

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, however, 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 nonbornen annelated alumolanes, which are supposedly formed by alkene cycloalumination with AlEt_3 catalyzed by Cp_2ZrCl_2 . Conformational analysis upon inversion of a five-membered ring for mono and polycyclic alumolanes is presented.

Keywords: alumolanes; conformation; metallocycle; self-association; Main III Group metals; multinuclear NMR spectroscopy; DFT



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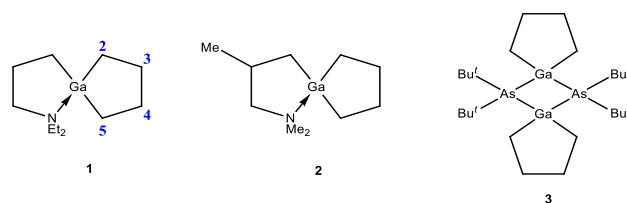


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1. Introduction

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, metallocycles 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 deuterolysis. 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 $i\text{-Bu}_2\text{AlH}$ catalyzed by Cp_2ZrCl_2 , was carried out exclusively on the basis of hydrolysis and deuterolysis products. Gallacyclopentanes, which are described by NMR spectroscopy, are not numerous and are represented in the review by three compounds 1–3 (Scheme 1). Gallacyclopentanes 1 and 2 are obtained by reacting gallium dichloride $\text{Et}_2\text{N}(\text{CH}_2)_3\text{GaCl}_2$ with $\text{Li}(\text{CH}_2)_4\text{Li}$ or $\text{BrMg}(\text{CH}_2)_4\text{MgBr}$ at -78°C in diethyl ether [2]. Compound 1 is a white solid at room temperature ($T_{\text{melt}} = 88^\circ\text{C}$, $T_{\text{bp}} = 125^\circ\text{C}$), while gallacyclopentane 2, structurally similar to it, is a viscous liquid ($T_{\text{bp}} = 53^\circ\text{C}$) under standard conditions. Metallocycle 3 has the form of white crystals at room temperature ($T_{\text{melt}} = 288\text{--}291^\circ\text{C}$), 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 C_2 -symmetric *twist* conformation. The signals of the cyclic methylene groups located in the α -position to the metal in metallocyclopentanes 1 and 2 in the ^1H and ^{13}C NMR spectra appear in the ranges of 0.3–0.9 ppm and 13.07–13.98 ppm, respectively. The signals of the cyclic β -methylene

groups of 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.

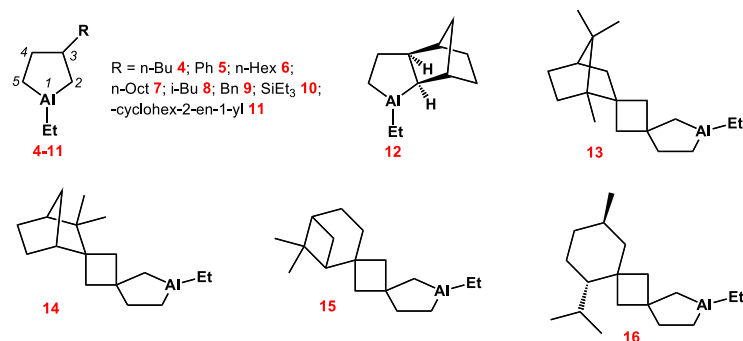


Scheme 1. Structure of gallacyclopentanes.

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 using alumolanes enabled the synthesis of a broad range of organic and heteroatom-containing compounds, including those that were 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 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 the atoms of cyclic OACs (for example, Figure 1). As follows from Figure 1, the signals of the 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.

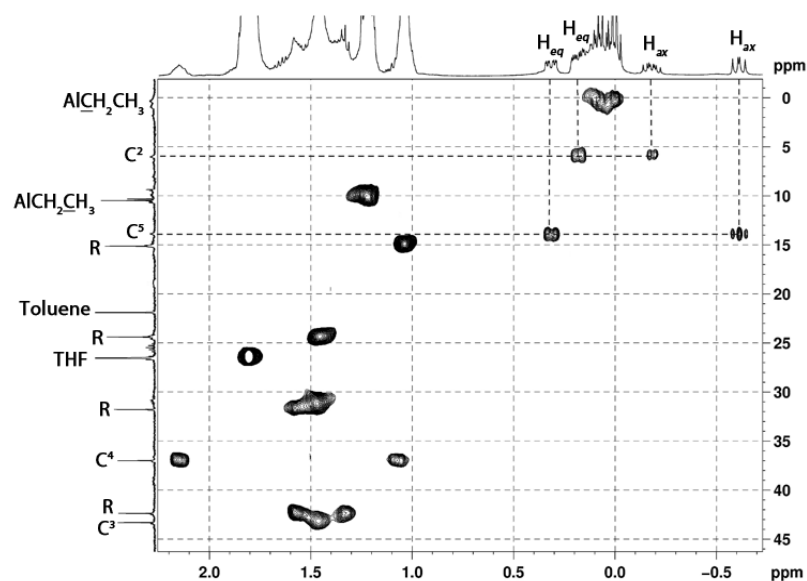


Figure 1. Fragment of the HSQC spectrum of 1-ethyl-3-butylalumolane 4 in THF- d_8 .

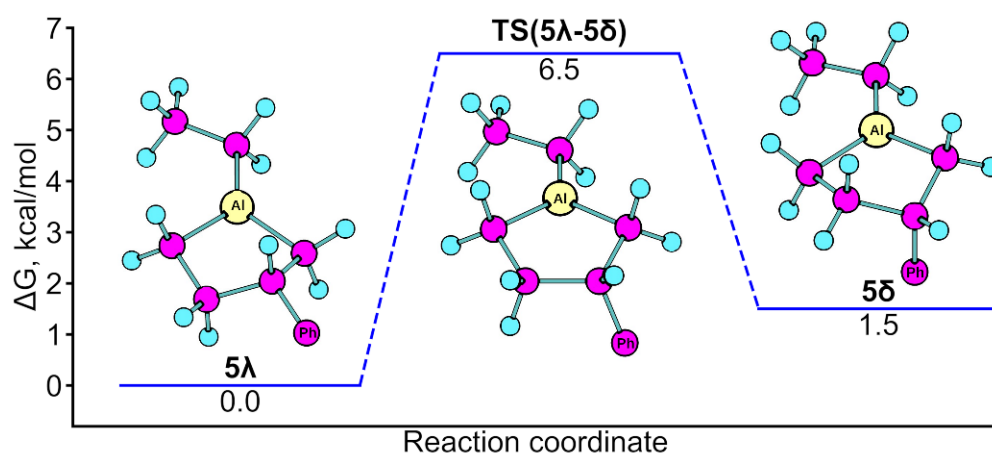
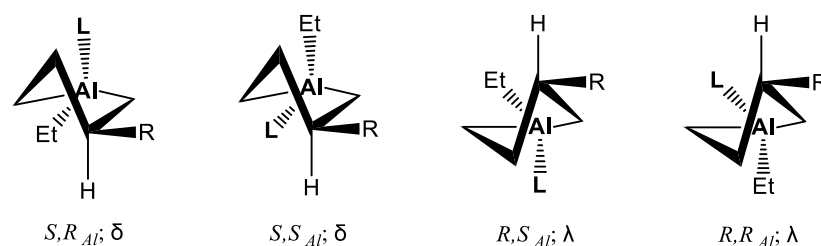


Figure 2. Conformational analysis of 3(S)-alumolane 5.

The conformational rigidity of the five-membered aluminacarbocycle made it possible for cyclic OACs to determine the direct heteronuclear constants $^1J(^1\text{H}-^{13}\text{C})$ from the data of two-dimensional experiments without proton suppression for the first time. Thus, the values of the constants for the methylene fragments in the α -position to the aluminum atom vary within $108 \div 116$ 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, indicates the existence of stereoelectronic effects within the aluminacarbocycle.

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: OAC·Py > OAC·THF > OAC·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 evaluation of the thermodynamic and activation parameters of the alumolane dimerization reaction using 1,3-diethylalumolane as an example.

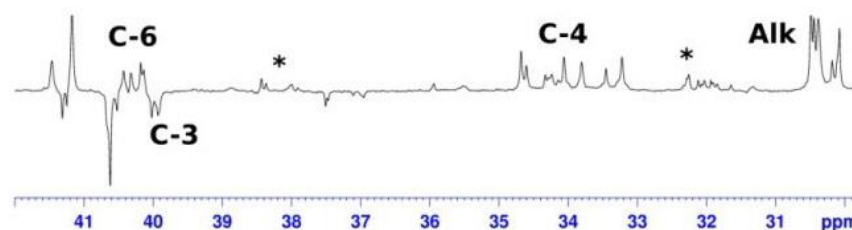


Figure 3. ¹³C NMR spectra (dept 135 of 1-ethyl-3-butylalumolane **4** in toluene (50% OAC): at T = 298 K (symbol * denotes minor carbalumination products).

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.

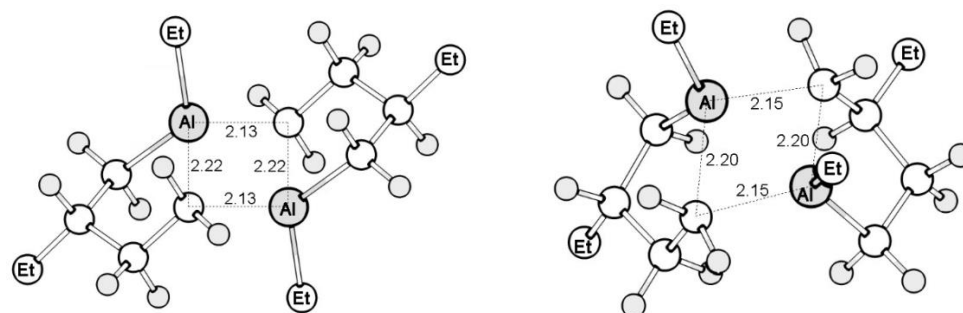


Figure 4. Optimized structures of the two most energetically favorable dimers of 1,3-diethylalumolane: anti-SR- $\delta\lambda$ ($\Delta G = -34.3$ kJ/mol) and $S_{Al}R_{Al}SS-\delta\delta$ ($\Delta G = -30.1$ kJ/mol).

As follows from the theoretical data that was obtained, stereoisomers of dimers should predominantly exist at room temperature, in which bridging bonds are formed with the participation of the 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 non-bornen annelated alumolanes **12**–**16** [21]. The results are presented in Figure 5.

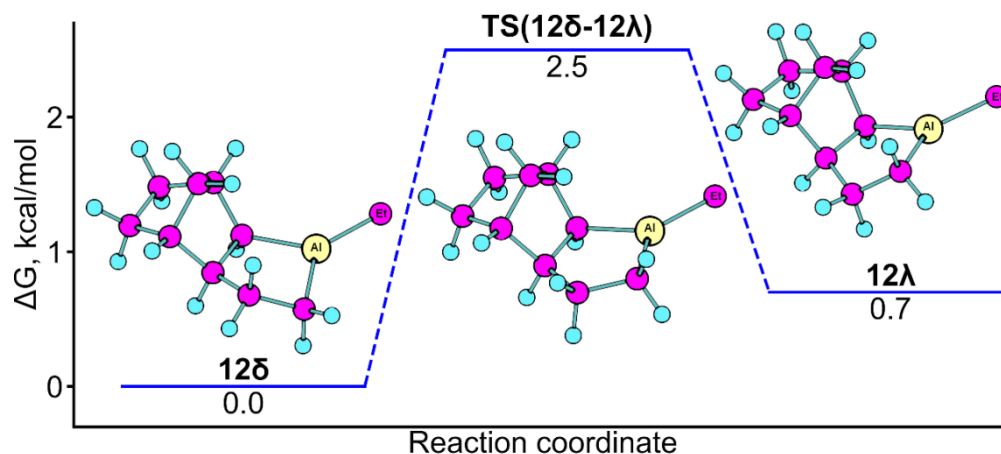


Figure 5. Conformational analysis of alumolane **12**.

As follows from Figure 5, conformations of alumolane *exo*-annelated with nonbornene were found on the potential energy surface of the molecule that differ in energy by 0.7 kcal/mol. Conformational dynamics are associated with the 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

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

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References

1. Dzhemilev, U.M.; Ibragimov, A.G.; Ermilova, O.E.; Sultanov, R.M.; Khalilov, L.M.; Kunakova, R.V.; Sharipova, A.Z. Method of Preparing 1-Chloro-trans-3,4-dialkyl Substituted Indium. Cyclopentanes. Patent RU2164227C2, 20 January 1999.
2. Schumann, H.; Just, O.; Seuß, T.D.; Görlitz, F.H.; Weimann, R. Intramolekular stabilisierte galla- und Indacyclohexane, -cyclopentane und -cyclopentene; Röntgenstrukturanalyse von $(\text{CH}_2)_5\text{Ga}(\text{CH}_2)_3\text{NM}$. *J. Organomet. Chem.* **1994**, *466*, 5–14. [\[CrossRef\]](#)
3. Cowley, A.H.; Corbelin, S.; Jones, R.A.; Lagow, R.J.; Nail, J.W. Synthesis and structure of $[(\text{CH}_2)_4\text{Ga}-\mu\text{-AstBu}_2]_2$. The first example of a gallacyclopentane. *J. Organomet. Chem.* **1994**, *464*, C1–C3. [\[CrossRef\]](#)
4. Ibragimov, A.G.; Khafizova, L.O.; Satenov, K.G.; Khalilov, L.M.; Yakovleva, L.G.; Rusakov, S.V.; Dzhemilev, U.M. Synthesis and transformations of metallacycles. *Russ. Chem. Bull.* **1999**, *48*, 1574–1580. [\[CrossRef\]](#)
5. Dzhemilev, U.M.; D'yakonov, V.A. Hydro-, carbo-, and cycloaluminum of unsaturated compounds. In *Modern Organoaluminum Reagents: Preparation, Structure, Reactivity and Use*; Woodward, S., Dagorne, S., Eds.; Springer Berlin Heidelberg: Berlin/Heidelberg, Germany, 2013; pp. 215–244.
6. D'yakonov, V.A. *Dzhemilev Reaction in Organic and Organometallic Synthesis*; Nova Science Publishers, Inc.: New York, NY, USA, 2010.
7. D'yakonov, V.A.; Makhamatkhanova, A.L.; Dilmukhametova, L.K.; Agliullina, R.A.; Tyumkina, T.V.; Dzhemilev, U.M. Catalytic cycloaluminum for the synthesis of norbornane-annulated phospholanes. *Organometallics* **2015**, *34*, 221–228. [\[CrossRef\]](#)
8. D'yakonov, V.A.; Makhamatkhanova, A.L.; Agliullina, R.A.; Dilmukhametova, L.K.; Tyumkina, T.V.; Dzhemilev, U.M. Aluminacyclopentanes in the synthesis of 3-substituted phospholanes and α,ω -bisphospholanes. *Beilstein J. Org. Chem.* **2016**, *12*, 406–412. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Khafizova, L.O.; Khusainova, L.I.; Tyumkina, T.V.; Dzhemilev, U.M. One-pot synthesis of borolanes by reaction of aluminacyclopentanes with $\text{BF}_3 \cdot \text{Et}_2\text{O}$. *Russ. J. Org. Chem.* **2012**, *48*, 755–760. [\[CrossRef\]](#)
10. Smith, M.B. The monomer–dimer equilibria of liquid aluminum alkyls: III. Trimethylaluminum: The monomer–dimer equilibria of liquid and gaseous trimethylaluminum and triethylaluminum. *J. Organomet. Chem.* **1972**, *46*, 31–49. [\[CrossRef\]](#)
11. Yamamoto, O. The Low Temperature NMR Spectrum of Triethylaluminum. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1125–1128. [\[CrossRef\]](#)
12. Yamamoto, O.; Hayamizu, K.; Yanagisawa, M. Bridge-terminal exchange of aluminum trialkyl dimers. *J. Organomet. Chem.* **1974**, *73*, 17–25. [\[CrossRef\]](#)
13. Ramey, K.C.; O'Brien, J.F.; Hasegawa, I.; Borchert, A.E. Nuclear Magnetic Resonance Study of Aluminum Alkyls. *J. Phys. Chem.* **1965**, *69*, 3418–3423. [\[CrossRef\]](#)
14. Dzhemilev, U.M.; Ibragimov, A.G.; Zolotarev, A.P.; Muslukhov, R.R.; Tolstikov, G.A. First preparative synthesis of alumocyclopentanes involving zirconium complexes. *Russ. Chem. Bull.* **1989**, *38*, 194–195. [\[CrossRef\]](#)
15. Muslukhov, R.R.; Khalilov, L.M.; Zolotarev, A.P.; Morozov, A.B.; Ibragimov, A.G.; Dzhemilev, U.M.; Tolstikov, G.A. Synthesis and conversions of metallocycles. 8. ^{13}C NMR spectra of aluminocyclopentanes. *Russ. Chem. Bull.* **1992**, *41*, 1646–1651. [\[CrossRef\]](#)
16. Dzhemilev, U.M.; Ibragimov, A.G. Regio- and stereoselective synthesis for a novel class of organoaluminum compounds—Substituted aluminacyclopentanes and aluminacyclopentenes assis. *J. Organomet. Chem.* **1994**, *466*, 1–4. [\[CrossRef\]](#)
17. Tyumkina, T.V.; Islamov, D.N.; Parfenova, L.V.; Khalilov, L.M.; Dzhemilev, U.M. Structure and conformations of 2-substituted and 3-substituted alumolanes in polar solvents: A direct NMR observation. *Magn. Reson. Chem.* **2016**, *54*, 62–74. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Benn, R.; Ruffiniska, A. High-Resolution Metal NMR Spectroscopy of Organometallic Compounds. *Angew. Chem. Int. Ed.* **1986**, *25*, 861–881. [\[CrossRef\]](#)
19. Wasano, T.; Agou, T.; Sasamori, T.; Tokitoh, N. Synthesis, structure and reactivity of a 1-bromoalumole. *Chem. Commun.* **2014**, *50*, 8148–8150. [\[CrossRef\]](#) [\[PubMed\]](#)
20. Stammler, H.-G.; Blomeyer, S.; Berger, R.J.F.; Mitzel, N.W. Trimethylaluminum: Bonding by Charge and Current Topology. *Angew. Chem. Int. Ed.* **2015**, *54*, 13816–13820. [\[CrossRef\]](#) [\[PubMed\]](#)
21. Tyumkina, T.V.; Idrisova, S.M.; Nurislamova, R.R.; Tullyabaeva, L.I. Multinuclear ^1H , ^{13}C , ^{27}Al and ^{31}P NMR spectroscopy in the study of the structure of the 3-spiro-substituted polycyclic borolanes, alumolanes and phospholanes. In Proceedings of the International Conferences “Modern Development of Magnetic Resonance” and “Spin Physics, Spin Chemistry, and Spin Technology”, Kazan, Russia, 25–30 September 2023.

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