

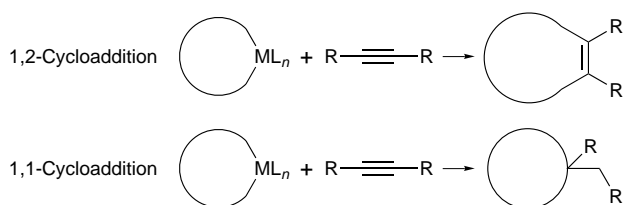
1,1-Cycloaddition of zirconacyclopentadienes to propynoates

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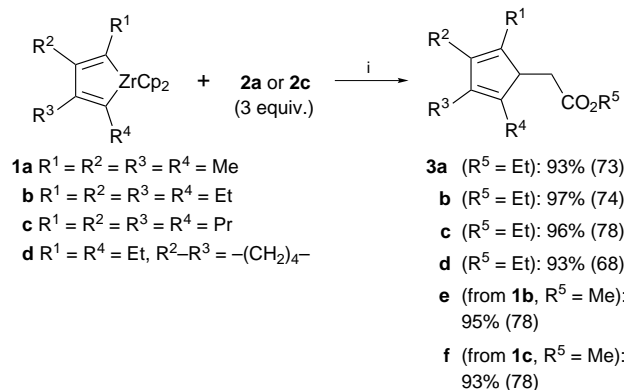
Zirconacyclopentadienes react with propynoates in a 1,1-cycloaddition manner to give pentasubstituted cyclopentadiene derivatives in high yields.

Metallacycles are convenient starting materials for the construction of carbocyclic compounds.¹ The formation of carbocycles can be accomplished by the addition reaction (or insertion reaction of) unsaturated compounds such as alkenes, alkynes, CO and RNC. It is well documented that CO or its synthetic equivalents act as one-carbon units. For alkenes or alkynes, two types of addition reaction, *i.e.* 1,2-cycloaddition or 1,1-cycloaddition, are considered to be possible as shown in Scheme 1. There have been many examples of the 1,2-cycloaddition of metallacycles to alkynes, in which the alkynes behave as two-carbon units.² In contrast, 1,1-cycloaddition to alkynes or related reactions in which alkynes act as a one-carbon unit is very rare.^{3,4} Here we report the 1,1-cycloaddition of zirconacyclopentadienes to propynoates to afford cyclopentadiene derivatives.

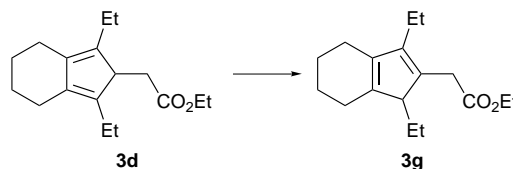


Scheme 1

In a typical example, the reaction of tetraethylzirconacyclopentadiene **1b** with ethyl propynoate **2a** (3 equiv.) provided the cyclopentadiene **3b** in 97% (GC) yield (Scheme 2). The best results were obtained by stirring the reaction mixture first at $-78\text{ }^\circ\text{C}$ for 1 h followed by stirring at $0\text{ }^\circ\text{C}$ for 1–3 h. Some further examples are presented in Scheme 2. In all cases yields of products were high. Monocyclic zirconacyclopentadienes afforded only the corresponding cyclopentadienes. In the case of bicyclic zirconacyclopentadiene **1d**, the desired product **3d** was easily isomerized to the more stable **3g** (Scheme 3) under the conditions used here. The reactions of

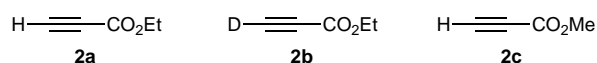


Scheme 2 Conditions: i, -78 to $0\text{ }^\circ\text{C}$, 1–3 h; H^+ . GC yields. Isolated yields are given in parentheses.

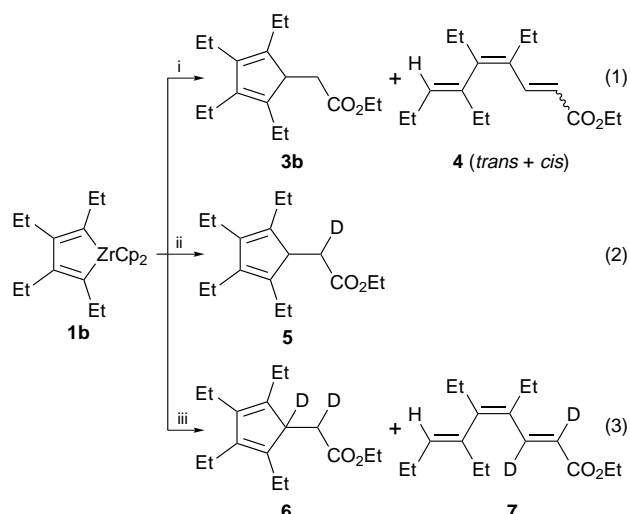


Scheme 3

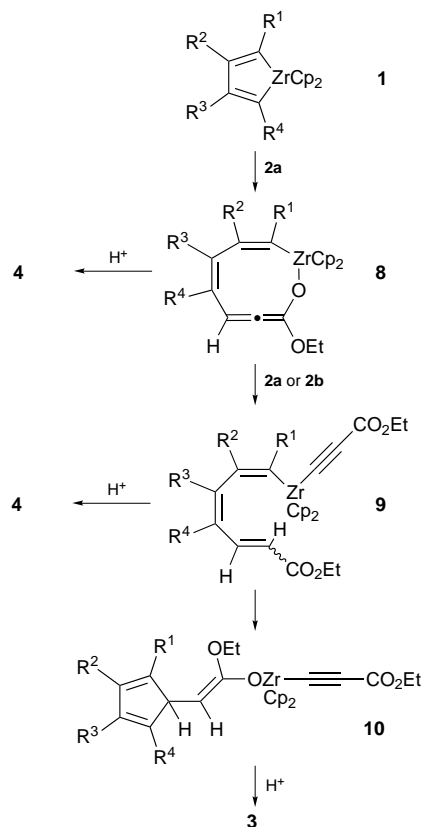
zirconacyclopentadienes **1b,c** with methyl propynoate **2c** gave similar products **3e** and **3f**, respectively. Thus, the formation of cyclopentadiene derivatives proceeds under relatively mild conditions in high yields. Although its scope is limited only to zirconacyclopentadienes bearing alkyl substituents, and zirconacyclopentadienes bearing phenyl or trimethylsilyl substituents at the α -position did not react, clarification of the mechanism of 1,1-cycloaddition of **1** to **2** should be informative.



To elucidate the reaction mechanism, the following experiments were conducted (Scheme 4). Firstly, the reaction was carried out at $-78\text{ }^\circ\text{C}$. Interestingly, trienes **4** were obtained in 78% yield (*trans*-**4** 38% + *cis*-**4** 40%) as major products along with **3b** (18%), whereas at $-40\text{ }^\circ\text{C}$ the reaction gave a different ratio of the products: **3b** (49%), *trans*-**4** (29%) and *cis*-**4** (16%). Secondly, the reaction of the zirconacyclopentadiene **1b** with ethyl propynoate at $-78\text{ }^\circ\text{C}$ for 1 h and then $0\text{ }^\circ\text{C}$ for 1 h afforded the monodeuterated cyclopentadiene **5** after deuterolysis with 3 M DCl. This result shows that the product of the reaction of **1b** with **2a** before hydrolysis contains only one Zr–C bond or one Zr-enolate moiety. One hydrogen atom must be transferred to the intermediate during the reaction. Obviously,



Scheme 4 Reagents and conditions: i, **2a**, $-78\text{ }^\circ\text{C}$, H^+ ; ii, **2a**, -78 to $0\text{ }^\circ\text{C}$, D^+ ; iii, **2b**, -78 to $0\text{ }^\circ\text{C}$, H^+



Scheme 5 Proposed reaction mechanism of the cyclopentadiene formation

the only compound capable of acting as a possible hydrogen donor is the propynoate having a weakly acidic hydrogen atom bound to the sp carbon of the triple bond. This is consistent with the fact that 3-substituted propynoates, which do not have the acidic hydrogen, do not give the desired products. To clarify this point, the reaction of the zirconacyclopentadiene **1b** with ethyl [3-²H]propynoate **2b**⁵ was carried out. Hydrolysis of the reaction mixture with 3 M HCl afforded the dideuterated cyclopentadiene **6** in 61% yield and the *trans* triene **7** in 17% yield. This clearly indicates that Michael addition of one Zr–C bond of the zirconacyclopentadiene to propynoate is the first step. It is noteworthy that this is the first example of direct Michael addition of organozirconocene compounds. So far, the Michael addition was observed only after transmetalation of organozirconium compounds to Cu²⁺⁶ or Ni⁷ compounds. This

demonstrated that a hydrogen (deuterium) atom is indeed transferred from the second propynoate (deuterated propynoate). It also explains why an excess of propynoate was necessary for this reaction and why 3-substituted propynoates did not give the desired products.

From these results, it is possible to propose the following reaction mechanism (Scheme 5). In the first step, the zirconacyclopentadiene **1** adds to the propynoate **2a** forming the nine-membered oxazirconacycle **8**. Hydrolysis of **8** gives the trienes **4**. Then, protonolysis **8** with the propynoate **2a** takes place forming the alkenylalkynyl zirconium compound **9**. Hydrolysis of **9** also affords trienes **4**. The intermediate **9** undergoes an intramolecular conjugate addition and forms **10** which, upon hydrolysis, affords **3**.

In conclusion, zirconacyclopentadienes unprecedentedly reacted with propynoates *via* inter- and intra-molecular Michael addition, resulting in a 1,1-cycloaddition to afford cyclopentadienes. This is in contrast to the reactions of late transition metal metallacyclopentadienes (*e.g.* Ir) which react with propynoates *via* vinylidene intermediates to yield stable organometallic compounds.^{4,8}

Footnote and References

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- (a) N. E. Schore, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier, Oxford, 1995, vol. 12; pp. 703–740; (b) D. B. Grothjahn, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier, Oxford, 1995, vol. 12, pp. 741–770; (c) E. Negishi, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 5, pp. 1163–1184; (d) H.-W. Frühauf, *Chem. Rev.*, 1997, **97**, 523; (e) M. Lautens, W. Klute and W. Tam, *Chem. Rev.*, 1996, **96**, 49.
- For example, for Zr see: T. Takahashi, M. Kotora and Z. Xi, *J. Chem. Soc., Chem. Commun.*, 1995, 361; for Ti: J. E. Hill, G. Balaich, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1993, **12**, 2911; for other metals see: K. P. C. Volhardt, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**; see also refs. 1(a) and 1(b).
- L. Miginiac, in *The Chemistry of Metal-Carbon Bond*, ed. F. R. Hartley and S. Patai, Wiley, New York, 1985, vol. 3, pp. 99–141.
- J. M. O'Connor, K. Hiibner, R. Merwin, P. K. Gantzel, B. S. Fong, M. Adams and A. L. Rheingold, *J. Am. Chem. Soc.*, 1997, **119**, 3631 and references cited therein.
- C. A. Townsend, A. M. Brown and T. T. Nguyen, *J. Am. Chem. Soc.*, 1983, **105**, 919.
- M. Yoshifuji, M. J. Loots and J. Schwartz, *Tetrahedron Lett.*, 1977, 1303; B. H. Lipshutz and M. Segi, *Tetrahedron*, 1995, **51**, 4407.
- M. J. Loots and J. Schwartz, *J. Am. Chem. Soc.*, 1977, **99**, 8045.
- J. M. O'Connor, K. Hiibner, R. Merwin and L. Pu, *J. Am. Chem. Soc.*, 1995, **117**, 8861.

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