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Selective Dimerization of Aryl-substituted Terminal Alkynes on Bis(indenyl)zirconocene Derivatives

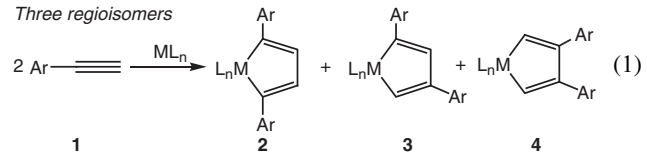
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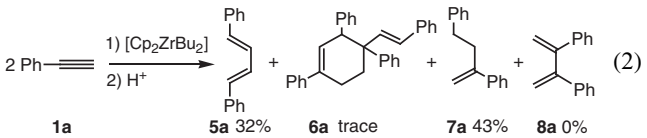
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Dimerization of aryl-substituted terminal alkynes on indenyl zirconium complexes occurred in a selective way. 1,4-Aryl-1,3-diene derivatives were formed exclusively after hydrolysis. It is in sharp contrast to the reaction on [Cp_2Zr] complexes.

Dimerization of aryl-substituted terminal alkynes **1** on low valent transition metal to metallacyclopentadienes is attractive since these metallacycles can be converted into various functionalized 1,3-dienes or substituted arenes.[1] However, formally there are three possible regioisomers **2** (α,α-diaryl), **3** (α,β-diaryl), and **4** (β,β-diaryl) as shown in eq 1, because of the orientations of two terminal alkynes for combining on the metal. And in most cases the α,β-diaryl isomer **3** was the major one,[1a,1c,1j,1k] to avoid the steric problems. Therefore, the β,β-diaryl isomer **4** and α,α-diaryl isomer **2** are relatively rare. Only one example has been shown for the selective dimerization of phenyl acetylene to α,α'-metallacyclopentadiene **2**, in the case of titanium using pyridinediamide ligand with 2,6-dimethylphenyl substituents on the imide nitrogen.[1c]



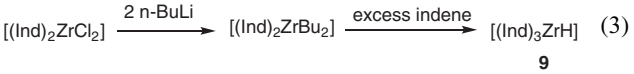
We then tested the dimerization of phenylacetylene using simple zirconocene complexes. Our study was started from conveniently generated Negishi reagent [Cp_2ZrBu_2].[2,3] In this example, phenylacetylene coupled with [Cp_2Zr] (in situ generated from [Cp_2ZrBu_2]) to form zirconacyclopentadiene. Protonolysis of the reaction mixture gave three products **5**–**7** as shown in eq 2.



Product **5a** was generated from the α,α-diaryl isomer in 32% yield. And both **6a** and **7a** were formed from the α,β-diaryl isomer in the combined yield of 43%. There was no related product from the β,β-diaryl isomer. Recently, Szymoniak reported similar result in a [Cp_2ZrCl_2]/Ln system.[4] A mixture of 1,4- and 1,3-diphenylbutadiene in a ratio of 2.5 to 1 was obtained. This clearly shows that dimerization of phenylacetylene on the [Cp_2Zr] system is not selective.

However, when we used [$(Ind)_3ZrH$] (**9**) for dimerization of phenylacetylene, we found that α,α'-metallacyclopentadiene with indenyl ligand **10** was selectively formed. In addition, [$(Ind)_2Zr(CO)_2$] (**11**) also showed the same selectivity for the dimerization of phenylacetylene.

Zirconium indenyl complex, [$(Ind)_3ZrH$] (**9**) was prepared by the reaction of [$(Ind)_2ZrBu_2$] and an excess of indene as shown in eq 3.



The complex **9** was prepared as pale-yellow powder in 64% yield. The structure of **9** was determined by X-ray analysis and its structure is shown in Figure 1.[5] Three indenyl ligands coordinate to zirconium in an η^3 fashion.[6] One hydride ligand was found on the Zr metal center.

In order to confirm the bonding mode of indenyl ligand, we compared the bond distances between zirconium and indenyl ligands. All of the distances between zirconium and C(1), C(2), C(3), C(10), C(11), C(12), C(19), C(20), C(21), are in the range from 2.48 to 2.60 Å. On the other hand, the Zr–C distances of Zr–C(4), Zr–C(9), Zr–C(13), Zr–C(18), Zr–C(22), and Zr–C(27) are relatively longer and ranged from 2.78 to 2.83 Å. This clearly shows that all of the three indenyl ligands are best described as η^3 ligands.[6]

^{1}H NMR of compound **9** showed one doublet peak at 5.79 ppm and one triplet peak at 2.03 ppm assignable to two protons of C(1) and C(3), and one proton of C(2), respectively, of 5-membered ring in indenyl ligands. One singlet peak was observed at 2.95 ppm assignable to H attached to zirconium.

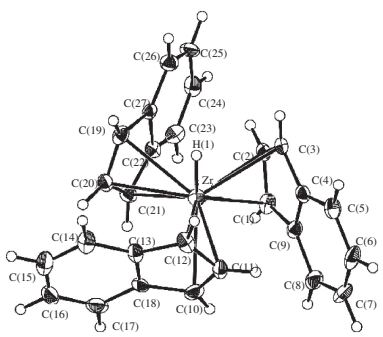


Figure 1. Molecular structure of hydridotris(indenyl)zirconium (**9**).

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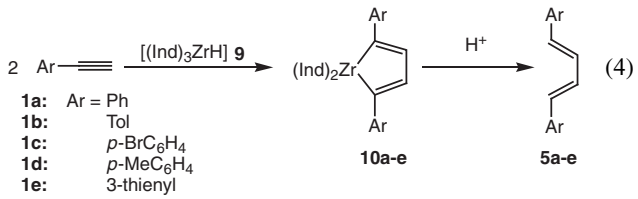
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Table 1. Selective formation of 1,4-diarylbutadiene **5a–5e**

Entry	Aryl–C≡CH	Product	NMR yield of **5**/%	
			by complex **9**	by complex **11**
1	**1a**	**5a**	68	77
2	**1b**	**5b**	77	60
3	**1c**	**5c**	38	51
4	**1d**	**5d**	49	83
5	**1e**	**5e**	55	75

Dimerization reaction of phenylacetylene using complex **9** was then carried out. Phenylacetylene reacted with the complex **9** in THF at room temperature to give zirconacyclopentadiene **10a** in 98% yield.[7] It is interesting to report that hydrolysis of the reaction mixture gave 1,4-diphenyl-1,3-diene **5a** exclusively in 68% yield. No formation of other isomer related compounds such as **6**, **7**, and **8** was observed.

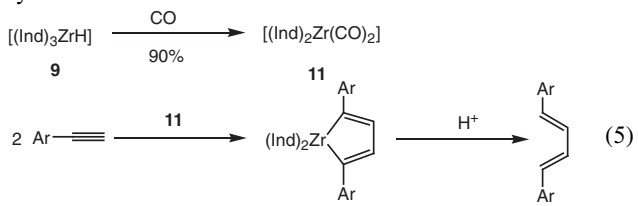
This unusual selective dimerization of coupling reaction was also observed for other aryl-substituted terminal alkynes such as *p*-tolylacetylene, (*p*-bromophenyl)acetylene, (*p*-methoxyphenyl)acetylene, and 3-thienylacetylene. In all cases, only 1,4-diaryl-1,3-dienes **5b–5e** were obtained in 77, 38, 49, and 55% yields, respectively, after hydrolysis. Results are shown in Table 1.



(4)

In the case of 3-thienylacetylene, the corresponding zirconacyclopentadiene **10e** was isolated as crystals. Its structure was determined by X-ray analysis. The structure is shown in Figure 2. It clearly shows that two 3-thienyl groups are at the α,α'-positions of zirconacyclopentadiene moiety.

According to the structure of **10e**, there is no interaction was observed between 3-thienyl group and indenyl ligand in the crystal structure.



(5)

In order to make clear the effect of the "[(Ind)$_2$Zr]" system for the selectivity, we used [(Ind)$_2$Zr(CO)$_2$] (**11**).[8]

Complex [(Ind)$_2$Zr(CO)$_2$] (**11**) was prepared by the reaction of complex **9** with CO in 90% yields which was higher than the known method.[8] By the reaction of **11** with phenylacetylene at room temperature in THF for 12 h, **5a** was exclusively obtained in 77% yield after hydrolysis of the reaction mixture. In the case of other aryl-substituted alkynes, comparable results were obtained which are shown in Table 1. Both [(Ind)$_3$ZrH] (**9**) and [(Ind)$_2$Zr(CO)$_2$] (**11**) gave similar results and 1,4-diarylbutadienes **5a–5e** were exclusively obtained. The formation of the other regioisomers or related products was not observed in these all examples.

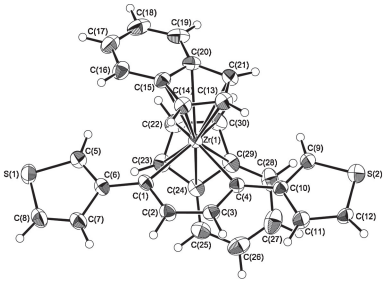


Figure 2. Molecular structure of dimerization product **10e** of thienylacetylene on hydridotris(indenyl)zirconium (**9**).

It is not clear but we believe the selectivity comes from the interaction of aryl groups with indenyl ligand. Therefore **5a–5e** were selectively formed. It is important to note that [(Ind)$_2$ZrBu$_2$] did not show similar selectivity. [(Ind)$_2$ZrBu$_2$] is not stable in the solution. Other complexes such as [(Ind)$_3$ZrH] and [(Ind)$_2$Zr(CO)$_2$] are stable in the solution. It is the major difference between [(Ind)$_2$ZrBu$_2$] and the other two complexes, **9** and **11**.[9]

This paper is in celebration of the 2010 Nobel Prize awarded to Professors Richard F. Heck, Akira Suzuki, and Ei-ichi Negishi.

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