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Regio- and Stereo-selective Synthesis of *trans*-3,4-Dialkyl-substituted Aluminacyclopentanes in the Presence of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$

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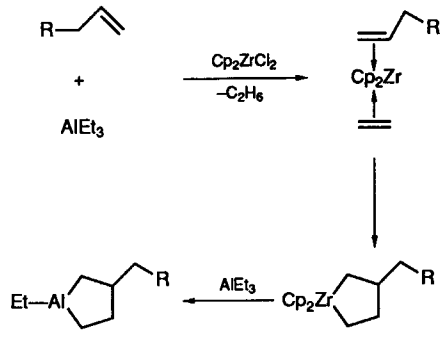
A novel cycloalumination of terminal alkenes using organoaluminium alkyls and halides in the presence of catalytic amounts of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ has been developed, giving *trans*-3,4-dialkyl-substituted aluminacyclopentanes in one stage.

An efficient method for the synthesis of a new class of organoaluminium compounds (OACs), 3-alkyl-substituted aluminacyclopentanes (ACPs), based on the cycloalumination of terminal alkenes with $AlEt_3$ in the presence of catalytic amounts of Cp_2ZrCl_2 ($Cp = \eta^5\text{-}C_5H_5$) was reported recently.[1,2] According to ref. 1, cyclometallation of the alkenes was carried out *via* the formation of zirconacyclopentane intermediates (Scheme 1). This reaction was studied for linear and cyclic mono- and di-alkenes. In relation to Scheme 1, we thought that the introduction of $AlEt_3$ into the reaction, along with other OACs and long-chain terminal alkenes, should enable substituted ACPs of various structures to be synthesized.

Therefore, in order to broaden the application of ACPs, to develop novel syntheses of OACs and to elucidate the possibility of insertion into the reaction of long-chain OAC and unsaturated compounds, we have investigated the interaction of OACs of the AlR_3, $EtAlCl_2$, RO—$AlCl_2$ and R_2N—$AlCl_2$

Mendeleev Commun., 1992, 2(1), 26–28



Scheme 1

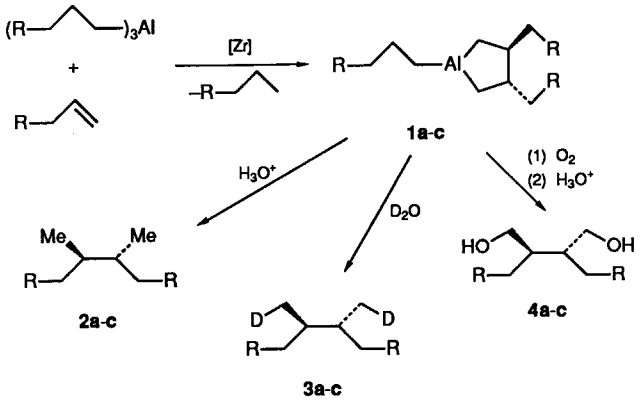
type with terminal alkenes. Cp_2ZrCl_2 was used as a catalyst, having the highest activity and selectivity in alkene cycloalumination with $AlEt_3$.[1,2]

Disubstituted ACPs **1a–c** were formed (Scheme 1) by the cycloalumination of hex-1-ene, oct-1-ene and undec-1-ene, using $(C_6H_{13})_3Al$, $(C_8H_{17})_3Al$ and $(C_{11}H_{23})_3Al$, respectively, in the presence of 5 mol% Cp_2ZrCl_2 in hydrocarbon solvents (20–25 °C, 10–12 h) in 55–80% yields.†

The pairwise coincidence of the signals from the carbon atoms in the cyclopentane ring and also the pairwise equivalence of the alkyl substituents were confirmed by ^{13}C NMR spectra of ACPs **1a–c**, thus demonstrating the formation of symmetric 3,4-dialkyl-substituted aluminacyclopentanes under the conditions of our experiments.

Taking into account the fact that 3,4-disubstituted ACPs, containing two chiral centres at C^3 and C^4, can coexist in the form of two geometric isomers with *cis*- and *trans*-positions of the alkyl substituents in the five-membered metallocycle, we have calculated conformation energies for these isomers using the molecular mechanics method MM2. It has been established that two degenerate conformations of an envelope form, with the Al atom out of the plane of the metallocycle, and in which the substituents have a *trans*-configuration (Fig. 1) is energetically more favourable for ACPs **1a–c**.

The ^{13}C NMR spectra of products of hydrolysis and deuterolysis of aluminacyclopentanes **1a–c** showed that the formation



a; R = Pr
b; R = C_5H_{11}
c; R = C_8H_{17}

Scheme 2

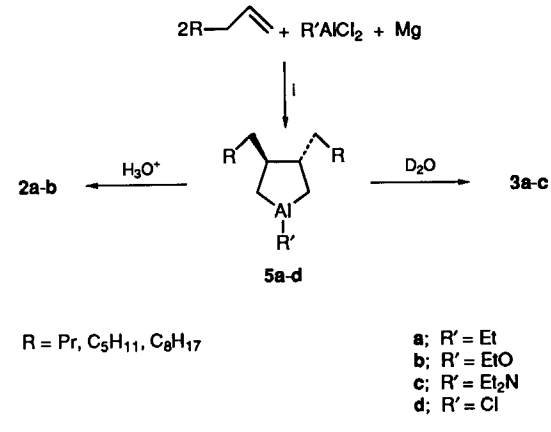
Fig. 1

of exclusively *threo*-dimethylalkanes **2a–c** or dideuteriodimethylalkanes **3a–c** was observed. The oxidation of ACPs **1a–c** by molecular O_2 led to *threo*-butane-1,4-diols **4a–c**. On the basis of the results obtained, **1a–c** were identified as 1-alkyl-*trans*-3,4-dialkyl-substituted ACPs.

Taking into account the fact that 'Cp_2Zr' is a key intermediate in the synthesis of ACPs, according to Scheme 1, we have developed an efficient approach to the generation of zirconium *in situ*, differing from those known,[6-9] *via* reduction of Cp_2ZrCl_2 using active Mg in the presence of organoaluminium halides, terminal alkenes and metallic magnesium. As a result, 1-ethyl-, 1-alkoxy-, 1-amino- and 1-halogeno-3,4-dialkyl-substituted aluminacyclopentanes **5a–d** were synthesized by the reaction of $EtAlCl_2$, $EtOAlCl_2$, $Et_2N—AlCl_2$ and $AlCl_3$, respectively, with hex-1-ene, oct-1-ene and undec-1-ene in a ratio of 1:2 at 20–25 °C for 6–8 h (Scheme 3).‡

Hydrolysis or deuterolysis of ACPs **5a–d** prepared by this method, as observed with ACPs **1a–c**, gave rise to the corresponding hydrocarbons **2a–c** and **3a–c** with exclusively *threo*-configurations, showing that the alkyl substituents of the ACPs formed are in a *trans*-configuration.

Determination of the structure of the synthesized ACPs, isolation and identification using ^{13}C NMR and a control synthesis of the intermediate zirconacyclopentanes, formed during the interaction of $AlEt_3$ with Cp_2ZrCl_2 and α-alkenes or of Cp_2ZrCl_2 with Mg and terminal alkenes, allows us to propose a possible scheme for the formation of 3,4-disubstituted ACP molecules (Scheme 4). The first step is the generation of 'Cp_2Zr' from Cp_2ZrCl_2. Subsequent coordination of the alkene at the central atom of a catalyst molecule leads to a π-complex of type **6**, followed by intramolecular oxidative coupling, gives the corresponding zirconacyclopentane **7**. Remetallation of the latter proceeds to form the ACP under the reaction conditions.



R = Pr, C_5H_{11}, C_8H_{17}

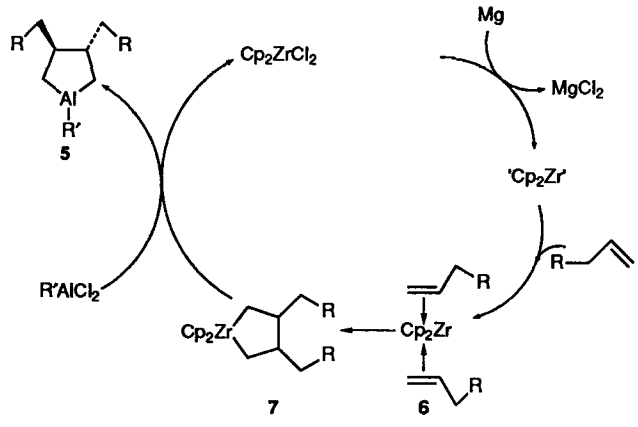
a; R′ = Et
b; R′ = EtO
c; R′ = Et_2N
d; R′ = Cl

Scheme 3 *Reagents and conditions:* i, Cp_2ZrCl_2 (5 mol%), THF, 20 °C, 8 h, 70–85%

† Into a glass reactor (50 ml) equipped with a magnetic stirrer, 0.146 g (0.5 mmol) of Cp_2ZrCl_2, tris(n-octyl)aluminium, prepared from 2.38 g (12 mmol) of Bu^i_3Al and 4.0 g (36 mmol) of oct-1-ene,[3] were loaded in hexane under dry argon. 1.12 g (10 mmol) of oct-1-ene was then added and the resulting solution was stirred for 10 h at room temperature (23–25 °C). Acid hydrolysis (5% HCl) of the reaction mixture led to 7,8-dimethyltetradecane in a yield of 1.55 g (69%).

‡ Into a glass reactor (50 ml), equipped with a magnetic stirrer, 0.146 g (0.5 mmol) of Cp_2ZrCl_2, 0.288 g (12 mmol) of magnesium powder, 20 mmol of the corresponding α-alkene, 15 ml tetrahydrofuran (THF) and 1.61 g (12 mmol) of $AlCO_3$ were loaded under dry argon at 0 °C. The temperature was raised to room temperature (23–25 °C) and the resulting solution was stirred for 10 h. Thus, 1-chloro-*trans*-3,4-dialkylsubstituted aluminacyclopentanes **5d** were prepared in ~80% yield.

Mendeleev Commun., 1992, 2(1), 26–28



Scheme 4

Therefore, we have developed a regio- and stereo-selective method for catalytic cycloalumination of terminal alkenes, organoaluminium alkyls and halides in the presence of zirconium complexes. This provides a promising new way to synthesize a class of OAC-*trans*-3,4-dialkyl-substituted alumina-cyclopentanes which have not been described previously.

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