

Proceeding Paper

DFT and Multinuclear NMR Spectroscopy in the Study of Five-Membered Saturated Metallocarbocycles of Main III Group Metals [†]

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Abstract: Five-membered saturated metallocarbocycles represent a large family of organometallic compounds, which are frequently postulated as reactive intermediates in catalysis or as precursors for the synthesis of a wide range of functionally substituted compounds, therefore, their NMR spectral data are incomplete and not systematized. Metallocarbocycles for Main III Group metals, which are spectroscopically characterized, are described in this article. Among these, of particular interest are 1-ethyl-3-substituted alumolanes, 3-spiro-substituted polycyclic alumolanes and non-bornen annelated alumolanes, which are supposed to be formed in alkene cycloaluminumation with AlEt₃ catalyzed by Cp₂ZrCl₂. Conformational analysis upon inversion of a five-membered ring for mono and polycyclic alumolanes is presented.

Keywords: alumolanes; conformation; metallacycle; selfassociation; Main III Group metals; multinuclear NMR spectroscopy; DFT

1. Introduction

Five-membered saturated metallocarbocycles for Main III Group metals, such as, alumolanes, gallolanes and indolanes (tallolanes are not described in the literature) are frequently postulated as precursors for the synthesis of functionally substituted compounds. In laboratory practice, as a rule, metallacycles are not isolated in pure form due to their high sensitivity to moisture and atmospheric oxygen; therefore, their identification is carried out by the products of subsequent oxidation and deuteration. For example, the identification of 1-chloro-3-alkyl-indacyclopentanes [1], which were synthesized in the reaction of α -olefins with indium chloride and magnesium metal using *i*-Bu₂AlH catalyzed by Cp₂ZrCl₂, was carried out exclusively on the basis of hydrolysis and deuteration products. Gallacyclopentanes, which are described by NMR spectroscopy, are not numerous and are presented in the review by three compounds 1–3 (Scheme 1). Gallacyclopentanes 1 and 2 are obtained by reacting gallium dichloride Et₂N(CH₂)₃GaCl₂ with Li(CH₂)₄Li or BrMg(CH₂)₄MgBr at –78 °C in diethyl ether [2]. Compound 1 is a white solid at room temperature (T_{melt} = 88 °C, T_{bp} = 125 °C), while gallacyclopentane 2, structurally similar to it, is a viscous liquid (T_{bp} = 53 °C) under standard conditions. Metallacycle 3 is white crystals at room temperature (T_{melt} = 288–291 °C), which made it possible to identify it using X-ray diffraction analysis [3]. It was shown that the five-membered rings in the dimeric structure of compound 3 are in the C₂-symmetric “twist” conformation. The signals of cyclic methylene groups located in the α -position to the metal in metallocyclopentanes 1 and 2 in the ¹H and ¹³C NMR spectra appear in the ranges of 0.3–0.9 ppm and 13.07–13.98 ppm, respectively. The signals of cyclic β -methylene groups of

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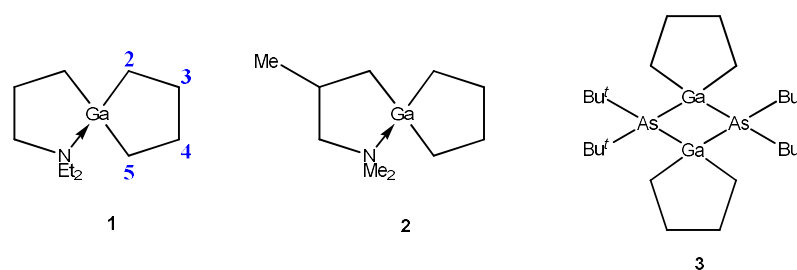
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gallacyclopentanes in the ^1H and ^{13}C NMR spectra were recorded in the regions of 1.55–2.65 and 30.28–34.48 ppm, respectively.

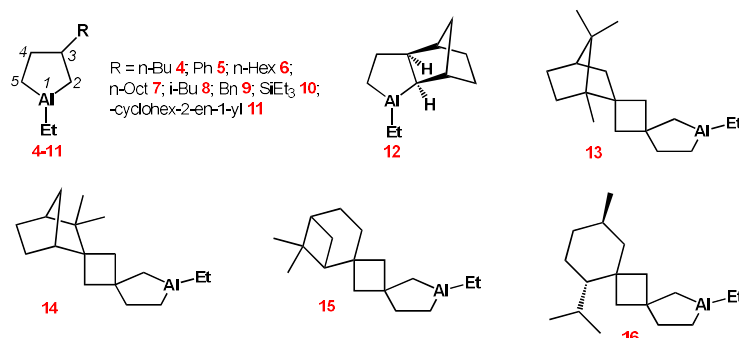


Scheme 1. Structure of gallacyclopentanes.

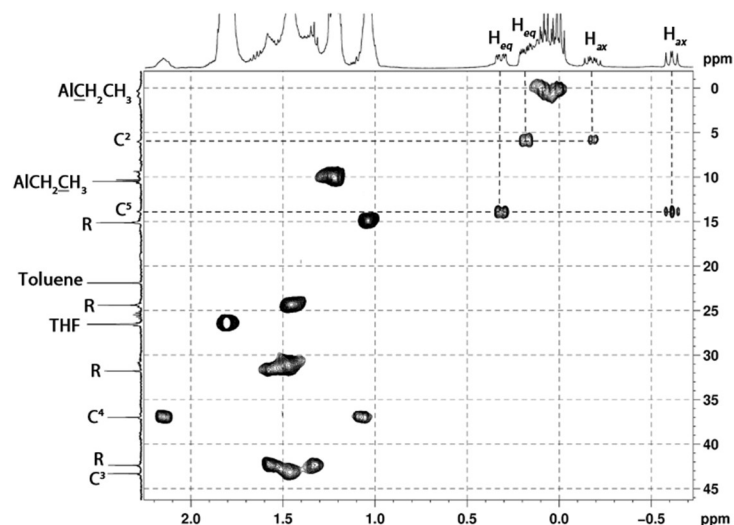
Among the five-membered cyclic organic compounds containing an aluminum atom in their structure, 1-ethyl-3-substituted alumolanes are known, which are formed in the cycloalumination of α -olefins with AlEt_3 catalyzed by Cp_2ZrCl_2 [4]. This method through alumolanes enabled the synthesis of a broad range of organic and heteroatom-containing compounds, including those difficult to synthesize before [5, 6]. To date, the latest data indicate the possibility of using the reaction in the one-pot synthesis of phospholanes [7, 8] and borolanes [9]. Since alumolanes are viscous homogeneous liquids, multinuclear ^1H , ^{13}C and ^{27}Al NMR spectroscopy is the only reliable tool for the structural studies. Unlike acyclic alkylalanes AlR_3 ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, i\text{-Bu}$), which have been structurally studied in detail [10–13], ring organoaluminum compounds (OACs) have received much less attention [14–16]. Recently, we carried out a systematic structural high-resolution multinuclear NMR study of alumolanes in polar solvents [17] and in non-polar media, where self-association processes take place similarly to acyclic alkylalanes.

2. Results and Discussion

A systematic analysis of a number of 1-ethyl-3-R-substituted alumolanes ($\text{R} = n\text{-Bu}$, $n\text{-Hex}$, $n\text{-Oct}$, $i\text{-Bu}$, Ph , Bn , SiMe_3 , SiEt_3 , cyclohex-2-en-1-yl) in polar (Et_2O , THF, pyridine) and nonpolar (toluene, cyclohexane) solvents by multinuclear ^1H , ^{13}C , and ^{27}Al NMR spectroscopy was carried out using two-dimensional (COSY, HSQC, HMBC) techniques (Scheme 2). We have assigned all the observed NMR signals of atoms of cyclic AOCs (for example, Figure 1). As follows from Figure 1, the signals of carbon atoms located in the α -position to the metal atom are significantly broadened and appear in the high-field region of the spectrum: $\delta\text{C-2} = 13.6$ ppm and $\delta\text{C-5} = 5.7$ ppm. The two pairs of methylene protons corresponding to them are diastereotopic and appear in the two-dimensional COZY and HSQC spectra as geminal partners bound together in pairs. Analysis of the experimental $^3J_{\text{HH}}$ and $^4J_{\text{HH}}$ in the ^1H NMR spectra (Figure 1), as well as theoretical conformational analysis showed that the 3-substituted five-membered aluminum carbocycle in solution (Figure 2) is predominantly in the *twist* conformation with a *pseudo*-equatorial substituent in the third position.



Scheme 2. Structure of alumolanes.

Figure 1. Fragment of the HSQC spectrum of 1-ethyl-3-butylaluminacyclopentane 4 in THF- d_8 .

The conformational rigidity of the five-membered aluminacyclopentane made it possible for the first time for cyclic AOCs to determine the direct heteronuclear constants $^1J(^1\text{H}-^{13}\text{C})$ from the data of two-dimensional experiments without proton suppression. Thus, the values of the constants for methylene fragments in the α -position to the aluminum atom vary within 108–116 Hz. The lower value of the constants compared to those for ordinary $\text{C}^{\text{sp}^3}\text{-H}$ carbon-hydrogen bonds (~ 120 Hz) is explained by the lower electron density on carbon atoms due to the influence of the metal atom. The stereospecificity of direct heteronuclear constants at C^2H_2 , C^5H_2 , where $^1J(^1\text{H}_{\text{eq}}-^{13}\text{C}) > ^1J(^1\text{H}_{\text{ax}}-^{13}\text{C})$, was established, which indicates the existence of stereoelectronic effects within the aluminacyclopentane.

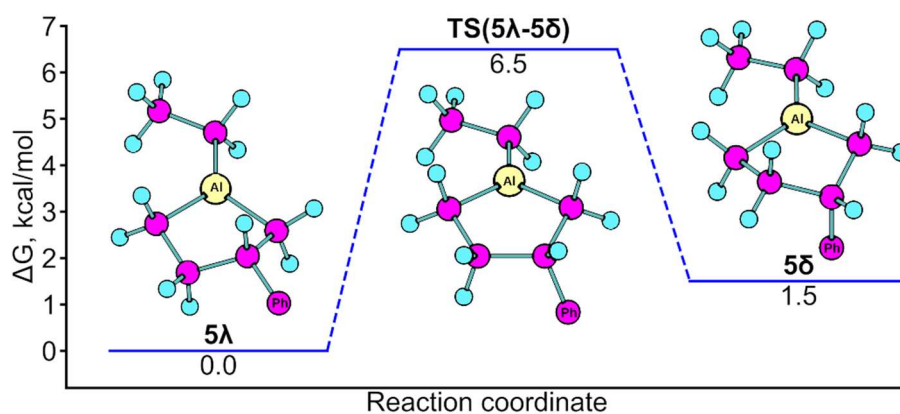
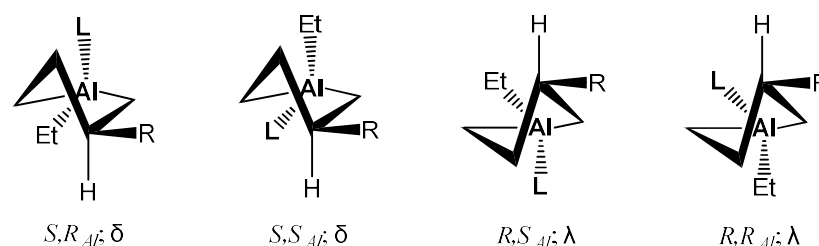


Figure 2. Conformational analysis of 3(S)-alumolane 5.

The ^{27}Al NMR signals of the spectra of 1-ethyl-3-R-substituted alumolanes in THF are observed in the region of δAl 178–185 ppm and in toluene $\delta\text{Al}(\mathbf{4}) = 146.3$ ppm ($W_{1/2} = 5.8$ kHz), which indicates the presence of a four-coordinated aluminum atom in the molecular structure [18]. Despite the formation of diastereomers (Scheme 3) due to the complexation with Et_2O , THF, and Pyr solvent molecules at the metal atom, diastereomers were not observed even when the temperature was lowered to 200 K due to the rapid epimerization of the stereogenic center on Al.



Scheme 3. Diastereomers of solvated alumolane.

We calculated the thermodynamic parameters of complex formation reactions for each of the isomers using 1,3-diethylalumolane as an example. A comparative analysis of the calculated ΔG for the complexes of the model compound showed that the thermodynamic stability of the complexes decreases in the series: AOC·Py > AOC·THF > AOC·Et₂O. The most stable is the pyridine complex, in which the "lifetime" of the ligand on the metal atom is the longest. It is natural that only in the ¹³C NMR spectra of pyridine solutions of 1-ethyl-3-phenyl(butyl)alumolanes did we manage to detect the signals of two diastereomers.

A distinctive feature of the ¹H and ¹³C NMR spectra of 1-ethyl-3-R-alumolanes in toluene is the presence of a large number of signals for each carbon atom of the molecule (Figure 3). As the temperature rises to 333 K, the spectrum simplifies due to the coalescence of a number of signals. We performed a quantum chemical assessment of the thermodynamic and activation parameters of the alumolane dimerization reaction using 1,3-diethylalumolane as an example.

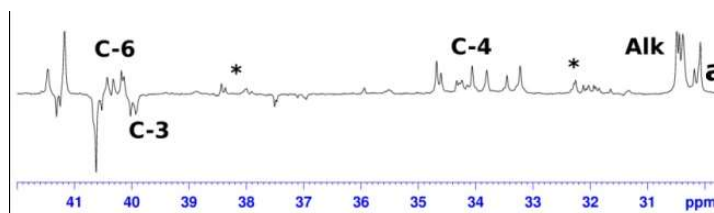


Figure 3. ¹³C NMR spectra (dept 135) of 1-ethyl-3-butylalumolane **4** in toluene (50% AOC): at T = 298 K (symbol * denotes minor carbalumination products).

As a result, possible isomer structures were calculated taking into account configurational and conformational isomerism, of which 20 dimeric forms can be stable at room temperature ($\Delta G \leq 0$). The two most energetically favorable structures are shown in Figure 4.

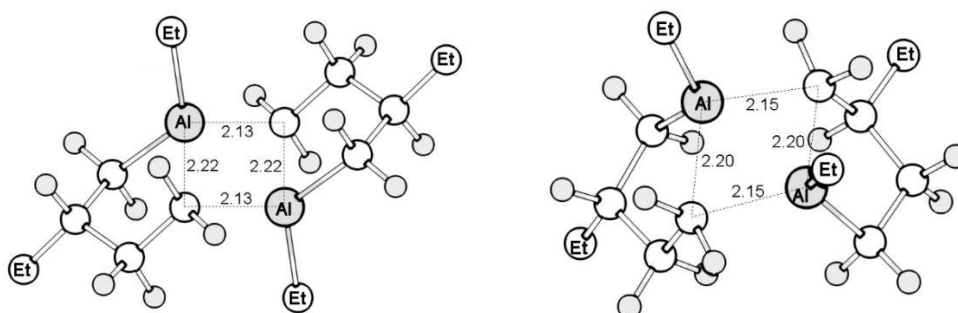


Figure 4. Optimized structures of the two most energetically favorable dimers of 1,3-diethylalumolane: anti-SR- $\delta\lambda$ ($\Delta G = -34.3$ kJ/mol) and SAIRAISS- $\delta\delta$ ($\Delta G = -30.1$ kJ/mol).

As follows from the theoretical data obtained, stereoisomers of dimers should predominantly exist at room temperature, in which bridging bonds are formed with the

participation of metal–carbon bonds of the five-membered ring. The bonds formed in alumolane dimers, by analogy with alumols (according to PCA experiments [19]) and AlMe_3 (according to new electron spectroscopy data [20]), should be interpreted in terms of multicenter binding.

We found that the theoretical and experimental data are consistent, so we also performed a conformational analysis for 3-spiro-substituted polycyclic alumolanes and nonbornen annelated alumolanes **12**–**16** [21]. The results are presented in Figure 5.

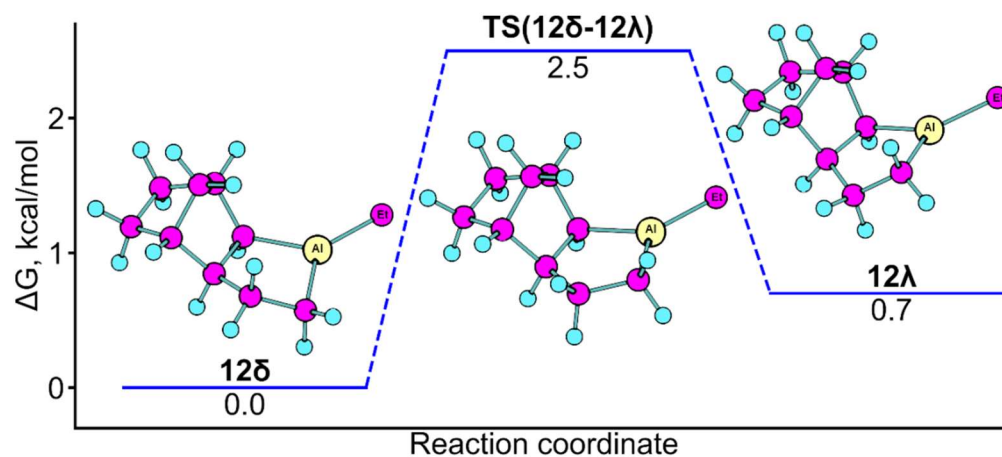


Figure 5. Conformational analysis of alumolane **12**.

As follows from Figure 5, conformations of alumolane exo-annelated with non-bornene were found on the potential energy surface of the molecule that differ in energy by 0.7 kcal/mol. Conformational dynamics are associated with vibration ($\Delta G^\ddagger = 2.5$ kcal/mol) of the methylene fragment (Al-CH_2 -) of the five-membered ring. The inversion of metal-lacycle in a spiro-linked compound requires significantly more energy; for example, the energy barrier for the conformational transition in alumolane **15** is 7.4 kcal/mol.

3. Conclusions

NMR data of five-membered saturated metallocarborcycles for Main III Group metals are summarized. Particular attention is paid to 1-ethyl-3-substituted alumolanes. The equilibrium mixture of metallocyclic dimers are formed *via* coordination of Al-C ring bonds in nonpolar solvents. A multicenter character of metal and C atoms binding in alumolane dimers has been shown. In polar solvents, solvates of alumolanes with solvent molecules are formed. Aluminacarborcycle adopts a chiral *twist* conformation with a *pseudo-equatorial* 3-substituent position. Comparative conformational analysis upon inversion of a five-membered ring for mono and polycyclic alumolanes was carried out.

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

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