

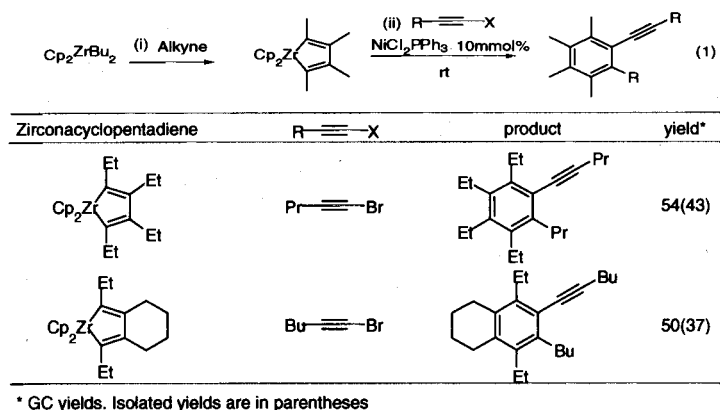
1301 Nickel Catalyzed Benzene Derivatives Formation from Zirconacyclopentadienes

(Catalysis Research Center and Graduate School of Pharmaceutical Science, Hokkaido Univ.)

○Hui Wang, Fu-Yu Tsai, Tamotsu Takahashi

Transition-metal-catalyzed or -mediated coupling of three alkynes to give benzene derivatives has been well established in organic synthesis. We have reported benzene formation from zirconacyclopentadienes and third alkyne in the presence of stoichiometric amount of CuCl or NiX₂(PPh₃)₂. Here, we would like to report nickel-catalyzed coupling reaction of zirconacyclopentadienes with two equiv of 1-halo alkyne as shown in eq(1).

To the solution of zirconacyclopentadiene prepared in situ was added the 1-bromo or chloro alkyne and 10 mmol% NiCl₂(PPh₃)₂ at rt for 24h, benzene derivatives were formed in moderate yield.



1302 Preparation of Dihydropyridazines from Zirconacyclopentadienes

(Catalysis Research Center, Hokkaido University; Aichi University of Education)

○Feng Xu, Yuanhong Liu, Kiyohiko Nakajima, Tamotsu Takahashi*

Zirconacyclopentadienes are very useful intermediates in organic synthesis. It can be conveniently prepared from two different alkynes with high selectivity. In recent years, our group has developed several new synthetic reactions using zirconacyclopentadienes as reactive organometallic intermediates.

In this paper, we will report novel method for preparation of dihydropyridazine derivatives by the reaction of zirconacyclopentadienes with N=N moieties with electron-withdrawing group. A typical experimental procedure is shown in the following equation: zirconacyclopentadienes reacted with azodicarboxylate to give substituted dihydropyridazines in moderate to good yields.

