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

**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%).

**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 alkynes. 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 \( M_n = 24 \text{ 400 Da} \) was obtained.

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(C) Stereoselective Macrocyclization
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 zirconacyclopen-
tadienes 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 zir-
conocene and a 1,4-bis(trimethylsilyl(ethynyl))benzene 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%.

(D) Ligand Exchange with Phosphino-Acetylene
Bis(diphenylphosphino)acetylene was used in the reaction with
Cp2Zr(py)(Me3Si≡CSiMe3) to form a dinuclear complex with an
isolated yield of 63%. A four-membered heterometallacycle was
observed in solution that is in equilibrium with the dinuclear com-
plex.

(E) Ligand Exchange with Azobenzenes
Kaleta et al. showed that azobenzenes react in a ligand-exchange
process to yield diazazirconacyclopropanes. The reaction was car-
ried out in toluene, and after 18 h, orange crystals were isolated in a
yield of 68%.

(F) Ligand Exchange with Sulfurdiimides
Four-membered zirconacycles containing nitrogen and sulfur were
prepared by ligand exchange with sulfurdiimides. The complex
was analyzed by mass spectrometry, IR spectroscopy, elemental
analysis, and NMR spectroscopy. NMR analysis showed the dia-
magnetic character.

(G) Formation of Hetero-Zirconacycloallenes
The synthesis of azazirconacycloallenes by the reaction of the zir-
conocene Cp2Zr(py)(Me3Si≡CSiMe3) with carbodiimides was re-
ported. Almost no byproducts were formed during the reaction,
and the products were isolated in yields of up to 86%. The mecha-
nism is proposed to proceed via Si–C bond cleavage, insertion of the
carbodiimide into the newly formed Zr–Si bond, and C–C coupling.

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**References**