February 3, 1995)

Reactions of diynes RCC-X-CCR with zirconocene ethylene complex $\text{Cp}_2\text{Zr}(\text{CH}_2=\text{CH}_2)$ were investigated. When X was C_6H_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.¹ Zirconacyclopentenes could be converted into functionalized compounds such as cyclopentenones,^{1a,2} heterocycles³ and other zirconacycles.^{1a,c} However, preparation of bridged compounds from the two functionalized products is rather difficult. For example, α,α' -bridged cyclopentenones are difficult to prepare from two cyclopentenones, since the substitution reaction method at the α -carbon is limited.⁴ 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**⁵ with diynes such as RCC-X-CCR (**2**: R = *n*-Bu, X = 1,4- C_6H_4 ; **3**: R = *n*-Bu, X = 1,3- C_6H_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 = Me_3Si , 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 α,α' -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 Cp_2ZrCl_2 (2.4 mmol, 0.70 g) and 2 equiv of EtMgBr (4.8 mmol, 1.0 mmol/dm³, 4.8 cm³) 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.

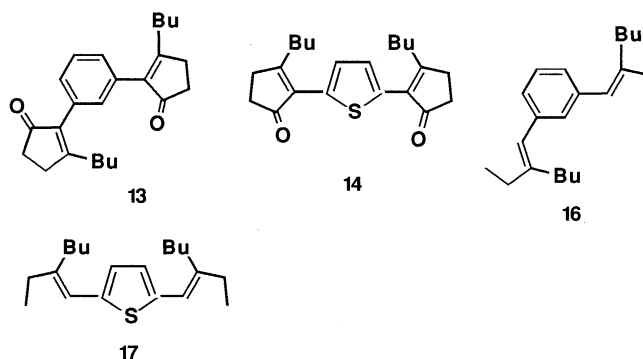


Table 1. Comparison of ¹³C NMR data for bridged zirconacyclopentenes **9-11**, bridged cyclopentenones **12-14**, and hydrolysis products **15-17**

Bridged zirconacyclopentenes	Yield /% ^a	¹³ C NMR data ^b			
		9 ^c	12 ^d	15	
 9	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	81	10 ^c	13 ^d	16	
		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	76	11 ^c	14 ^d	17	
		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		

^aNMR yields. ^b*n*-Butyl groups were omitted. ^cAssignment for C3 and C5 was not clear. ^dAssignment for C4 and C5 was not clear.

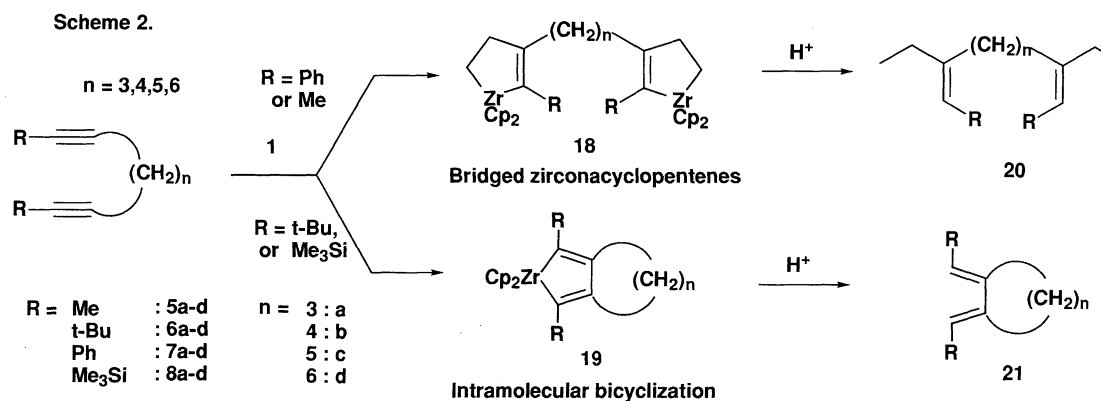


Table 2. Reaction of Diynes $\text{RCC}(\text{CH}_2)_n\text{CCR}$ with $\text{Cp}_2\text{ZrEt}_2^a$

n	R	Yield of 20 /%	Yield of 21 /%
3	Me	89 (65) ^b	0
4	Me	71 (68) ^b	0
5	Me	92 (74) ^b	0
6	Me	92 (71) ^b	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 ₃ Si	0	81 (67)
4	Me ₃ Si	0	87 (71)
5	Me ₃ Si	5	83 (61)
6	Me ₃ Si	10	20

^aAll reactions were carried out at 0°C. Yields were based on diynes. Isolated yields were given in the parentheses.

^bCombined 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 α, α' -bridged cyclopentenone **12** in 73% yield.

It is noteworthy that NMR spectrum of **9 - 11** showed the selective formation of bridged zirconacyclopentenes. Their ¹³C 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 α -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.¹ 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 α -carbon of cyclopentenone is limited,⁴ selective formation of α, α' -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 Cp_2ZrCl_2 and metal amalgam⁶ or Negishi reagent ($\text{Cp}_2\text{ZrCl}_2 + 2\text{BuLi}$)⁷ 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** selectively¹ 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

- 1 a) T. Takahashi, M. Kageyama, V. Denisov, R. Hara, and E. Negishi, *Tetrahedron Lett.*, **34**, 687 (1993); b) T. Takahashi, Z. Xi, C. J. Rousset, and N. Suzuki, *Chem. Lett.*, **1993**, 1001 and references therein; c) Z. Xi, R. Hara, and T. Takahashi, *J. Org. Chem.*, submitted.
- 2 E. Negishi, "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), Vol. 5, p 1163 and references therein.; M. Mori, N. Uesaka, and M. Shibasaki, *J. Org. Chem.*, **57**, 3519 (1992); G. Agnel, Z. Owczarczyk, and E. Negishi, *Tetrahedron Lett.*, **33**, 1543 (1992); G. Agnel and E. Negishi, *J. Am. Chem. Soc.*, **113**, 7424 (1991).
- 3 P. J. Fagan and W. A. Nugent, *J. Am. Chem. Soc.*, **110**, 2310 (1988); P. J. Fagan, W. A. Nugent, and J. C. Calabrese, *J. Am. Chem. Soc.*, **116**, 1880 (1994); T. V. RajanBabu, W. A. Nugent, D. F. Tabor, and P. J. Fagan, *J. Am. Chem. Soc.*, **110**, 7128 (1988).
- 4 E. Negishi and K. Akiyoshi, *Chem. Lett.*, **1987**, 1007. Recently an α, α' -bridged cyclopentenone has been prepared by Pauson Khand reaction using Co.; See B. Y. Lee, Y. K. Chung, N. Jeong, Y. Lee, and S. H. Hwang, *J. Am. Chem. Soc.*, **116**, 8793 (1994).
- 5 T. Takahashi, N. Suzuki, M. Kageyama, Y. Nitto, M. Saburi, and E. Negishi, *Chem. Lett.*, **1991**, 1579.
- 6 E. Negishi, S. J. Holmes, J. M. Tour, and J. A. Miller, *J. Am. Chem. Soc.*, **107**, 2568 (1985); W. A. Nugget, D. L. Thorn, and R. L. Harlow, *J. Am. Chem. Soc.*, **109**, 2788 (1987). See also, S. Thanedar and M. F. Faron, *J. Organomet. Chem.*, **235**, 65 (1982).
- 7 E. Negishi, F. E. Cederbaum, and T. Takahashi, *Tetrahedron Lett.*, **27**, 2829 (1986).