Cycloaddition of Zirconacyclopentadienes to Alkynes using Copper Salts: Formation of Benzene Derivatives

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Reaction of zirconacyclopentadienes with alkynes such as dimethyl acetylenedicarboxylate gives benzene derivatives in the presence of CuCl/LiCl.

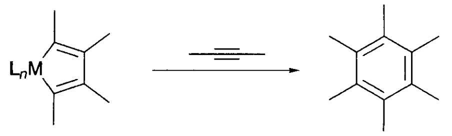
Metallacyclopentadienes containing transition metals such as cobalt, rhodium or titanium have been known to react with 1 equiv. of alkynes to give benzene derivatives [eqn. (1)].[1] This type of reaction is very attractive and very useful, since metallacyclopentadienes can be easily prepared from 2 equiv. of alkynes.

One of the major problems of this reaction concerns the control of combination of alkynes. It has been difficult to prepare cleanly the unsymmetrical metallacyclopentadienes using these metals by the *inter*molecular coupling of two different alkynes. This is the reason why there have been no reports for the selective formation of benzene derivatives from three different alkynes. Recently a variety of unsymmetrical zirconacyclopentadienes have been prepared by several methods.[2] However, unfortunately, there is no precedent of the cycloaddition reactions of these zirconacyclopentadienes to a third alkyne. In this paper we report the novel cycloaddition reaction of zirconacyclopentadienes to alkynes in the presence of a stoichiometric amount of CuCl/LiCl.

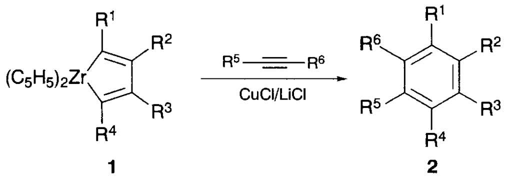
The typical procedure was as follows: zirconacyclopentadiene **1a** was prepared by the method reported using the Negishi reagent[3] {1 mmol of $[\mathrm{Cl_2Zr(C_5H_5)_2}]$ (0.29 g) and 2 equiv. of Bu^{n}Li} and 2 mmol of hex-3-yne in 5 ml of THF. To a solution of **1a** in THF was added 2.0 mmol of CuCl and 2.0 mmol of dimethyl acetylenedicarboxylate **3**. The mixture was stirred for 1 h at room temperature. GC analysis of the reaction mixture indicated the corresponding benzene derivative **2a** was formed in 84% yield. After the usual work-up, distillation or column chromatography gave the pure compound in 59% yield.

Results are shown in Table 1; in the absence of copper salts the starting material **1a** was unreactive. With a stoichiometric amount of copper(I) salts the cycloaddition reaction of zirconacyclopentadienes to dimethyl acetylenedicarboxylate proceeded. Unsymmetrical zirconacyclopentadienes (**1b–d**) were prepared using the Negishi reagent, ethylene and two different alkynes. Dimethyl acetylenedicarboxylate **3** gave good results while methyl but-2-ynecarboxylate **4** afforded the corresponding product **5** in low yield (17%) and diphenylacetylene did not react at all. A zirconacycle compound **1f**[4] prepared from benzyne and hex-3-yne gave the naphthalene derivative **2f** in 80% yield. Although the range of alkynes which could be usefully employed was limited, this is, to the best of our knowledge, the first example of cycloaddition reactions of zirconacyclopentadienes, and the benzene derivatives (**2b–d**) arise from three different alkynes.

Cycloaddition reactions of **1** occurred not only with alkynes but also with alkenes such as **6**. The corresponding product **8** was formed in 70% yield (48% isolated yield).

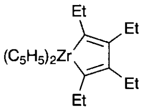
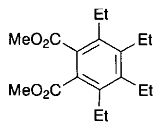
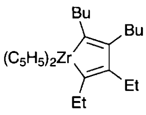
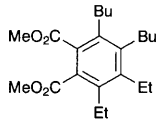
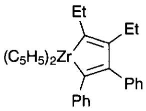
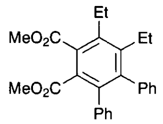
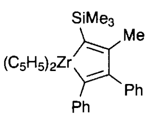
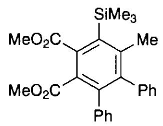
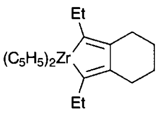
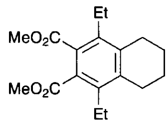
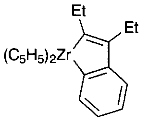
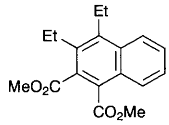


(1)



(2)

Table 1 Cycloaddition reactions of zirconacyclopentadienes to dimethyl acetylenedicarboxylate[a]

Zirconacyclopentadiene[b]		Product		Yield[c]
	**1a**		**2a**	84 (59)
	**1b**		**2b**	90 (71)
	**1c**		**2c**	95 (63)
	**1d**		**2d**	(56)
	**1e**		**2e**	93 (64)
	**1f**		**2f**	80 (54)

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[a] It was not necessary to add LiCl, since LiCl was formed in the reaction of $[\mathrm{Cl_2Zr(C_5H_5)_2}]$ (1 mmol) with 2 equiv. of Bu^{n}Li. All reactions were carried out at room temperature for 1 h using CuCl (2 mmol) and **3** (2 mmol). [b] Zirconacyclopentadienes were prepared according to the literature [ref. 3 for **1a** and **1e**; ref. 2(*e*) for **1b–d**; ref. 4 for **1f**]. [c] GC yields (%); isolated yields are given in parentheses.

$\mathrm{MeO_2C{-}C{\equiv}C{-}CO_2Me}$

3

$\mathrm{Me{-}C{\equiv}C{-}CO_2Et}$

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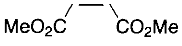

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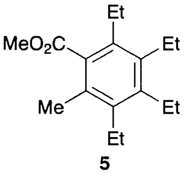

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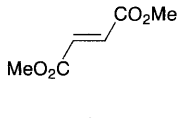

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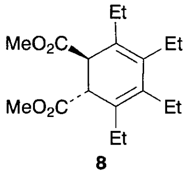

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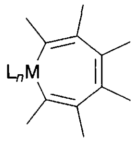
Recently we have reported copper catalysed carbon–carbon bond formation reactions of zirconacycles such as zirconacyclopentadienes[5a] and zirconacyclopentenes.[5b] In these reactions sp^2 and sp^3 carbons on zirconocene were transferred from zirconium to copper(I).[5] The novel reaction reported here requires a stoichiometric amount of copper salt with transmetallation from zirconium to copper(I) being an important step. In general, the mechanism proposed for cycloaddition reactions of metallacyclopentadienes [eqn. (1)] involves either a stepwise or a concerted carbon–carbon bond formation *via* intermediates **9** or **10**. In the cycloaddition reported here carbon–carbon bond formation is stepwise, since **6** and **7** gave the same product **8**. A plausible mechanism of this reaction involves the formation of **11** as an intermediate followed by an intramolecular coupling of the alkenyl moiety and precipitation of metallic copper was observed in all cases. Further investigations are now in progress to elucidate the mechanism, scope and limitations of this reaction.



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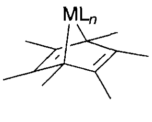

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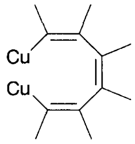

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2 For intermolecular cross-coupling reactions of alkynes with zirconocene, see: (*a*) T. Takahashi, D. R. Swanson and E. Negishi, *Chem. Lett.*, 1987, 623; (*b*) S. L. Buchwald and R. B. Nielsen, *J. Am. Chem. Soc.*, 1989, **111**, 2870; (*c*) B. C. V. Wagenen and T. Livinghouse, *Tetrahedron Lett.*, 1989, **30**, 3495; (*d*) T. Takahashi, M. Kageyama, V. Denisov, R. Hara and E. Negishi, *Tetrahedron Lett.*, 1993, **34**, 687; (*e*) Z. Xi, R. Hara and T. Takahashi, submitted to *J. Org. Chem.*

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