

# SYNLETT Spotlight 1

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

## Bis(cyclopentadienyl)titanium(III) Chloride<sup>1</sup>

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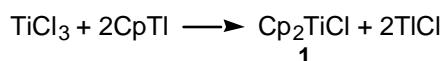
Helen J. Gold received her D.Phil from the University of Sussex, under the supervision of Professor Philip Parsons. She is currently carrying out postdoctoral studies with Professor Steven Ley at the University of Cambridge.



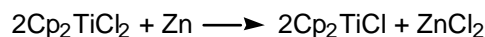
Bis(cyclopentadienyl)titanium(III) chloride **1** - Nugent's reagent - exists as a chloride-bridged dimer in its solid state, but dissociates to its monomeric species in the presence of donor solvents (eg. THF) to afford a loosely solvated 'transition-metal-centred-radical'. The very mild nature of Nugent's reagent, and its selective one-electron reduction of epoxides results in its compatibility with highly functionalised compounds. The reactivity of the carbon-centred radical formed by initial C-O homolysis of the epoxide can be tuned depending on the reacting partner.

**Preparation:** (comparable yields have been obtained for reactions using the in situ reagent versus isolated Cp<sub>2</sub>TiCl)

1) Isolated Cp<sub>2</sub>TiCl (yellowish green solid) is prepared by the treatment of titanium(III) chloride with thallium cyclopentadienide.<sup>2</sup>

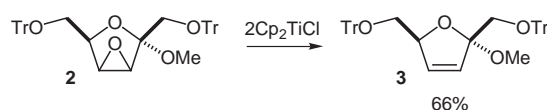


2) In situ Cp<sub>2</sub>TiCl (lime green solution) is prepared quantitatively from titanocene dichloride and powdered zinc in THF.<sup>1</sup>

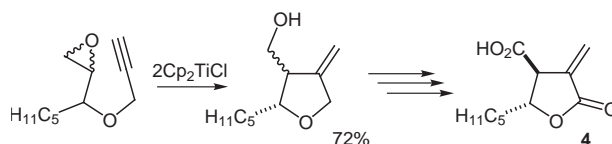


## Abstracts

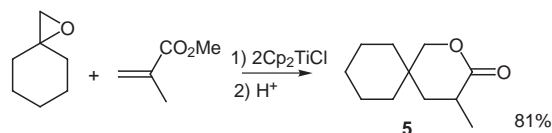
A) The deoxygenation of methyl furanoside **2** to its corresponding olefinic product **3** has been the target of extensive synthetic efforts. The mildness of this deoxygenation procedure is attested by the fact that even the acidic impurities in CDCl<sub>3</sub> are sufficient for conversion to the fully aromatic product.<sup>3</sup>



B) The stereoselective total synthesis of (+/-)-methylenolactocin **4** used Nugent's reagent in the key intramolecular epoxyheptyne radical cyclisation step.<sup>4</sup>



C) The intramolecular addition of epoxides to activated olefins utilizes Nugent's reagent to effect homolysis of the epoxide C-O bond. The δ-hydroxy ester formed on work-up cyclises to the spirolactone **5**.<sup>5</sup> (Interestingly, under the reaction conditions no further addition or polymerisation of methyl methacrylate occurred)



## References

- (1) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986.
- (2) Manzer, L. *Inorg. Synth.* **1982**, *21*, 84.
- (3) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1990**, *112*, 6408.
- (4) Matti, G.; Roy, S. C. *J. Chem. Soc., Perkin Trans 1* **1996**, 403.
- (5) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1989**, *111*, 4525.