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Proceeding Paper

AlCl$_3$-Catalyzed Synthesis of Zirconacyclopentadienes from Alkynes, Cp$_2$ZrCl$_2$ and Mg [†]

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Abstract: A new convenient preparative procedure for the preparation of zirconacyclopentadienes was developed based on the use of AlCl$_3$-catalyzed reactions of alkyl-, aryl- and silyl-substituted alkynes with the Cp$_2$ZrCl$_2$–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 AlCl$_3$ 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

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1. Introduction

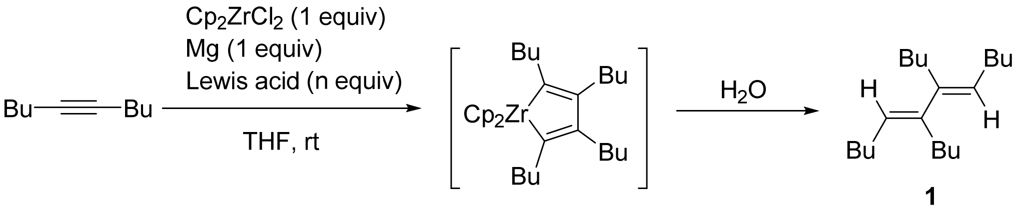
One-step synthesis of bis-η^5-cyclopentadienylzirconacyclopentadienes by reduction of Cp$_2$ZrCl$_2$ with amalgamated magnesium in the presence of various alkynes is a well-established reaction. However, this procedure has not received wide synthetic application for the preparation of diene derivatives and is currently superseded by procedures using Negishi ("Cp$_2$ZrBu$_2$") [1] and Takahashi ("Cp$_2$ZrEt$_2$") [2] reagents which are generated by reacting Cp$_2$ZrCl$_2$ with BuLi or EtMgBr. Indeed, the literature describes procedures for the preparation of zirconacyclopentadienes from 3-hexyne using stoichiometric amounts of HgCl$_2$ 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 Cp$_2$ZrCl$_2$–Mg reagent system for the preparation of diene derivatives and cyclization of enynes.

2. Results and Discussion

We found that 10 mol % of AlCl$_3$ 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 Cp$_2$ZrCl$_2$ and Mg in THF in the presence of 10 mol % of AlCl$_3$ 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 Cp$_2$ZrCl$_2$ and Mg in THF at room temperature without AlCl$_3$ does not proceed even overnight. The use of catalytic amounts of Me$_3$SiCl,

$InCl_3$ or $SnCl_4$ instead of $AlCl_3$ 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 Me_3SiCl instead of $AlCl_3$. The addition of catalytic amounts of $TiCl_4$ instead of $AlCl_3$ 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 decine-5 with Cp_2ZrCl_2 and Mg (Table 1, Entry 11).

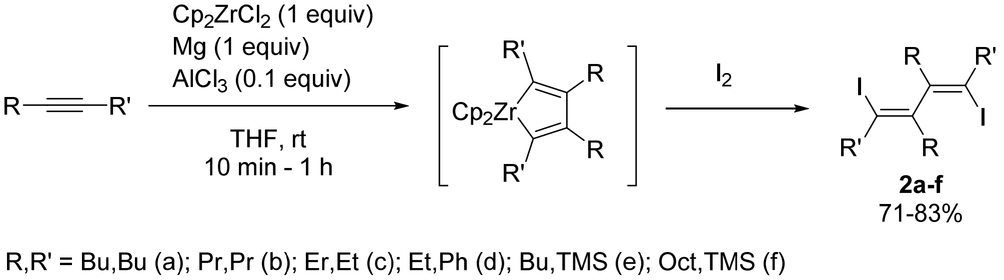
Table 1. The cyclozirconation of 5-decyne with Cp_2ZrCl_2–Mg reagent system.



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_3SiCl	0.1	5 h	nd
6	Me_3SiCl	1	1 h	22
7	Me_3SiCl	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] Et_2O was used instead of THF. [3] Hexane was used instead of THF. [4] 50 °C.

Similarly, catalytic amounts of $AlCl_3$ accelerate the reaction with alkyl-, aryl- and silyl-substituted alkynes giving after iodinolysis the corresponding iodine-containing homo-coupling products in good yield. (Scheme 1).



Scheme 1. The cyclozirconation of alkyl–, aryl– and silyl–substituted alkynes with Cp_2ZrCl_2–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 ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (100.62 MHz for ^{13}C and 400.13 MHz for ^1H). When recording the ^1H and ^{13}C NMR spectra, $SiMe_4$ and $CDCl_3$ were used as internal standards, respectively. Mass spectra were measured using a 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 a Carlo Erba elemental analyzer, model 1106.

(5Z,7Z)-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 were added at room temperature. After stirring for 15 min, CuCl (0.99 mg, 1 mmol) and the solution of I_2 (0.508 mg, 2 mmol) in 3 mL of THF were added at 0 °C. After stirring for 30 min at room temperature, the reaction mixture was diluted with 5 mL of Et_2O, 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 $CaCl_2$ 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 $AlCl_3$-catalyzed reactions of alkyl-, aryl- and silyl-substituted alkynes with the Cp_2ZrCl_2–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.

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

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