

Proceedings

AlCl₃-Catalyzed Synthesis of Zirconacyclopentadienes from Alkynes, Cp₂ZrCl₂ and Mg[†]

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Abstract: A new convenient preparative procedure for the preparation of zirconacyclopentadienes has been developed based on the use of AlCl₃-catalyzed reactions of alkyl-, aryl- and silyl-substituted alkynes with the Cp₂ZrCl₂-Mg reagent system, which excludes the use of both pyrophoric organometallic compounds and salts of toxic metals. In addition, the new procedure can significantly reduce the reaction time. We found that 10 mol % of AlCl₃ significantly accelerates the cyclozirconation of alkyl-, aryl- and silyl-substituted alkynes giving after iodinolysis the corresponding iodine-containing homo-coupling products in a quantitative yield.

Keywords: alkynes; cyclometallation; zirconocene; zirconacyclopentadienes

1. Introduction

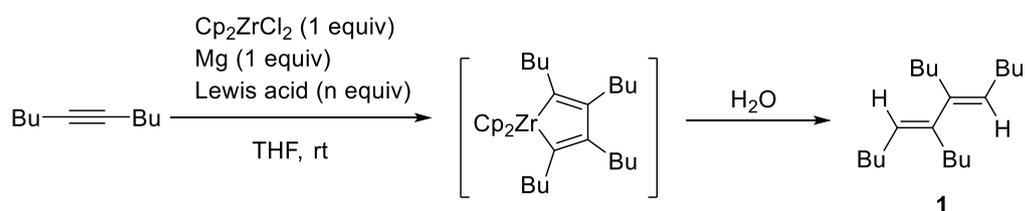
One-step synthesis of bis-η⁵-cyclopentadienylzirconacyclopentadienes by reduction of Cp₂ZrCl₂ with amalgamated magnesium in the presence of various alkynes is well established reaction. However, this procedure has not received wide synthetic application for the preparation of diene derivatives and is currently superseded by procedures using Negishi (“Cp₂ZrBu₂”) [1] and Takahashi (“Cp₂ZrEt₂”) [2] reagents which are generated by reacting Cp₂ZrCl₂ with BuLi or EtMgBr. Indeed, the literature describes procedures for the preparation of zirconacyclopentadienes from 3-hexyne using stoichiometric amounts of HgCl₂ that makes this methodology unattractive for widespread use [3,4]. Thus the development of a new effective method for the homo-coupling of alkynes which excludes the use of both pyrophoric organometallic compounds and salts of toxic heavy metals could contribute to a wider use of the Cp₂ZrCl₂-Mg reagent system for the preparation of diene derivatives and cyclization of enynes.

2. Results and Discussion

We found that 10 mol % of AlCl₃ significantly accelerates the cyclozirconation of alkyl-substituted alkynes giving after iodinolysis the corresponding iodine-containing homo-coupling products in a quantitative yield. Thus, the reaction of 5-decyne with one equivalent each of Cp₂ZrCl₂ and Mg in THF in the presence of 10 mol % of AlCl₃ proceeds with complete conversion of alkyne into zirconacyclopentadiene at room temperature in less than 10 min (Table 1). The best results were obtained using THF as a solvent. At the same time, the reaction of 5-decyne with Cp₂ZrCl₂ and Mg in THF at room temperature without AlCl₃ does not proceed even overnight. The use of catalytic amounts of Me₃SiCl, InCl₃ or SnCl₄ instead of AlCl₃ also did not lead to the formation of the

dimerization product after 5 h at room temperature. The conversion of 5-decyne was 42% in 5 h using one equivalent of Me₃SiCl instead of AlCl₃. The addition of catalytic amounts of TiCl₄ instead of AlCl₃ leads to the formation of an isomeric mixture of dimerization products with full conversion of 5-decyne. It was also found that an increase in the reaction temperature significantly accelerates the rate of interaction of decyne-5 with Cp₂ZrCl₂ and Mg (Table 1, Entry 11).

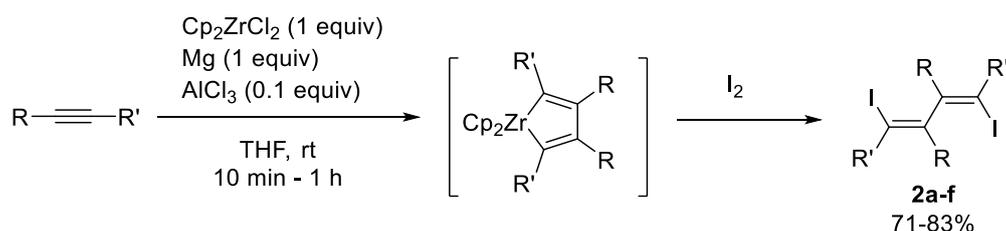
Table 1. The cyclozirconation of 5-decyne with Cp₂ZrCl₂-Mg reagent system.



Entry	Lewis Acid	Equiv.	Time	GC Yield of 1, %
1	AlCl ₃	0.1	10 min	95
2	-	-	18 h	nd
3	InCl ₃	0.1	5 h	nd
4	SnCl ₄	0.1	5 h	nd
5	Me ₃ SiCl	0.1	5 h	nd
6	Me ₃ SiCl	1	1 h	22
7	Me ₃ SiCl	1	5 h	42
8	TiCl ₄	0.1	5 h	90 ¹
9	AlCl ₃	0.1	5 h	41 ²
10	AlCl ₃	0.1	5 h	nd ³
11	AlCl ₃	0.1	2 h	92 ⁴

¹ The mixture of isomers was formed. ² Et₂O was used instead of THF. ³ Hexane was used instead of THF. ⁴ 50 °C.

Similarly, catalytic amounts of AlCl₃ accelerates the reaction with alkyl-, aryl- and silyl-substituted alkynes giving after iodinolysis the corresponding iodine-containing homo-coupling products in good yield. (Scheme 1).



R,R' = Bu,Bu (a); Pr,Pr (b); Er,Et (c); Et,Ph (d); Bu,TMS (e); Oct,TMS (f)

Scheme 1. The cyclozirconation of alkyl-, aryl- and silyl-substituted alkynes with Cp₂ZrCl₂-Mg reagent system.

3. Experimental Part

Commercially available reagents were used. The reactions were carried out in a dry argon atmosphere. THF was distilled over DIBAL-H. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 400 spectrometer (100.62 MHz for ¹³C and 400.13 MHz for ¹H). When recording the ¹H and ¹³C NMR spectra, SiMe₄ and CDCl₃ were used as an internal standards, respectively. Mass spectra were measured using Finnigan 4021 instrument with an ionizing electron energy of 70 eV and an

ionization chamber temperature of 200 °C. The elemental analysis of the samples was determined on Carlo Erba elemental analyzer, model 1106.

(5*Z*,7*Z*)-6,7-Dibutyl-5,8-diiodododeca-5,7-diene (**2a**)

To the mixture of magnesium powder (0.243 mg, 1 mmol), Cp₂ZrCl₂ (0.292 g, 1 mmol) and AlCl₃ (0.013 mg, 0.1 mmol), the solution of 5-decyne (0.138 mg, 1 mmol) in 3 mL of THF was added at room temperature. After stirring for 15 min, CuCl (0.99 mg, 1 mmol) and the solution of I₂ (0.508 mg, 2 mmol) in 3 mL of THF was added at 0 °C. After stirring for 30 min at room temperature, the reaction mixture was diluted with 5 mL of Et₂O, and 3 mL of water was added dropwise while cooling the flask in an ice bath. The precipitate was collected on a filter paper. The aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous CaCl₂ and concentrated in vacuo to give the crude product that was purified by flash chromatography (silica gel, hexane) to afford a viscous yellowish oil; yield: 220 mg, (83%); *R*_f = 0.8 (hexane).

4. Conclusions

A new convenient preparative procedure for the preparation of zirconacyclopentadienes has been developed based on the use of AlCl₃-catalyzed reactions of alkyl-, aryl- and silyl-substituted alkynes with the Cp₂ZrCl₂-Mg reagent system, which excludes the use of both pyrophoric organometallic compounds and salts of toxic metals. In addition, the new procedure can significantly reduce the reaction time.

Author Contributions: Conceptualization, I.R.R. and U.M.D.; methodology, F.T.S.; software, X.X.; validation, F.T.S., T.P.Z. and A.R.R.; formal analysis, F.T.S.; investigation, F.T.S.; resources, T.P.Z.; data curation, A.R.R.; writing—original draft preparation, I.R.R.; writing—review and editing, I.R.R.; visualization, X.X.; supervision, I.R.R.; project administration, U.M.D.; funding acquisition, I.R.R. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Negishi, E.; Holmes, S.J.; Tour, J.M.; Miller, J.A.; Cederbaum, F.E.; Swanson, D.R.; Takahashi, T. Novel Bicyclization of Enynes and Diynes Promoted by Zirconocene Derivatives and Conversion of Zirconabicycles into Bicyclic Enones via Carbonylation. *J. Am. Chem. Soc.* **1989**, *111*, 3336–3346, doi:10.1021/ja00191a035.
2. Negishi, E.; Cederbaum, F.E.; Takahashi, T. Reaction of Zirconocene Dichloride with Alkylolithiums or Alkyl Grignard Reagents as a Convenient Method for Generating a “Zirconocene” Equivalent and Its Use in Zirconium-Promoted Cyclization of Alkenes, Alkynes, Dienes, Enynes, and Diynes. *Tetrahedron Lett.* **1986**, *27*, 2829–2832, doi:10.1016/S0040-4039(00)84653-5.
3. Thanedar, S.; Farona, M.F. A One-Step Synthesis of Bis(H5-Cyclopentadienyl)Zirconacyclopentadiene Compounds. *J. Organomet. Chem.* **1982**, *235*, 65–68, doi:10.1016/S0022-328X(00)85720-4.
4. Hong, J.H. Synthesis and NMR-Study of the 2,3,4,5-Tetraethylsilole Dianion [SiC 4Et 4] 2-•2[Li] +. *Molecules* **2011**, *16*, 8033–8040, doi:10.3390/molecules16098033.

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