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Synthesis and transformations of metallacycles
23.* Cp_2TiCl_2-Catalyzed cyclometallation of fullerene C_{60} with $EtAlCl_2$

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1-Ethyl-2,3-fullerenoaluminacyclopropanes $(EtAl)_n(\eta^2\text{-}C_{60})$ were synthesized by the reaction of fullerene C_{60} with an excess of $EtAlCl_2$ in the presence of Mg and using Cp_2TiCl_2 as the catalyst in a THF—toluene solution at ~20 °C. Deuterolysis of fullerenoaluminacyclopropanes afforded a mixture of deuteriofullerenes $C_{60}D_m$, where m = 6—12.

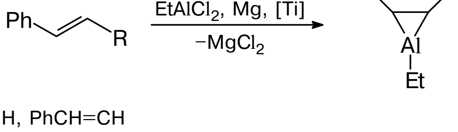
Key words: catalysis, organoaluminum compounds, fullerenes, cyclometallation, hydrolysis, deuterolysis.

Recently, fullerene C_{60} has been subjected to catalytic cyclometallation with an excess of $AlEt_3$ in the presence of Cp_2ZrCl_2 to form 2,3-fullerenoaluminacyclopentanes in a total yield of ~80%.[2]

As part of continuing studies of cyclometallation of carbon clusters and in an attempt to develop promising procedures for the synthesis of organometallic derivatives of fullerene C_{60}, we studied for the first time the reaction of C_{60} with $EtAlCl_2$ in the presence of Ti-containing complex catalysts with the aim of preparing cluster compounds containing aluminacyclopropane fragments.

The reaction was carried out under conditions of cycloalumination of arylalkenes studied previously[3] with the use of $EtAlCl_2$ in the presence of Cp_2TiCl_2 as the catalyst. The reaction gave rise to substituted aluminacyclopropanes (ACP) according to Scheme 1.

Scheme 1



R = H, PhCH=CH

It appeared that the reaction of C_{60} with an excess of $EtAlCl_2$ [C_{60} : [Al] = 1 : (60 : 300)] in the presence of Cp_2TiCl_2 as the catalyst (0.3—1 mol.% with respect to [Al]) in a toluene—THF solution (20—22 °C, 12 h) afforded C_{60}-containing organoaluminum compounds (OAC) (**1**). The conversion of the starting fullerene was 80—95% (according to the data from HPLC of deuterolysis products). Studies of the reaction mixture by ^1H NMR spectroscopy demonstrated that methylenated fullerenes $C_{60}(CH_2)_k$ (**2**) were present along with polyhydrofullerenes $C_{60}H_m$ (m = 6—12) among the hydrolysis products of OAC **1** as evidenced by high-field multiplet signals at δ 1.03—2.83 with the maxima at δ 1.06, 1.14, 1.25, 2.17, 2.26, 2.41, 2.52, 2.60, 2.68, and 2.70. With the aim of searching for optimum conditions for selective cycloalumination of C_{60}, we studied the effects of the reaction conditions, the reagent ratio, and the concentration of the catalyst on the yield and compositions of the reaction products of fullerene C_{60} with $EtAlCl_2$ in the presence of the catalyst Cp_2TiCl_2 in a toluene—THF mixture.

We found that the total yield of by-products, *viz.*, methylenated fullerenes $C_{60}(CH_2)_k$, depended only slightly on the reaction conditions, while it depended to a greater extent on the mode of workup of the reaction mixture after completion of cycloalumination. In particular, the yields of methylenated fullerenes **2** upon hydrolysis of OAC **1** with 10% HCl in the light without prior removal of THF from the reaction mixture was the higher the longer was the time of contact of hydrofullerenes (**3**) resulted from hydrolysis of OAC **1** with the initial solvent (toluene+THF). On the other hand, if the reaction of compound **1** with 10% HCl was carried out

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* For Part 22, see Ref. 1.

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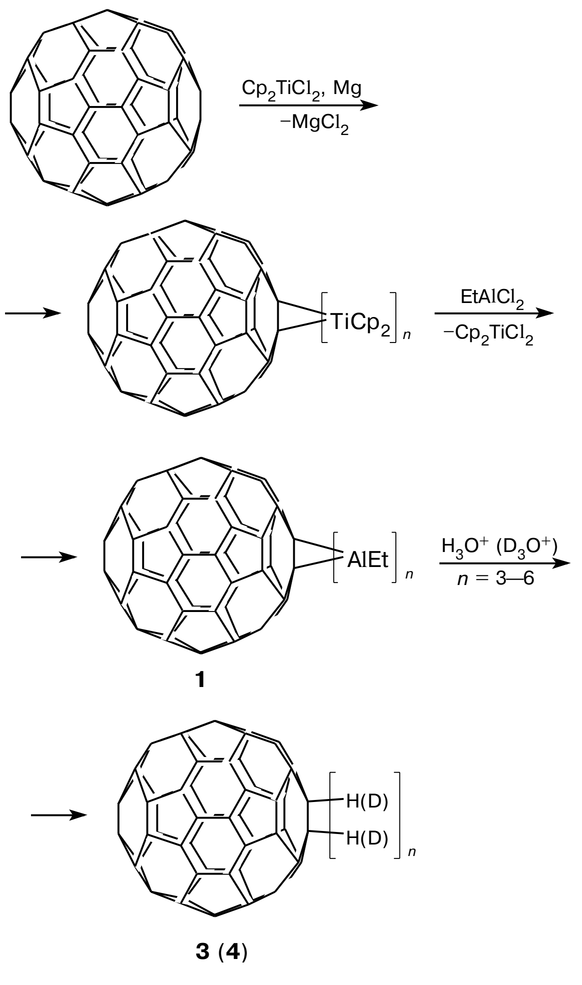
under an atmosphere of an inert gas in the dark and THF was rapidly removed from the reaction mixture, methylenated fullerenes **2** were not virtually formed. These results suggest that under conditions of hydrolysis of OAC **1**, hydrofullerenes **3** react with THF under the action of light and atmospheric oxygen to yield methylenated derivatives **2**. Actually, the formation of methylenated fullerenes **2** was observed in the reaction of a mixture of hydrofullerenes **3** with THF. The yields of fullerenes **2** increased as the reaction time was increased. Our suggestions were supported by the data[4] on the ability of hydrofullerenes to cleave the THF molecule giving rise to reactive methylene fragments $(CH_2)_k$, which add to fullerene C_{60}. According to the data published previously,[5] methylenated derivatives of C_{60} were also formed upon boiling of C_{60} in THF.

In this connection, all subsequent experiments, hydrolysis (deuterolysis) of the reaction mixture, and isolation of the target products were performed under an atmosphere of argon in the dark and the solvents were evaporated *in vacuo*. Hydrogenated (deuterated) fullerenes **3** and **4** were identified by ^1H NMR and IR spectroscopy and negative-ion mass spectrometry (the resonant electron capture $E_e \approx 0$ eV).

Scheme 2



The negative-ion mass spectrum of deuterolysis products **4** measured at 325 °C and $E_e \approx 0$ eV contains lines with the following values of m/z (I_{rel} (%)): 720 $[C_{60}]$ (45), 732 $[C_{60}D_6]$ (40), and 744 $[C_{60}D_1]$ (100), which indicates that fullerenes with three or six aluminacyclopropane fragments were formed under the reaction conditions. In the ^1H NMR spectrum, the signals of hydrogenated fullerenes **3** are observed in a broad region (δ 3.20—7.10) with the maxima at δ 3.57, 4.90, 5.76, 5.84, 6.26, 6.43, 6.65, and 7.06. The IR spectra of hydrolysis products **3** have bands in the C—H stretching vibration region at 2925 and 2855 cm^{-1}, which is typical of fullerene hydrides.[6]

We failed to identify signals for nonequivalent sp^2-hybridized C atoms in the ^{13}C NMR spectra of a mixture of hydrogenated (deuterated) fullerenes **3** (**4**) due to their substantial splitting.

It can be suggested that 1-ethyl-2,3-fullerenoaluminacyclopropanes **1** are formed *via* 2,3-fullerene-substituted titanacyclopropane intermediates $Cp_2Ti(\eta^2\text{-}C_{60})$ generated *in situ*. Transmetallation of the latter with the starting reagent $EtAlCl_2$ afforded metal-containing clusters **1** according to the scheme which we have proposed previously.[3] Recently, $CpTi(\eta^2\text{-}C_{60})$ has been synthesized[7] and its structure has been established, which is an additional supporting evidence for the scheme of titanium(zirconium) → aluminum transmetallation proposed previously.[3]

Experimental

HPLC analysis of hydrolysis and deuterolysis products was performed on a Hewlett—Packard chromatograph (model 1050) equipped with a UV detector at $\lambda = 254$ nm. Separation was carried out on a metal column (250×3 mm) with Diasorb 130 (8 μm) modified with cyanodecyl groups as the sorbent. Hexane was used as the elunet (the flow rate was 0.2 mL min^{-1}). The ^1H and ^{13}C NMR spectra were recorded on Jeol FX (90 and 22.5 MHz, respectively) and Bruker AM-300 (300 and 75 MHz, respectively) spectrometers with $CDCl_3$, C_6D_6, or deuterioacetone as the solvents. The negative-ion mass spectra were obtained on a modified MI-1201 mass spectrometer[8] with direct inlet of the samples into the ion source. The pressure outside the collision chamber was no higher than 10^{-6}—10^{-7} mbar, which corresponds to conditions of single collisions. The effusing molecule beam in the ionization chamber and the computer-controlled monokinetic electron beam of variable energy $E_e \approx 0.80$ eV, which was generated with a trochoidal electron monochromator, crossed each other at the right angle. Throughout the experiment, the energy distribution of the electron beam at the half-height was $\Delta E \approx 200$—300 meV at the electron current of 300—500 mA. The low energy resolution and, correspondingly, the large electron current were determined by the low intensities of the signals. Calibration and monitoring of the linearity of the E_e electron energy scale were performed by recording effective yield curves of SF_6^-/SF_6 and NH_2^-/NH_3. The IR spectra were recorded on an IR-75 spectrometer (film).

Cyclometallation of C_{60} with $EtAlCl_2$—Mg—Cp_2TiCl_2. A magnesium powder (0.12 g, 5 mg-at.) and Cp_2TiCl_2 (0.01 g, 0.0375 mmol) were added to a solution of C_{60} (0.036 g, 0.05 mmol) in toluene (30 mL) and THF (5 mL) in an atmosphere of argon. Then $EtAlCl_2$ (0.95 g, 7.5 mmol) was added at ~0 °C. The reaction mixture was stirred at ~20 °C for 12 h, unconsumed Mg was separated, and THF and ~1/3 of toluene were evaporated *in vacuo* without heating. The reaction mixture was treated (an Ar or N_2 atmosphere, in the dark) with 10% HCl or DCl. The organic layer was dried with $MgSO_4$ and purified by chromatography (a graphite powder or Al_2O_3), the solvent was evaporated *in vacuo*, and the residue was analyzed.

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