The first example of synthesis of aluminacyclopropanes catalysed by $(\eta^5\text{-}C_5H_5)_2TiCl_2$

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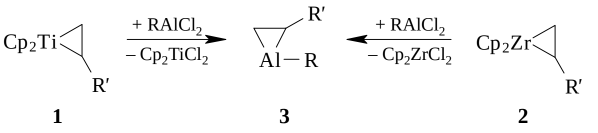
The synthesis of a series of cyclic organoaluminium compounds, aluminacyclopropanes, which have never previously been described, has been carried out by α-olefin cyclometallation with $EtAlCl_2$ in the presence of a chlorine ion acceptor, metallic magnesium and Cp_2TiCl_2 ($Cp = \eta^5\text{-}C_5H_5$) catalyst.

Recently we have developed regio- and stereoselective methods to synthesize aluminacyclopentanes,[1–7] aluminacyclopent-2-enes[8,9] and 1,4-dialuminium compounds[10] using zirconium catalysts. The reactions were assumed to proceed in the presence of zirconium-containing metallacycles as key intermediates.

To extend the study on the catalytic cyclometallation of olefins by alkylalanes to five-member organoaluminium compounds (OAC) and to understand the possibilities of applying this approach to the synthesis of aluminacyclopropanes we have studied the cyclometallation of α-olefins with $EtAlCl_2$–Mg reagent in the presence of Cp_2TiCl_2 catalyst.

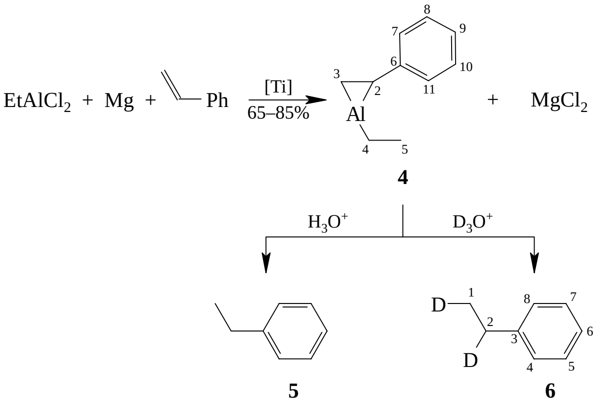
The catalyst for cycloalumination of α-olefins to cyclic OAC were chosen in the expectation that titana- **1** or zircona-cyclopropane **2** intermediates[11–15] generated *in situ* would be transmetallated with $EtAlCl_2$ to give substituted alumina-cyclopropanes **3**.



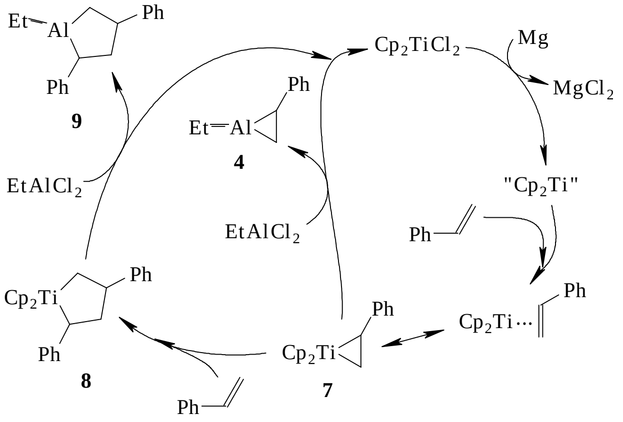
To confirm the supposition proposed, we have studied the cyclometallation of styrene by $EtAlCl_2$–Mg effected by Cp_2ZrCl_2 and Cp_2TiCl_2 with high selectivity and catalytic activity in reactions of hydro-, carbo- and cyclo-metallization of olefins.[3,16–18]

As a result we have found that Cp_2ZrCl_2 (under the chosen conditions) promoted the generation of aluminacyclopentanes,[5] whereas Cp_2TiCl_2 directed the reaction towards formation of aluminacyclopropanes. Thus, 1-ethyl-2-phenylaluminacyclopropane **4** was formed in the interaction of styrene with equimolar amounts of $EtAlCl_2$ and Mg (powder) in the presence of catalytic amounts of Cp_2TiCl_2 (3–5 mol%) in THF for 6–8 h at room temperature (22–23 °C) in 65–85% yield. The latter was isolated by distillation under reduced pressure in an inert atmosphere The product was colourless, readily decomposed in air and was stable in an inert atmosphere. Each experiment gave 5–10% of 1-ethyl-2,4-diphenylaluminacyclopentane together with **4**.[†]

Ethylbenzene **5** was formed in the hydrolysis of the reaction mixture by 5% HCl, and 1,2-dideuterioethylbenzene **6** was formed in deuteriolysis, the latter being identified by spectral methods. The structure of **4** was confirmed by NMR spectroscopy.[‡] The ^{13}C NMR spectrum of **4** contains two pairs of broaded signals in the high field region. A wide triplet signal at 1.80 ppm and a quartet signal at 9.20 ppm might be assigned to the ethyl group on the aluminium atom. Methylene and methyne carbon atoms of the aluminacyclopropane fragment had an intense broadened triplet at 1.50 ppm and a doublet at 9.92 ppm.



According to the literature data and our experimental results we suppose that titanacyclopropane **7** was formed initially in the cycloalumination reaction under the chosen conditions and that it was then transmetallated with $EtAlCl_2$ to give **4**. Subsequent incorporation of a styrene molecule into **7** with respect to the Ti–C bond gave titanacyclopentane **8**. Transmetallation of the latter with the initial $EtAlCl_2$ was found to promote formation of a minor (5–10%) product **9**.

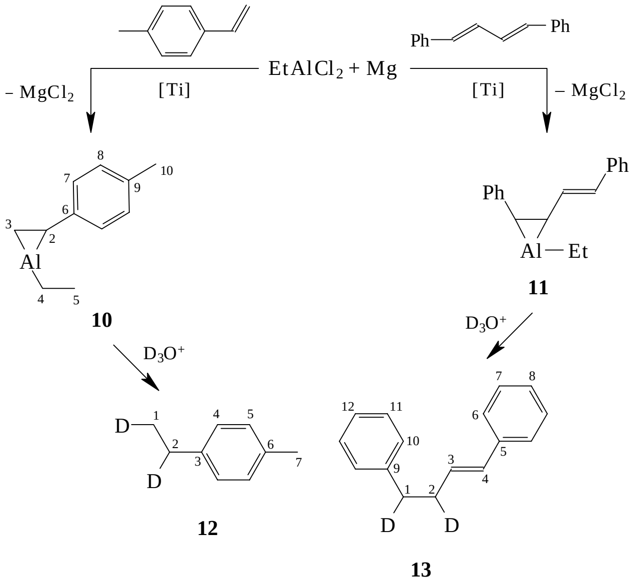


[†] A 50 ml flask equipped with a magnetic stirrer under dry argon at 0 °C was charged with styrene (1.04 g, 10 mmol), THF (10 ml), Mg powder (0.288 g, 12 mmol), Cp_2TiCl_2 (0.10 g, 0.5 mmol) and $EtAlCl_2$ (1.524 g, 12 mmol), and the temperature was increased to room temperature (22–23 °C). The reaction mixture was stirred for 8 h, then treated with 5% HCl or DCl/D_2O.

[‡] *Spectral data* for 1-ethyl-2-phenylaluminacyclopropane **4**: ^{13}C NMR (C_6D_6, 22.5 MHz, Jeol FX 90Q) δ: 1.50 (br. t, C^3), 1.80 (br. t, C^4), 9.20 (q, C^5), 9.92 (br. d, C^2), 126.44 (d, C^9), 128.53 (d, C^8, C^{10}), 129.12 (d, C^7, C^{11}), 137.73 (s, C^6).

For 1,2-dideuterioethylbenzene **6**: ^1H NMR ($CDCl_3$, 300 MHz, Bruker AM300) δ: 1.16 (d, CH_2D, $^3J_{H-H}$ 7.6 Hz), 2.57 (t, CHD, $^3J_{H-H}$ 7.6 Hz), 7.02–7.24 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$, 75 MHz, Bruker AM300) δ: 15.35 (t, C^1, J_{C-D} 22.0 Hz), 28.57 (t, C^2, J_{C-D} 22.0 Hz), 125.65 (C^6), 127.90 (C^4, C^8), 128.37 (C^5, C^7), 144.23 (C^3).

To extend the field of application of styrene cycloalumination to **4** under the chosen conditions (5 mol% of Cp_2TiCl_2, THF, 22–23 °C, 8 h) we carried out cycloalumination of *p*-methylstyrene and 1,4-diphenylbuta-1,3-diene with $EtAlCl_2$ to give aluminacyclopropanes **10** and **11** in 80% yield.



The structures of **10** and **11** were confirmed by spectral methods and deuteriolysis of the latter to hydrocarbons **12** and **13**.[§]

Cycloalumination of alkyl-, cycloalkyl- and Si- and Sn-containing α-olefins effected by Cp_2TiCl_2 will be discussed in future publications.

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[§] *Spectral data* for **10**: ^{13}C NMR (C_6D_6, 22.5 MHz, Jeol FX 90Q) δ: 10.03 (br. d, C^2), 2.63 (br. t, C^3), 1.59 (br. t, C^4), 9.84 (q, C^5), 135.24 (s, C^6), 128.06 (d, C^7), 128.52 (d, C^8), 136.30 (s, C^9), 21.03 (q, C^{10}).

For **12**: ^{13}C NMR ($CDCl_3$, 75 MHz, Bruker AM300) δ: 15.52 (t, C^1, J_{C-D} = 19.05 Hz), 28.13 (t, C^2, J_{C-D} = 19.05 Hz), 141.22 (s, C^3), 127.82 (d, C^4), 129.06 (d, C^5), 135.04 (s, C^6), 21.04 (q, C^7).

For **13**: ^{13}C NMR ($CDCl_3$, 75 MHz, Bruker AM300) δ: 35.63 (t, C^1, J_{C-D} = 19.60 Hz), 34.55 (t, C^2, J_{C-D} = 19.60 Hz), 129.71 (d, C^3), 126.88 (d, C^4), 137.59 (s, C^5), 130.34 (d, C^6), 128.41 (d, C^7), 125.84 (d, C^8), 141.55 (s, C^9), 128.41 (d, C^{10}, C^{11}), 125.96 (d, C^{12}).

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