Zirconocene Hydrochloride

“Schwartz Reagent”

Compiled by Eduardo Fernández-Megía

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK.

Eduardo Fernández-Megía was born in Vigo (Spain) in 1967 and obtained his Ph. D. (1995) from the Universidad de Santiago de Compostela under the supervision of Dr. F. Javier Sardina. He is currently carrying out postdoctoral studies with Professor Steven V. Ley at the University of Cambridge.

Zirconocene Hydrochloride (C₅H₅N₂ZrHCl, 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-alkenyIzirconocenes (2) where the Zr is attached to the less hindered carbon atom. The polarization of the Zr-C bond in 1 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 C₅H₅N₂ZrCl₂ with LiAl(O(tBu))₃H, Red-Al or LiAlH₄ (Buchwald procedure). In situ generation procedures with 'BuMgCl and LiEt₂BH allow the preparation of I 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.

References


This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.