SYNLETT Spotlight 7

Zirconocene Hydrochloride
“Schwartz Reagent”

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Zirconocene Hydrochloride (Cp₂ZrHCl, 1), also known as “Schwartz reagent”, is a solid with low solubility in commonly used organic solvents. Carbon-carbon multiple bonds insert into the Zr-H bond of 1 in a syn fashion to give alkyl and E-alkenylzirconocenes (2) where the Zr is attached to the less hindered carbon atom. The polarization of the Zr-C bond in 2 is comparable to Grignard reagents, however, due to steric crowding around the Zr atom, only reaction with CO, isonitriles and halogen sources can be effected directly. Transmetallations (mostly to Al, Zn, Pd, B, Cu and Ni) are also possible to give new organometallics which are synthetically useful in other carbon-carbon bond forming reactions.

The rate of hydrozirconation decreases from terminal alkyne > terminal alkene ~ internal alkyne > disubstituted alkene.

Preparation: 1 is prepared by reduction of Cp₂ZrCl₂ with LiAl(O'Bu)₃H, Red-Al or LiAlH₄ (Buchwald procedure). In situ generation procedures with ‘BuMgCl’ and LiEt₂BH, that allow the preparation of 1 and the hydrozirconation to take place in one pot, have also been reported. For a discussion of the advantages and disadvantages of the in situ procedures, also for alternative preparation and functional group compatibility see ref 2.

Abstracts

1. Alkyl and alkenyl zirconocenes react readily with CO to give intermediate acylzirconocenes (3) that can be elaborated to aldehydes or carboxylic acid derivatives depending on reaction conditions. Very recently it has been reported that 3 can react as an unmasked acyl anion with aldehydes or in Pd catalysed cross coupling reactions.

2. Alkenyl zirconocenes may be easily transmetallated to the corresponding organomagnesium compounds and added to aldehydes in a process promoted by the resulting zirconocene byproducts. If catalytic amounts of chiral aminothiols are present, good enantioselectivities are obtained with aromatic aldehydes.

3. The Pd catalysed coupling of alkyl zirconocenes with vinyl halides or allylic halides/acetates is an excellent method for the construction of conjugated and 1,4-dienes. Although the Zr to Pd transmetallation in alkyl zirconocenes is slow, addition of ZnCl₂ promotes the formation of coupling products.

References


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