

# SYNLETT Spotlight

## Rosenthal's Zirconocene

Compiled by Julian Linshoeft



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

Julian Linshoeft was born in Stade, Germany, and studied chemistry at Kiel University. He spent a few months in Nantes, France, as an ERASMUS student and obtained his diploma degree in 2010 at Kiel University. Currently, he is working towards his Ph.D. at the Otto-Diels-Institute for Organic Chemistry under guidance of Professor Dr. Anne Staubitz. His research focuses on main group heterocycles for semiconducting polymers.

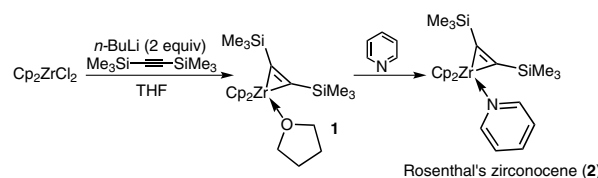
Otto-Diels-Institut für Organische Chemie, Universität Kiel, Otto-Hahn-Platz 4, 24098 Kiel, Germany  
E-mail: jlinshoeft@oc.uni-kiel.de

### Introduction

The complex  $\text{Cp}_2\text{Zr}(\text{py})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$  is a dark purple to black solid and was first synthesized by Uwe Rosenthal and co-workers in 1995.<sup>1</sup> The applications are to some extent similar to those of the Negishi reagent,<sup>2</sup> but Rosenthal's zirconocene provides some considerable advantages:<sup>3</sup> 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 zirconacyclopenta-

dienes that can be transformed into a variety of different heterocycles.<sup>4</sup>

Rosenthal's zirconocene **2** can be prepared in a one-pot procedure, starting with  $\text{Cp}_2\text{ZrCl}_2$ .<sup>3,5</sup> The THF intermediate **1** is unstable and difficult to isolate.<sup>1</sup> Therefore, this complex is treated in situ with pyridine, giving high yields of **2** (up to 85%).

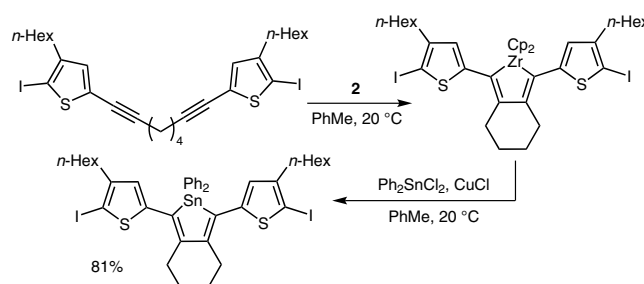


**Scheme 1** Preparation of Rosenthal's reagent.

### Abstracts

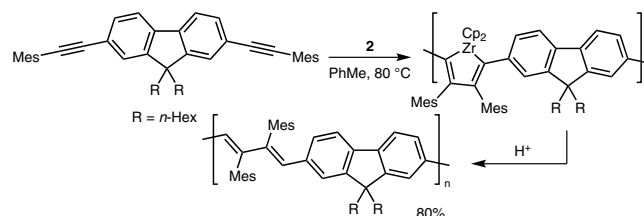
#### (A) Reductive Coupling of Halide-Functionalized Alkynes

Rosenthal's zirconocene shows a much lower reactivity than the comparable Negishi reagent.<sup>3</sup> This mild reactivity not only allows the reductive coupling of bromide-functionalized alkynes,<sup>6</sup> but also of iodide-substituted species.<sup>3</sup> 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%.



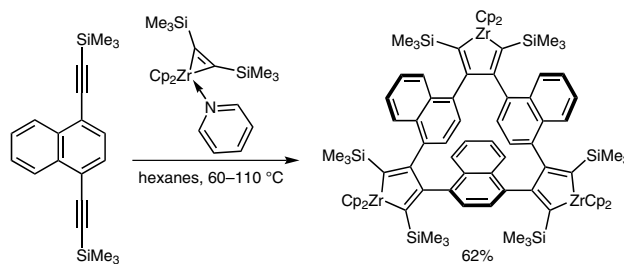
#### (B) Regioselective Polymerization

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.<sup>7</sup> 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  $M_n = 24\,400$  Da was obtained.



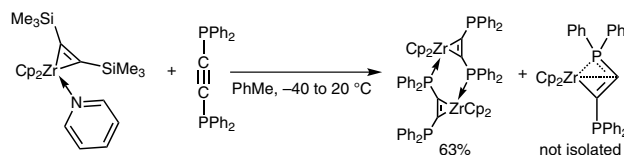
## (C) Stereoselective Macrocyclization

One option for the synthesis of macrocycles is high dilution in order to avoid polymerization.<sup>8</sup> 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.<sup>9</sup> The '2 up, 1 down' diastereomer was isolated after purification in a yield of 62%.



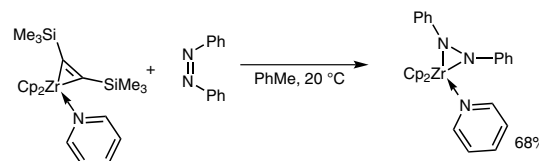
## (D) Ligand Exchange with Phosphino-Acetylene

Bis(diphenylphosphino)acetylene was used in the reaction with  $\text{Cp}_2\text{Zr}(\text{py})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$  to form a dinuclear complex with an isolated yield of 63%.<sup>10</sup> A four-membered heterometallacycle was observed in solution that is in equilibrium with the dinuclear complex.



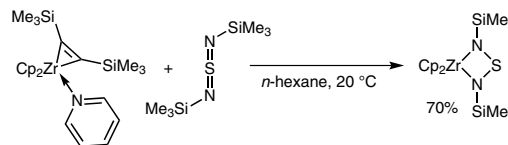
## (E) Ligand Exchange with Azobenzenes

Kaleta et al. showed that azobenzenes react in a ligand-exchange process to yield diazazirconacyclopropanes.<sup>11</sup> The reaction was carried out in toluene, and after 18 h, orange crystals were isolated in a yield of 68%.



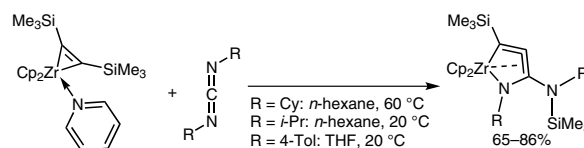
## (F) Ligand Exchange with Sulfurdiimides

Four-membered zirconacycles containing nitrogen and sulfur were prepared by ligand exchange with sulfurdiimides.<sup>12</sup> The complex was analyzed by mass spectrometry, IR spectroscopy, elemental analysis, and NMR spectroscopy. NMR analysis showed the diamagnetic character.



## (G) Formation of Hetero-Zirconacycloallenes

The synthesis of azazirconacycloallenes by the reaction of the zirconocene  $\text{Cp}_2\text{Zr}(\text{py})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$  with carbodiimides was reported.<sup>13</sup> Almost no byproducts were formed during the reaction, and the products were isolated in yields of up to 86%. The mechanism is proposed to proceed via Si–C bond cleavage, insertion of the carbodiimide into the newly formed Zr–Si bond, and C–C coupling. The structures of the products were confirmed by X-ray analysis.



## Acknowledgement

Julian Linshoeft gratefully acknowledges a Ph.D. scholarship from the Deutsche Bundesstiftung Umwelt (DBU).

## References

- (1) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 77.
- (2) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.
- (3) Linshoeft, J.; Baum, E. J.; Hussain, A.; Gates, P. J.; Näther, C.; Staubitz, A. *Angew. Chem. Int. Ed.* **2014**, DOI: 10.1002/anie.201407377.
- (4) (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.
- (5) Nitschke, J. R.; Zürcher, S.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 10345.
- (6) Lucht, B. L.; Buretea, M. A.; Tilley, T. D. *Organometallics* **2000**, *19*, 3469.
- (7) Miller, A. D.; Tannaci, J. F.; Johnson, S. A.; Lee, H.; McBee, J. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 4917.
- (8) Parker, D. *Macrocyclic Synthesis: A Practical Approach*; Oxford University Press: Oxford, **1996**.
- (9) Tannaci, J. F.; Kratter, I. H.; Rider, E. A.; McBee, J. L.; Miller, A. D.; Tilley, T. D. *Chem. Commun.* **2009**, 233.
- (10) Haehnel, M.; Hansen, S.; Schubert, K.; Arndt, P.; Spannenberg, A.; Jiao, H.; Rosenthal, U. *J. Am. Chem. Soc.* **2013**, *135*, 17556.
- (11) Kaleta, K.; Arndt, P.; Beweries, T.; Spannenberg, A.; Theilmann, O.; Rosenthal, U. *Organometallics* **2010**, *29*, 2604.
- (12) Kaleta, K.; Ruhmann, M.; Theilmann, O.; Roy, S.; Beweries, T.; Arndt, P.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. *Eur. J. Inorg. Chem.* **2012**, 611.
- (13) Kaleta, K.; Ruhmann, M.; Theilmann, O.; Beweries, T.; Roy, S.; Arndt, P.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. *J. Am. Chem. Soc.* **2011**, *133*, 5463.