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Naphthalene formation by allylation of zirconaindenes in the ZnX_2–$Pd(PPh_3)_4$ system

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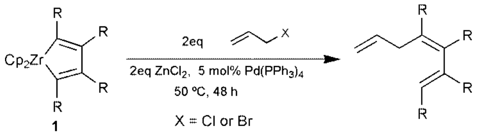
Received (in Cambridge, UK) 24th April 2001, Accepted 10th July 2001
First published as an Advance Article on the web 16th August 2001

Zirconaindenes reacted with allyl halides in the presence of ZnX_2 (X = Cl or Br) and a catalytic amount of $Pd(PPh_3)_4$ to give naphthalene derivatives in good yield.

It has been believed for a long time that zirconacyclopentadienes are inert toward C–C bond formation reactions. Recently, we found that transmetalation reactions of zirconacyclopentadienes to copper,[1] nickel[2] and lithium[3] could open a way to various carbon–carbon bond formation reactions. In this paper we would like to report the novel naphthalene formation reaction[4] of zirconaindenes in the presence of ZnX_2 and a catalytic amount of $Pd(PPh_3)_4$.[5]

When we investigated novel transmetalation to Zn, we tried the allylation reaction of zirconacyclopentadienes, since double allylation of zirconacyclopentadienes[1] proceeded in the presence of either a catalytic or stoichiometric amount of CuCl.[1] When only the zinc salts were used, the reactions were very sluggish. However in the presence of a catalytic amount of $Pd(PPh_3)_4$ the reaction dramatically changed. Monoallylation products were clearly formed. The formation of double allylation products was not observed [eqn. (1)].

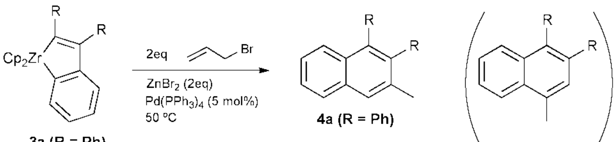


1

2a R = Et 75% (57%)
2b R = Pr 77% (57%)

(1)

This is in sharp contrast to the allylation in the presence of CuCl.[1] Then our attention was turned to the allylation reaction of zirconaindenes. It is interesting to note that, when zirconaindene[6] **3a** was used, substituted naphthalene **4a** was clearly formed as a single product [eqn. (2)].† The formation of regioisomer **5a** was not observed. The use of only a catalytic amount of $Pd(PPh_3)_4$ without zinc salt did not give a clean reaction, although **4a** was formed in 33% GC yield.



3a (R = Ph)

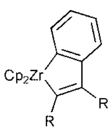
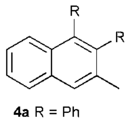
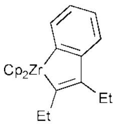
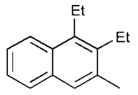
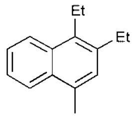
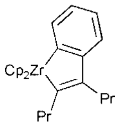
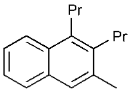
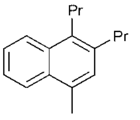
4a (R = Ph)
85% GC yield
(59% isolated yield)

5a (R = Ph)
Not observed

(2)

The structure of the compound **4a** was confirmed by X-ray analysis.‡ It clearly shows that the allylation reaction proceeded selectively at the benzene-carbon attached to Zr. When $MeOC_6H_4$- and MeC_6H_4- were used as substituents instead of the Ph group, the similar perfect regiocontrol was observed as shown in Table 1. This perfect regioselectivity is attributed to the high reactivity of the benzene-carbon attached to Zr compared with the carbon of the –C(Ph)=C(Ph) group attached to Zr. It is interesting to note that when the nucleophilic property of the carbon in the –C=C group attached to Zr was enhanced by introducing alkyl groups such as the Et group and the Pr group instead of the Ph groups, carbon–carbon bond formation with allyl halides at the –C(R)=C(R), R = Et or Pr, was observed. The isomers **5d** and **5e** were obtained in the case of **3d** and **3e**, respectively.

Table 1 The formation of naphthalene derivatives

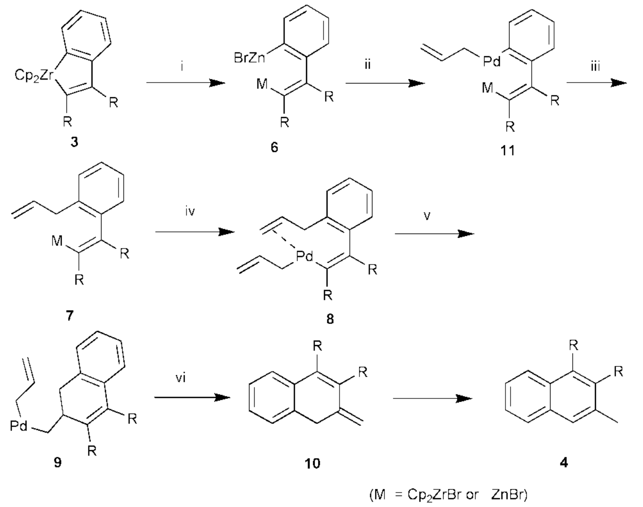
Zirconacyclopentadienes	Product	Yield (%)[a]
 **3a** R = Ph **3b** R = C_6H_4OMe **3c** R = C_6H_4Me	 **4a** R = Ph **4b** R = C_6H_4OMe **4c** R = C_6H_4Me	85(59) 61(42) 68(40)
 **3d**	 **4d** +  **5d**	79(47) 1.9:1
 **3e**	 **4e** +  **5e**	77(51) 3:1

[a] GC yields. Isolated yields are given in parentheses.

A possible mechanism of the naphthalene formation involves (i) transmetalation of the Zr-phenyl carbon bond to Zn giving **6**, (ii) transmetalation of **6** with an allylpalladium halide formed by oxidative addition of allyl halide to a Pd^0 complex, (iii) reductive elimination to give allylated intermediate **7**, (iv) transmetalation of the second Zr–C bonds to Pd forming **8**, (v) insertion of the vinyl group into the Pd–C bond (vi) β-hydrogen elimination to give *exo*-methylene derivative **10** that isomerizes to the corresponding naphthalene **4** (Scheme 1).

Further investigations on mechanism and selectivity are currently in progress.

DOI: 10.1039/b103674m



Scheme 1

Notes and references

† *Typical procedure*: to zirconaindene **3a** prepared according to the literature were added 2 eq. of $ZnBr_2$, a catalytic amount of $Pd(PPh_3)_4$ (5 mol%) and 2 eq. allyl bromide. The mixture was stirred at 50 °C for 12 h. Only **4a** was formed in 85% GC yield. After isolation and purification by column chromatography, **4a** was obtained in 59% isolated yield.

‡ *Crystallographic data of* **4a**: colorless prisms, monoclinic, space group $C2/c$, $a = 21.312(1)$, $b = 10.6981(6)$, $c = 16.2781(8)$ Å, $\beta = 117.713(4)°$, $Z = 8$, $R = 0.044$, GOF = 1.84. CCDC 165561. See http://www.rsc.org/suppdata/cc/b1/b103674m/ for crystallographic files in .cif or other electronic format.

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