

Synthesis of 1-Ethyl-*cis*-2,3-dialkyl(aryl)aluminacyclopent-2-enes. A Novel Class of Five-membered Organoaluminium Compounds

Usein M. Dzhemilev*, Askhat G. Ibragimov and Aleksei P. Zolotarev

Institute of Organic Chemistry, Ural Branch of the Russian Academy of Sciences, 450054 Ufa, Russian Federation.

Fax: +7 347 234 2914

A method has been developed to synthesize a novel class of organoaluminium compounds, 1-ethyl-*cis*-2,3-dialkyl(aryl)aluminacyclopent-2-enes, starting from disubstituted acetylenes and AlEt₃ assisted by catalytic amounts (3–5 mol %) of Cp₂ZrCl₂ (Cp = η⁵-C₅H₅).

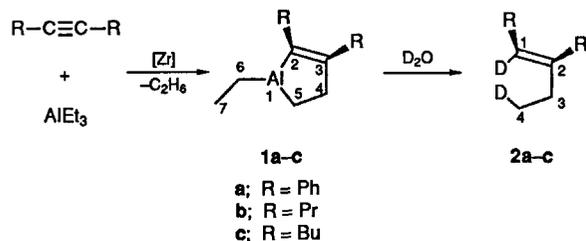
Recently, we created an original method for the regio- and stereo-selective synthesis of 3-alkyl-^{1,2} and *trans*-3,4-dialkyl-substituted^{3–5} aluminacyclopentanes, based on cyclometallation of alkenes by trialkylaluminium compounds assisted by catalytic amounts of Cp₂ZrCl₂ (Cp = η⁵-C₅H₅) in practically quantitative yields.

This paper concerns a novel reaction of AlEt₃ with disubstituted acetylenes in the presence of catalytic amounts of Cp₂ZrCl₂, leading to 1-ethyl-*cis*-2,3-disubstituted aluminacyclopentenes.

At the beginning of this work, we proceeded from an assumption that, during the interaction of disubstituted acetylenes and zirconium alkyl derivatives (formed under the reaction conditions *in situ* from Cp₂ZrCl₂ and AlEt₃),⁶ mixed Zr π-complexes included in the coordination sphere of a control metal atom by one ethylene and an associated acetylene molecule may be formed. The following intramolecular oxidative coupling was expected to lead to the related zirconacyclopentenes, which would then undergo remetalation by the initial AlEt₃ to form aluminacyclopentenes.

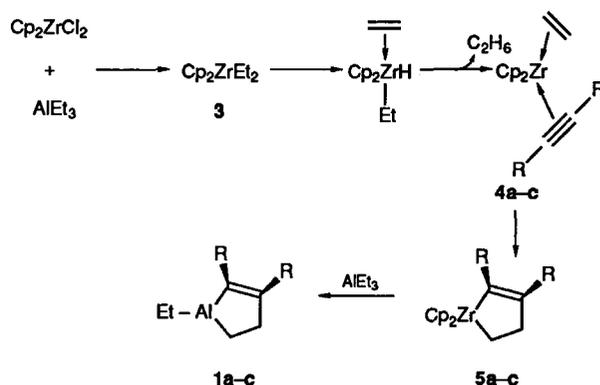
In fact, our study of the cyclometallation of disubstituted acetylenes with AlEt₃, by analogy with α-alkenes,^{1–5} and an investigation of the main features of this reaction showed that on the interaction of 1,2-diphenylacetylene or dialkylacetylenes with AlEt₃ (acetylene: Al = 1:2.5) in the presence of 3–5 mol % Cp₂ZrCl₂ (23–25°C, 10–12 h) the related 1-ethyl-*cis*-2,3-diphenyl(alkyl)aluminacyclopent-2-enes were formed in 75–90% yields.† The reaction was accompanied by the evolution of an equimolar amount of ethane. In the absence of a catalyst cyclometallation was not observed (Scheme 1).

The resulting aluminacyclopentenes **1a–c** and deuterolysis products **2a–c** were unambiguously assigned by spectroscopic methods. Thus, in the ¹³C NMR spectrum of aluminacyclopentene **1a**, a signal broadened due to interaction with a quadrupole nuclear ²⁷Al singlet (δ_C 145.18) may be assigned to the C² atom, and the most low-field singlet (δ_C 158.73) to the C³ atom. The triplet signals of the C⁵ (δ_C 3.14) and C⁶ (δ_C 2.35) atoms were broadened and had a diamagnetic shift. The signal of the C⁴ atom (δ_C 37.73) was shifted downfield in relation to the chemical shift of the related C³ atom (δ_C 33.38) of the deuteroly-



Scheme 1

† 0.146 g (0.5 mmol) Cp₂ZrCl₂, 2.85 g (25 mmol) AlEt₃ and 1.38 g (10 mmol) dec-5-yne were placed in a 50 ml glass reactor equipped with a magnetic stirrer in a dry argon atmosphere, then the solution was stirred for 10 h at room temperature (23–25°C). Protonolysis (5% HCl) of the reaction mixture led to *cis*-5-ethyldec-5-ene [1.38 g (82%)].



Scheme 2

sis product **2a**. The chemical shift of the C³ atom (δ_C 33.38) of **2a** confirmed unambiguously the *cis*-orientation of the phenyl substituents.

Based on the experimental results obtained and on literature data,⁶ the formation of aluminacyclopentenes from disubstituted acetylenes, AlEt₃ and catalytic amounts of Cp₂ZrCl₂ may be expressed by the mechanism in Scheme 2. The first stage is the interaction of Cp₂ZrCl₂ and AlEt₃ to form zirconium-alkyl complex **3**. The latter is probably transformed into π-complexes of the type **4a–c** with elimination of ethane under the reaction conditions. Intramolecular cyclometallation of ethylene and the disubstituted acetylene, entering into the coordination sphere of the central atom of a catalyst molecule, gives zirconacyclopentenes **5a–c**. Remetalation of the latter by AlEt₃ leads to the related aluminacyclopentenes **1a–c**.

It should be noted that in previous work^{7,8} the authors did not observe the formation of cyclic organoaluminium compounds on carbalumination of disubstituted acetylenes with R₃Al, catalysed by Cp₂ZrCl₂ or Cp₂TiCl₂. Evidently, this was caused by the use of halogen-containing solvents (CH₂Cl₂, ClCH₂CH₂Cl) for the carbalumination. The formation⁷ of zirconium dialkyl derivatives responsible for the cyclometallation of both the disubstituted acetylenes and alkenes does not take place in such solvents.^{1,2}

Thus, we have carried out the cyclometallation of disubstituted acetylenes with AlEt₃ in the presence of catalytic amounts of Cp₂ZrCl₂ to form 1-ethyl-*cis*-2,3-dialkyl(aryl)aluminacyclopent-2-enes, for the first time, in high yields.

References

- U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 207 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, 194).
- U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2831.
- U. M. Dzhemilev, A. G. Ibragimov, A. B. Morozov, L. M. Khalilov, R. R. Muslukhov and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1141 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, 1022).

- 4 U. M. Dzhemilev, A. G. Ibragimov, A. B. Morozov, R. R. Muslukhov and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1607 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, 1425).
- 5 U. M. Dzhemilev, A. G. Ibragimov and A. B. Morozov, *Mendeleev Commun.*, 1992, 26.
- 6 W. Kaminsky and H. Sinn, *Liebigs Ann. Chem.*, 1975, 3, 424.
- 7 D. E. Van Horn and E. Negishi, *J. Am. Chem. Soc.*, 1978, **100**, 2252.
- 8 D. E. Van Horn, L. F. Valente, M. J. Idacavage and E. Negishi, *J. Organomet. Chem.*, 1978, **156**, C20.

Received: Moscow, 10th January 1992
Cambridge, 6th March 1992; Com. 2/002801