Reductive elimination of α-alkynyl substituted zirconacyclopentenes: formation of cyclobutene derivatives

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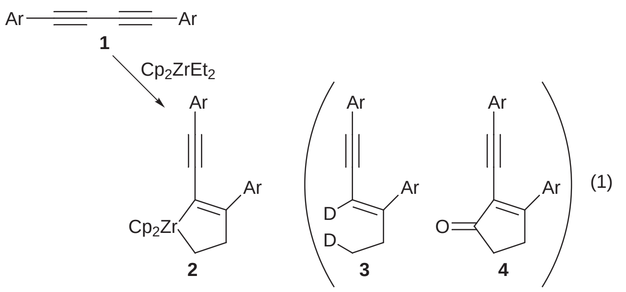
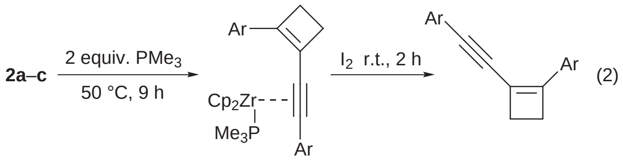
Reductive elimination of α-alkynyl substituted zirconacyclopentenes, prepared from diaryldiynes and Cp_2ZrEt_2, proceeded upon heating or in the presence of dimethyl acetylenedicarboxylate to give alkynylcyclobutene derivatives.

Reductive elimination of two organic groups on metals is a basic reaction step for making new C–C bonds.[1] Although this step has been intensively investigated for late transition metal compounds, it has not been well studied for early transition metal compounds such as zirconium. To the best of our knowledge, only a few reductive couplings of two organic groups of organozirconium compounds have been reported, such as photolysis or oxidation of diphenylzirconocene producing biphenyl,[2] CO insertion into organozirconocenes or zirconacycles followed by migration giving ketone derivatives,[3] or an alkynyl–phenyl coupling *via* ate-complexation.[4] Here we report that the reductive coupling of α-alkynyl substituted zirconacyclopentenes, prepared by the reaction of diaryldiynes with Cp_2ZrEt_2, proceeded upon heating or in the presence of additives such as dimethyl acetylenedicarboxylate to give alkynylcyclobutene derivatives.

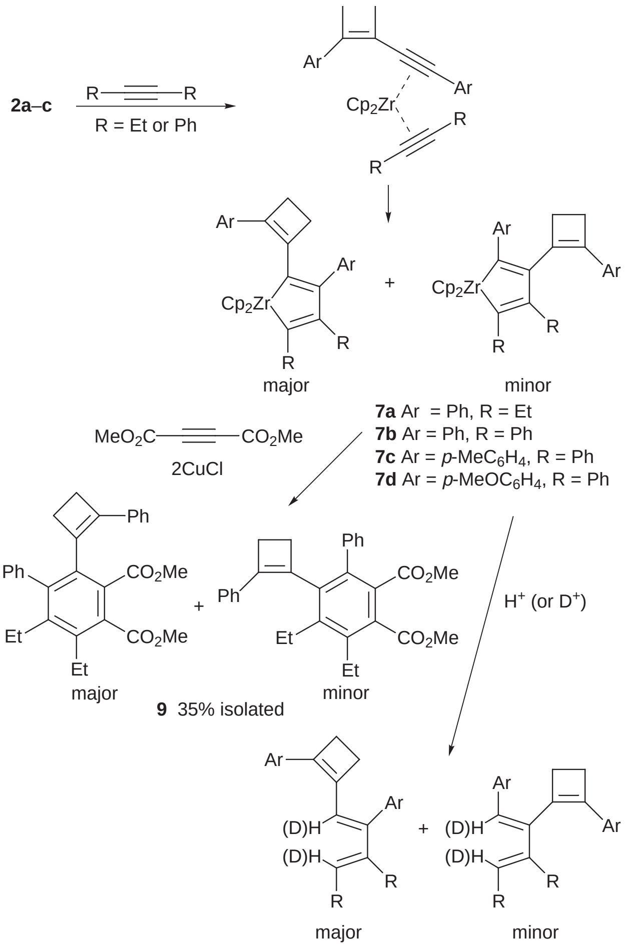


We have already reported that a reaction of diynes with $Cp_2Zr(CH_2{=}CH_2)$ *in situ* prepared from Cp_2ZrEt_2 afforded α-alkynylzirconacyclopentenes (**2**) which gave a dideuterated enyne **3** after deuterolysis [5] and α-alkynylcyclopentenones **4** by treatment with CO/I_2 [reaction (1)].[6] Here we find that, upon heating **2a**–**c** in THF at 50 °C for 9 h in the presence of 2 equiv. of PMe_3, a reductive elimination reaction of **2a**–**c** proceeds to afford the complexes **5a**–**c** in 61–86% NMR yields. Treatment of **5a**–**c** with an excess of I_2 produced alkynylcyclobutenes **6a**–**c** in 70–84% NMR yields based on diynes [reaction (2)]. This indicates that reductive elimination of **2a**–**c** took place to give cyclobutene derivatives. The Cp_2Zr^{II} species formed by the reductive elimination were trapped as alkyne complexes stabilized by PMe_3 and **6a**–**c** to give **5a**–**c**.[7]‡ This is the first example of the direct formation of cyclobutene derivatives from zirconacyclopentenes, to the best of our knowledge.[8]



2a Ar = Ph	**5a** 86%	**6a** 84% (70% isolated)
2b Ar = p-MeC_6H_4	**5b** 82%	**6b** 83% (72%)
2c Ar = p-$MeOC_6H_4$	**5c** 61%	**6c** 70% (62%)
	(NMR yield)	

In the presence of 1 equiv. of hex-3-yne instead of PMe_3, zirconacyclopentadienes **7a**–**d** were formed.[9] After hydrolysis of **7a**–**d**, cyclobutenyldienes **8a**–**d** were obtained in 74–85% yields as mixtures of two regioisomers in a ratio of 3 : 1 as expected (Scheme 1). Deuterolysis of **7a** instead of hydrolysis afforded a dideuterated product with > 98% deuterium incorporation. The zirconacyclopentadiene **7a** was further converted into benzene derivatives **9** as a mixture of two



7a Ar = Ph, R = Et
7b Ar = Ph, R = Ph
7c Ar = p-MeC_6H_4, R = Ph
7d Ar = p-$MeOC_6H_4$, R = Ph

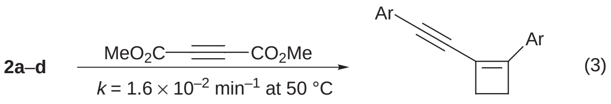
9 35% isolated

8a 74% (65% isolated) (3:1)
8b 80% (73%) (9:1)
8c 76% (75%) (11:1)
8d 85% (72%) (14:1)

Scheme 1

regioisomers by the reaction with dimethyl acetylenedicarboxylate by our method.[10] The structure of minor isomer **9** was determined by X-ray analysis.§

Addition of dimethyl acetylenedicarboxylate to **2a–d** induced the direct formation of free **6a–d** in 64, 63, 62 and 69% NMR yields, respectively [reaction (3)]. Although the zirconium species trapped by dimethyl acetylenedicarboxylate was not clearly detected in this reaction, NMR study of this reaction revealed that the cyclobutene formation from **2a** at 50 °C obeys the first order rule and the reaction rate was 1.6×10^{-2} min^{-1}. This indicates that the presence of dimethyl acetylenedicarboxylate does not cause the reductive elimination. Dimethyl acetylenecarboxylate liberates **6** from zirconium.

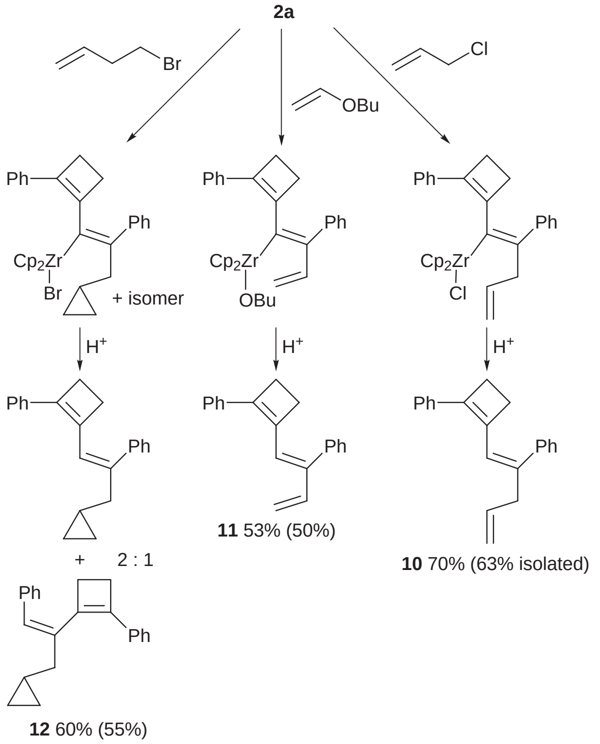


(3)

2d Ar = *o*-MeOC$_6$H$_4$

6a 64% (62% isolated)
6b 63% (59%)
6c 62% (62%)
6d 69% (63%)

Note that the cyclobutene formation was also induced by the reaction of **2a** with allyl chloride,[11] vinyl butyl ether,[12] and a homoallyl bromide[13] as shown in Scheme 2. Hydrolysis of these reaction mixtures gave the corresponding products **10–12** in 70, 53 and 60% yields, respectively.



Scheme 2

Notes and References

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‡ *NMR data* for **5a**: δ_H(C$_6$D$_6$ 1.18 (d, *J* 6.2, 9 H), 2.65 (br, 2 H), 2.79 (br, 2 H), 5.54 (br, 10 H), 6.92–7.66 (m, 10 H); δ_C(C$_6$D$_6$) 17.12(d), 25.89, 29.97, 102.91, 124.46, 124.74, 125.83, 126.08, 128.08, 128.50, 129.79, 138.62, 142.68, 154.39, 156.04(d), 178.77(d).

§ *Crystal data* for **9** (minor isomer): $C_{30}H_{30}O_4$, M = 454.57, monoclinic, space group $P2_1/n$ (no. 14), a = 7.0458(3), b = 20.7179(6), c = 17.3291(8) Å, β = 94.627(6)°, U = 2521.4(2) Å^3, Z = 4, D_c = 1.20 g cm^{-3}, μ(Cu-Kα) = 5.9 cm^{-1}, 5565 measured reflections, 3950 reflections with $I > 3\sigma(I)$, R = 0.046. CCDC 182/826.

1 J. P. Collman, L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1980.
2 V. Skibbe and G. Erker, *J. Organomet. Chem.*, 1983, **241**, 15; M. J. Burk, W. Tumas, M. S. Ward and D. R. Wheeler, *J. Am. Chem. Soc.*, 1990, **112**, 6133.
3 F. Rosenfeldt and G. Erker, *Tetrahedron Lett.*, 1980, **21**, 1637; C. J. Rousset, D. R. Swanson, F. Lamaty and E. Negishi, *Tetrahedron Lett.*, 1989, **30**, 5105; E. Negishi, *Comprehensive Organic Synthesis*, ed. L. A. Paquette, Pergamon, 1991, vol. 5, 1163.
4 K. Takagi, C. J. Rousset and E. Negishi, *J. Am. Chem. Soc.*, 1991, **113**, 1440.
5 T. Takahashi, K. Aoyagi, V. Denisov, N. Suzuki, D. Choueiri and E. Negishi, *Tetrahedron Lett.*, 1993, **34**, 8301.
6 T. Takahashi, Z. Xi, Y. Nishihara, K. Kasai, S. Huo and E. Negishi, *Tetrahedron*, 1997, **53**, 9123.
7 T. Takahashi, D. R. Swanson and E. Negishi, *Chem. Lett.*, 1987, 623; S. L. Buchwald, B. T. Watson and J. C. Huffman, *J. Am. Chem. Soc.*, 1987, **109**, 2544.
8 Recently Negishi *et al.* reported the cyclobutene formation from 1,4-diiodobutene derivatives which were prepared from zirconacyclopentenes. See E. Negishi, F. Liu, D. Choueiry, M. M. Mohamud, A. Silveira, Jr. and M. Reeves, *J. Org. Chem.*, 1996, **61**, 8325.
9 E. Negishi, S. J. Holms, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson and T. Takahashi, *J. Am. Chem. Soc.*, 1989, **111**, 3336; S. L. Buchwald and R. B. Nielsen, *J. Am. Chem. Soc.*, 1989, **111**, 2870; Z. Xi, R. Hara and T. Takahashi, *J. Org. Chem.*, 1995, **60**, 4444.
10 T. Takahashi and M. Kotora, Z. Xi, *J. Chem. Soc., Chem. Commun.*, 1995, 361.
11 T. Takahashi, N. Suzuki, M. Kageyama, D. Y. Kondakov and R. Hara, *Tetrahedron Lett.*, 1993, **34**, 4811; N. Suzuki, D. Y. Kondakov, R. Hara, M. Kageyama, M. Kotora and T. Takahashi, *Tetrahedron*, 1995, **51**, 4519.
12 T. Takahashi, D. Y. Kondakov, Z. Xi and N. Suzuki, *J. Am. Chem. Soc.*, 1995, **117**, 5871.
13 T. Takahashi, D. Y. Kondakov and N. Suzuki, *Tetrahedron Lett.*, 1993, **34**, 6571.

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