SYNLETT Spotlight 3

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Zirconocene Dichloride and Related Reagents

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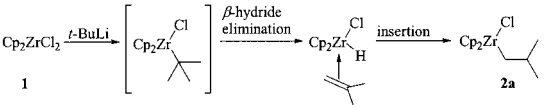
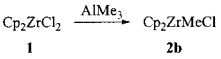
Although chemistry with arenes has a long tradition in organic synthesis, the use of transition metal containing reagents can lead to completely new reactivities and therefore to new functionalization strategies. One of the first syntheses of an aryne zirconocene complex of type **4** was published by Erker et al.[1]

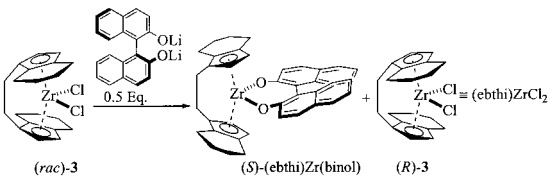
Bis(cyclopentadienyl)zirconium dichloride **1** is a commercially available and stable compound. It reacts in transmetallation reactions, either with *t*-BuLi, followed by a rearrangement to **2a**, or with trimethylaluminium, to **2b**.[2] Treatment of **2** with a lithiated arene results in zirconocene aryne complexes of type **4**. They react with different alkenes and alkynes yielding 1,2 bis-functionalized arenes.[3] The complexation and insertion properties of chiral zirconium compounds of type **3** with alkenes can also be used in stereoselective reactions.

Preparation:



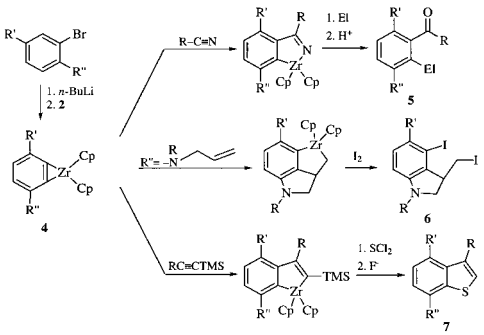


The first synthesis and resolution of (*rac*)-(ebthi)$ZrCl_2$ (ebthi = ethylenebis(tetrahydroindenyl) was described by Brintzinger and coworkers.[4]

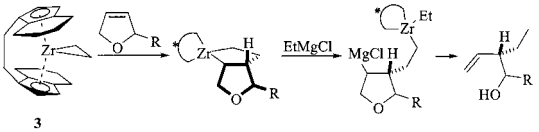


Abstracts

The reaction of **4** with nitriles yields imine derivatives which subsequently react with different electrophiles (El = H, I, S) and are hydrolysed to the corresponding ketones[5]. With respect to R′ and R″ *anti* Friedel Crafts acylation product can be obtained in good yields (> 50 %).
Access to 2,3-dihydroindoles[6] by reaction of **4** with allyl amines is very easy and good yields are obtained (65 - 70 %). The two iodo substituents allow a variety of further transformations.[5]
Regioisomeric control of the insertion of trialkylsilylacetylene is high (>20 : 1). Subsequent reaction with sulfur dichloride and treatment with tetrabutylammonium fluoride yields polysubstituted benzothiophenes[7].



Besides dihydrofurans, other heterocyclic alkenes either with nitrogen or oxygen as heteroatoms and different ring sizes react with **3** and show excellent enantiomeric excesses and yields.[6] Moreover Buchwald and coworkers published the stereoselective synthesis of allylic amines by using optically pure **3**.[7]



References

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(2) **4a**: Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *33*, 181. **4b**: Barr, K. J., Watson, B. T., Buchwald, S. L., *Tetrahedron Lett.* **1991**, *32*, 5465.
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