SYNLETT Spotlight 7

Zirconocene Hydrochloride "Schwartz Reagent"

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Zirconocene Hydrochloride (Cp_2ZrHCl , **1**), also known as "Schwartz reagent",¹ is a solid with low solubility in commonly used organic solvents.² 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.^{2,3} 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. Transmetalations (mostly to Al, Zn, Pd, B, Cu and Ni) are also possible to give

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.² Very recently it has been reported that **3** can react as an unmasked acyl anion with aldehydes⁹ or in Pd catalysed cross coupling reactions.¹⁰

2. Alkenyl zirconocenes may be easily transmetalated to the corresponding organozinc compounds and added to aldehydes in a process promoted by the resulting zirconocene byproducts.² If catalytic amounts of chiral aminothiols are present, good enantioselectivities are obtained with aromatic aldehydes.¹¹

3. The Pd catalysed coupling of alkenyl zirconocenes with vinyl halides or allylic halides/acetates is an excellent method for the construction of conjugated and 1,4-dienes.² Although the Zr to Pd transmetalation in alkenyl zirconocenes is slow, addition of ZnCl_2 promotes the formation of coupling products.^{2,12}

new organometallics which are synthetically useful in other carbon-carbon bond forming reactions.²

The rate of hydrozirconation decreases from terminal alkyne > terminal alkene ~ internal alkyne > disubstituted alkene.²

Preparation: **1** is prepared by reduction of Cp_2ZrCl_2 with $\text{LiAl}(\text{O}^i\text{Bu})_3\text{H}$,⁴ Red-Al⁵ or LiAlH_4 (Buchwald procedure).⁶ *In situ* generation procedures with $^i\text{BuMgCl}$ ⁷ and LiEt_3BH ,⁸ 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.

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