Rosenthal’s Zirconocene

Compiled by Julian Linshoef

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Introduction

The complex Cp₂Zr(py)(Me₃SiC≡CSiMe₃) is a dark purple to black solid and was first synthesized by Uwe Rosenthal and co-workers in 1995.¹ The applications are to some extent similar to those of the Negishi reagent,² but Rosenthal’s zirconocene provides some considerable advantages:³ it is stable in solutions of hydrocarbon solvents and as a solid, and it can be isolated and stored for several months in a glovebox without any noticeable decomposition. This lower reactivity of Rosenthal’s zirconocene in comparison with the Negishi reagent is accompanied by a higher selectivity, broadening the scope of its applications. It plays an important role in organic and inorganic synthesis, as it forms for example zirconacyclopentadienes that can be transformed into a variety of different heterocycles.⁴

Rosenthal’s zirconocene ² can be prepared in a one-pot procedure, starting with Cp₂ZrCl₂.³,⁵ The THF intermediate ¹ is unstable and difficult to isolate.¹ Therefore, this complex is treated in situ with pyridine, giving high yields of ² (up to 85%).

Scheme 1 Preparation of Rosenthal’s reagent.

Abstracts

(A) Reductive Coupling of Halide-Functionalized Alkynes
Rosenthal’s zirconocene shows a much lower reactivity than the comparable Negishi reagent.³ This mild reactivity not only allows the reductive coupling of bromide-functionalized alkynes,⁶ but also of iodide-substituted species.³ In the latter example, the zirconacyclopentadiene that was obtained was transformed in situ into a stannole by a Zr–Sn exchange, carried out in toluene, in an overall yield of 81%.

(B) Regioselective Polymerization
Regiochemistry has to be considered when a zirconacyclopentadiene is formed from unsymmetrical alkyne. Tilley and co-workers reported the reductive coupling of, amongst others, mesityl-substituted alkynes.⁷ The formation of fully regioselective products was observed, and the regioselectivity was attributed largely to steric effects. This led to the polymerization of a mesityl-terminated diyne, which was analyzed after demetalation. A bright yellow polymer with a high number-average molecular weight of Mₙ = 24 400 Da was obtained.
One option for the synthesis of macrocycles is high dilution in order to avoid polymerization. Another possibility is the synthesis under thermodynamic control. Because the formation of zirconacyclopentadienes is reversible, heating can give the thermodynamically more favored macrocycles in high yields. Using this strategy, a trimeric macrocycle was prepared by heating a solution of Rosenthal’s zirconocene and a 1,4-bis(trimethylsilyl(ethynyl))acene for 24 h at 60 °C and another 48 h at 110 °C. The ‘2 up, 1 down’ diastereomer was isolated after purification in a yield of 62%.

References