Regio- and stereoselective synthesis for a novel class of organoaluminium compounds — substituted aluminacyclopentanes and aluminacyclopentenes assisted by zirconium catalysts

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Abstract

A novel regio- and stereoselective method has been developed for the catalytic cyclometallation of olefins and acetylenes with alkylalanes in the presence of Cp_2ZrCl_2, to give in one stage high yields of 3-substituted aluminacyclopentanes and aluminacyclopentenes. Applications of these reactions to a wide range of linear and cyclic olefins and to those containing functional substituents have been studied. The transformation of the aluminacyclopentanes thus produced, into five-membered heterocycles, mono- and di-substituted cyclobutanes and cyclopropanes, has been demonstrated.

Key words: Alumina; Cyclopentane; Zirconium; Catalysis

Previously it was considered that the reactions of organoaluminium compounds (OAC) and olefins that are catalyzed by transition metals were essentially preliminaries to hydroaluminations with $LiAlH_4$ [1–4], $^iBu_2AlH$ [5–8], $(R_2N)_2AlH$ [9–11], $HAlCl_2$ [12], $^iBu_3Al$ [13], $^iBu_2AlCl$ [14,15] and to carbalumination with Et_2AlCl [16–18]. Organoaluminium compounds also appeared to be co-catalysts in reactions of olefin oligomerization and polymerization [19–22]. There was no literature on other types of catalytic transformations with OAC and olefins when we began our investigations.

We have found a novel route for the synthesis of aluminium-containing heterocycles, in particular aluminacyclopentanes (ACP), in the presence of Zr-containing catalysts. It is no exaggeration to state that the newly discovered catalytic reaction is a major achievement in organoaluminium chemistry on the scale of the last 15–20 years, as it permits synthesis of five-membered organoaluminium heterocycles with high regio- and stereoselectivity, which can hardly be synthesized by any other method.

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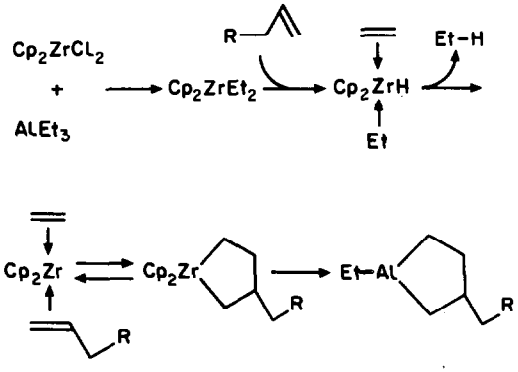
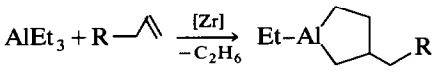
We proceeded from the assumption that low-valent zirconium complexes (zirconocene), formed from Cp_2ZrCl_2 and trialkylalanes in the course of the reaction, can be reacted with olefins according to the general pattern of intramolecular cyclometallation to give suitable zircona cyclopentanes [23–25]. The latter can react in the remetallation with an excess of alkylalane thus being transformed into aluminacyclopentanes according to the following scheme:



Suitable 3-alkylsubstituted aluminacyclopentanes **I** were found to be formed in 80–95% yields in the

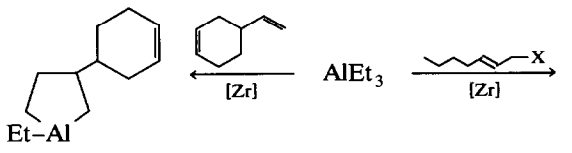
interaction of $AlEt_3$ with α-olefins (1-hexene, 1-octene, 1-undecene) in the presence of 2 mol% Cp_2ZrCl_2 at room temperature for 6–8 h with elimination of an equimolar amount of ethane.



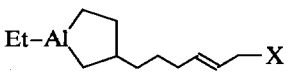
(Ia–c)

R = H–C_3H_7 (a), H–C_5H_{11} (b), H–C_8H_{17} (c)

A high selectivity for formation of only 3-substituted aluminacyclopentanes is a distinguishing feature of that reaction. The reaction was shown to apply to a rather wide range of α-olefins with alkyl, alkenyl, aryl substituents as well as of O-, N-, and S-containing functional groups. The scheme described considers that olefins react with $AlEt_3$ only by a monosubstituted double bond. From a series of olefins with disubstituted C=C bonds the only ones to be reactable are those in which the bonds are sufficiently activated, for example, norbornene and some of its derivatives.



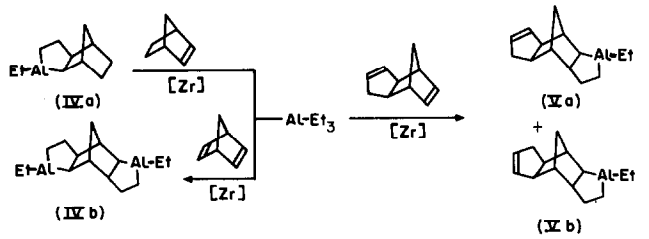
(II)



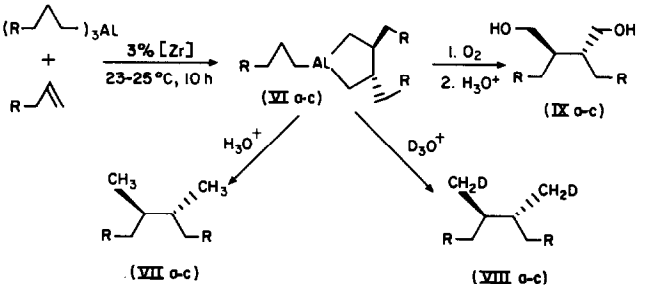
(IIIa–d)

X = NEt_2 (a), OCH_3 (b), OH (c), SBu (d)

The polycyclic Al-containing compounds of the following structure (IV, V) were synthesized from norbornene, norbornadiene and dicyclopentadiene.

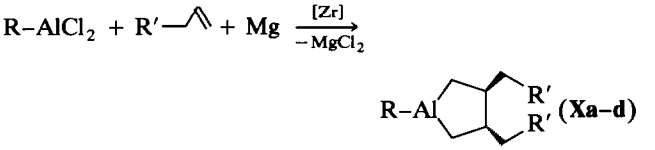


trans-3,4-Dialkylsubstituted aluminacyclopentanes (VI) were selectively formed (50–75% yields) in the cycloalumination discussed, when $AlEt_3$ was substituted by the highest tri(n-alkyl)alanes. Stereoconfiguration of the alkyl substituents was determined by ^{13}C NMR spectroscopy as well as by identification of hydrolysis (VII), deuterolysis (VIII), and oxidation (IX) products of the ACP initiated.



R = C_3H_7 (a), C_5H_{11} (b), C_8H_{17} (c)

We then developed an alternative approach to a synthesis of *trans*-3,4-dialkylaluminacyclopentanes based on the reaction of α-olefins with $AlEtCl_2$ in the presence of metallic magnesium and catalytic amounts (5 mol%) of Cp_2ZrCl_2 or $ZrCl_4$. Similarly, $AlCl_3$, $RO–AlCl_2$ and $R_2N–AlCl_2$ may all be involved in cycloalumination. N-, O-, Cl-containing *trans*-3,4-dialkylaluminacyclopentanes (X b–d) were all formed (70–90% yield) from halogenealanes, powdered Mg and a suitable α-olefin in TGF solution.

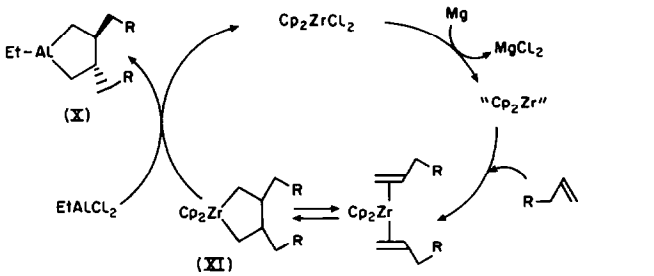


(Xa–d)

R = Et (a), Cl (b), C_4H_9O (c), Et_2N (d);

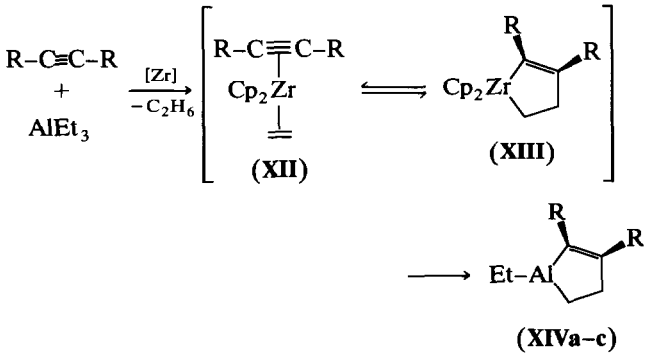
R′ = C_3H_7, C_5H_{11}, C_9H_{19}, Ph

A possible mechanism for the catalytic cycloalumination of α-olefins with $RAlCl_2$ includes, as we have considered, the generation of "Cp_2Zr" from Cp_2ZrCl_2 [26,27]. The subsequent coordinating and oxidative addition of olefin to "Cp_2Zr" give zirconium cyclopentane intermediate XI. Remetallation of XI with the formation of 3,4-dialkylsubstituted aluminacyclopentanes X is a final stage.



Subsequent experiments have found that disubstituted acetylenes could be involved in the cycloalumination with $AlEt_3$, catalyzed by Cp_2ZrCl_2. A study of the main regularities of the reaction encourages the proposal that a key stage of cycloalumination is the generation of zirconocene XII with the further formation of

zirconiumcyclopentene **XIII**. *cis*-2,3-Dialkyl(phenyl)-aluminacyclopent-2-enes **XII** of 75–90% yield, not previously described, were prepared by the cycloalumination of disubstituted acetylenes with an excess of $AlEt_3$ in the presence of 3–5% Cp_2ZrCl_2 at room temperature for 10–12 h, with high regio- and stereoselectivity. The reaction was followed by elimination of an equimolar amount of ethane. The reaction does not proceed in the absence of a catalyst. The reported reaction [28,29] of carbalumination of acetylenes with R_3Al is carried out in halogen-containing solvents (CH_2Cl_2, $ClCH_2CH_2Cl$).

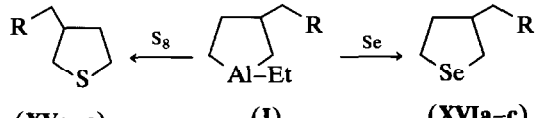


(XIVa–c)

R = Ph (**a**), C_3H_7 (**b**), C_4H_9 (**c**)

We consider that cycloaluminations of α-olefins and disubstituted acetylenes lead naturally to a novel approach to a catalytic synthesis of aluminium-containing heterocycles.

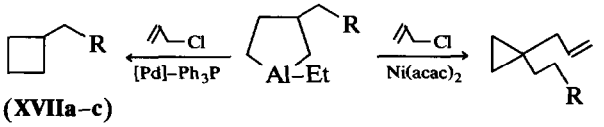
The properties of aluminacyclopentanes have been poorly studied due to the difficulty of their preparation. The first investigations of reactivity of synthesized aluminacyclopentanes have shown them to be one of the most interesting organoaluminium compounds with considerable practical value. For example, when heated in benzene (80°C, 6 h), with elemental sulfur and selenium in a 1:3 ratio, 3-alkylsubstituted aluminacyclopentanes produce 3-substituted tetrahydrothiophenes **XV** and selenofenes **XVI** in 60–85% yields with high selectivity.



(XVa–c) **(I)** **(XVIa–c)**

R = C_3H_7 (**a**), C_4H_9 (**b**), C_7H_{15} (**c**)

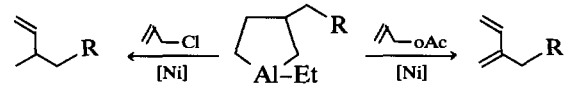
Aluminacyclopentanes behave in catalyzed reactions with allylhalogenides in different ways from trialkylalanes. The interaction of allylchloride and **I** in a mole ratio of 3:1, respectively, in ether solution in the presence of 5 mol% of catalytic $Pd(acac)_2$–Ph_3P (6–8 h, 0–20°C) gives alkylsubstituted cyclobutanes **XVII**. The substitution of the phosphine complex of Pd to $Ni(acac)_2$ under analogous conditions leads to 1,1-disubstituted cyclopropanes **XVIII**. An equimolar amount of propylene is eliminated in the course of the reaction.



(XVIIa–c) **(XVIIIa–c)**

R = C_3H_7 (**a**), C_5H_{11} (**b**), C_8H_{17} (**c**)

The study of catalytic transformation of disubstituted aluminacyclopentanes **I** in the presence of allylic compounds led to the development of a novel regioselective method of reducing β-vinylation of α-olefins. 3-methyl-1-alkenes **XIX** were found after hydrolysis of the reaction mass to be formed by the reaction (for 10 h at 20°C) of **I** with a three-fold excess of allylchloride in hexane catalyzed by 5 mol% $Ni(acac)_2 + Ph_3P + {}^iBu_2AlH$ (1:4:8). The substitution of allylchloride to allylacetate under analogous conditions leads to suitable 2-alkyl-1,3-dienes **XX** in *ca.* 85% yield.



(XIXa–c) **(XXa–c)**

R = C_3H_7 (**a**), C_4H_9 (**b**), $C_{13}H_{27}$ (**c**)

The development of novel syntheses of aluminacyclopentanes and of their further transformations is under study. We wish to make progress in that direction, which is of scientific and practical interests.

1. Experimental details

Cycloalumination of olefins and acetylenes was carried out under argon. The compounds obtained were analyzed by a Chrom-5 chromatograph in an He current, 1200 × 3 mm column packed with 5% of SE-30 and 15% of PEG-6000 on Chromosorb N-AW. ^{13}C-NMR spectra of aluminacyclopentanes were recorded on Jeol-FX 90 Q (22.5 MHz) and Bruker AM-300 (^{13}C-75,46 MHz, ^1H-300 MHz) spectrometers in regimes of complete and off-resonance decoupling of protons. The diluted solutions were used in absolute Et_2O with the addition of C_6D_6 for the internal stabilization of a field. TMC is the internal standard.

1.1. Synthesis of 1-ethyl-3-alkylaluminacyclopentanes (I)

Cp_2ZrCl_2 (0.0524 g, 0.2 mmol), $AlEt_3$ (1.368 g, 12 mmol), followed by α-olefins (1-hexene, 1-octene, 1-undecene) (10 mmol) were put into a glass reactor (50 ml) equipped with a magnetic stirrer, under inert gas. The mixture was stirred at room temperature for 6–8 h.

1-ethyl-3-butylaluminacyclopentane (1a) was individually isolated by vacuum rectification.

1.2. Synthesis of 1-ethyl-trans-3,4-dialkyl-aluminacyclopentanes (Xa)

Cp_2ZrCl_2 (0.0876 g, 0.3 mmol), magnesium powder (0.24 g, 10 g atom), olefin (20 mmol), TGF (15 ml) and $EtAlCl_2$ (1.27 g, 10 mmol) were put into a reactor at 0°C under argon. The mixture was warmed to room temperature (23–25°C) and stirred for 10 h.

1.3. Synthesis of 1-chlor-trans-3,4-dialkylaluminacyclopentanes (Xb)

Cp_2ZrCl_2 (0.0876 g, 0.3 mmol), magnesium powder (0.24 g, 10 g atom), α-olefin (20 mmol), TGF (15 ml) and $AlCl_3$ (1.34 g, 10 mmol) were put into a reactor at 0° under argon. The mixture was warmed to room temperature and stirred for 10 h.

1.4. Synthesis of 1-butoxy-trans-3,4-dialkylaluminacyclopentanes (Xc)

Cp_2ZrCl_2 (0.3 mmol), magnesium powder (10 g atom), olefin (20 mmol), TGF (10 ml), butoxyaluminiumchloride (10 mmol), and $EtAlCl_2$ (10 mmol) and BuOH previously mixed in 5 ml of TGF were put into a reaction under argon. The reaction mass stirred at room temperature for 8–10 h.

1.5. Synthesis of 1-ethyl-cis-2,3-dibutylaluminacyclopent-2-ene (XIV)

Cp_2ZrCl_2 (0.146 g, 0.5 mmol), $AlEt_3$ (2.85 g, 25 mmol) and disubstituted acetylene (10 mmol) were put into a reactor under argon. The mixture was stirred at room temperature for 10 h.

1.6. Synthesis of 3-methyl-1-alkene (XIX)

Cp_2ZrCl_2 (0.0524 g, 0.2 mmol), $AlEt_3$ (1.368 g, 12 mmol), then α-olefin (10 mmol) were put into a reactor under argon. The mixture was stirred at room temperature for 10 h, cooled to 0°C, and then the following were added in sequence, allylchloride (36 mmol), catalyst prepared by previous mixing of $Ni(acac)_2$ (0.1285 g, 0.5 mmol), PPh_3 (0.524 g, 2 mmol), and i-Bu_2AlH (0.568 g 4 mmol) in 2 ml hexane. The mixture was stirred at room temperature for 10 h. The reaction was followed by propylene isolation. The reaction mass was treated with 5% HCl at 0°C, and extracted by ether. The target product was isolated by vacuum rectification.

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