Organometallic Chemistry

Synthesis and transformations of metallacycles. 18.* Cp_2ZrCl_2-catalyzed cyclometallation of C_{60} fullerene with $AlEt_3$

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Cyclometallation of C_{60} fullerene with excess $AlEt_3$ in the presence of Cp_2ZrCl_2 (2 mol % with respect to [Al]) in a toluene solution at 22—23 °C was carried out. The reaction gave 2,3-fullerene-substituted aluminacyclopentanes, whose hydrolysis led to a mixture of hydrogen-containing ethylfullerenes of the type $H_mC_{60}Et_m$ containing 1 to 12 ethyl groups.

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

The majority of publications concerned with fullerenes[2,3] have been devoted to their synthetic transformations involving conventional electrophilic and nucleophilic reagents.[4—7] However, virtually no data on the use of homogeneous metal complex catalysts in the reactions of fullerenes with organometallic reagents can be found in the literature. This study is the first attempt to extend the reaction of catalytic cycloalumination of unsaturated compounds, which we discovered previously,[8—10] to the reaction of C_{60} fullerene with $AlEt_3$ in the presence of zirconium complexes.

Tentative experiments have shown that the metallation of C_{60} with $AlEt_3$ under conditions selected for cycloalumination of α-olefins in our previous studies[8—10] ([Al] : C_{60} = 1 : 1, Cp_2ZrCl_2 as the catalyst (2 mol. %), toluene, 22—23 °C, 2 h) did not give organoaluminum fullerene derivatives; the initial C_{60} was recovered in all experiments.

However, when C_{60} was made to react with excess $AlEt_3$ ([Al] : C_{60} = 30 : 1) in the presence of Cp_2ZrCl_2 (2 mol. % relative to $AlEt_3$) in a toluene solution (22—23 °C, 36 h), a mixture of organoaluminum compounds was obtained in a total yield of ~80% (according to HPLC of the deuterolysis products). Deuterolysis of the reaction

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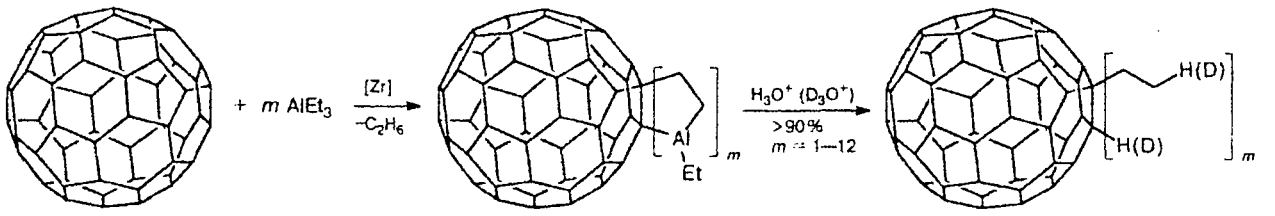
Scheme 1



1 2 (3)

mixture gives a mixture of partially deuterated ethylfullerenes **3** (*m/z* 751 $(C_{60}EtD)^{+\cdot}$, 752 $[C_{60}(C_2H_4D)D]^{+\cdot}$, 783 $[C_{60}(C_2H_4D)D_2Et]^{+}$), indicating that the reaction has yielded fullerenes **1** containing up to two aluminacyclopentane fragments in the molecule (Scheme 1). The number of aluminacyclopentane fragments in a molecule of C_{60} fullerene increases to 12; (according to the data of HPLC of hydrolysis products, the total yield is 90%) when the ratio [Al] : C_{60} ≈ 300 : 1 and the reaction is carried out in the presence of 2 mol. % Cp_2ZrCl_2 for 36 h at 22—23 °C.

The structures of hydrolysis products **2** and deuterolysis products **3** were proved by NMR and mass spectra. Thus the mass spectra of positive (EI, energy of electrons E_e ~70 eV) and negative ions (resonance capture of electrons, E_e ~0 eV) recorded at equal temperatures of the direct-introduction tube contain virtually identical sets of peaks with equal relative intensities. For example, the negative-ion mass spectrum of hydrolysis products **2** recorded at 325 °C and E_e ~0 eV exhibits mass lines, whose *m/z* (I_{rel} (%)) values correspond, in our opinion, to the molecular ions of hydrogen-containing ethylfullerenes and are equal to 720 [C_{60}] (38), 750 $[C_{60}EtH]^-$ (22), 780 $[C_{60}Et_2H_2]^-$ (40), 808 $[C_{60}Et_3H]^-$ (90), 810 $[C_{60}Et_3H_3]^-$ (92), 836 $[C_{60}Et_4]^-$ (25), 838 $[C_{60}Et_4H_2]^-$ (20), 840 $[C_{60}Et_4H_4]^-$ (100), 866 $[C_{60}Et_5H]^-$ (80), 868 $[C_{60}Et_5H_3]^-$ (84), 870 $[C_{60}Et_5H_5]^-$ (40), 896 $[C_{60}Et_6H_4]^-$ (8), 900 $[C_{60}Et_6H_6]^-$ (11), 926 $[C_{60}Et_7H_3]^-$ (21), 928 $[C_{60}Et_7H_5]^-$ (33), 930 $[C_{60}Et_7H_7]^-$ (12), 954 $[C_{60}Et_8H_2]^-$ (30), 956 $[C_{60}Et_8H_4]^-$ (30), 958 $[C_{60}Et_8H_6]^-$ (6), 984 $[C_{60}Et_9H_3]^-$ (30), 986 $[C_{60}Et_9H_5]^-$ (4), 1010 $[C_{60}Et_{10}]^-$ (30), 1012 $[C_{60}Et_{10}H_2]^-$ (10), 1040 $[C_{60}Et_{11}H]^-$ (28), 1042 $[C_{60}Et_{11}H_3]^-$ (15), and 1044 $[C_{60}Et_{11}H_5]^-$ (20). The relative intensities of ions in the mass spectrum of **2** depends appreciably on the temperature of the inlet system. At 308 °C, the most intense peaks correspond to ions with the general formula $C_{60}Et_8H_n^{+\cdot}$ (n = 2—8). Even the $C_{60}Et_{12}H_n^{+\cdot}$ ions with relative intensities of <1% (n = 2—10) were detected under these conditions. As the temperature increases, the maximum yield of ion peaks shifts toward fullerene ions containing fewer ethyl substituents. For example, at 360—370 °C, the maximum yields of ions of the $C_{60}Et_2H_n^{+\cdot}$ (n = 0, 2) and $C_{60}EtH^{+\cdot}$ types are attained. The ion peaks corresponding to hydrogen-containing ethylfullerenes containing more than four ethyl groups are totally missing from these spectra. Perhaps, hydrogen-containing ethylfullerenes decompose under these conditions. This assumption is consistent with the fact that an increase in the temperature results in higher relative yields of ions derived from the $C_{60}Et_nH_{n-2}$ molecules, *i.e.*, under these conditions (308—370 °C), the initial hydrogen-containing ethylfullerenes undergo dehydrogenation and decompose.

The ^{1}H NMR spectrum of hydrolysis products **2** contains a set of signals due to hydrogen atoms of ethyl groups: 0.8—1.3 m (CH_3), 1.42—2.48 m (CH_2). The hydrogen atoms bound directly to the C_{60} fullerene cage are responsible for two broadened multiplets centered at 4.86 and 4.98 ppm and a multiplet at about 5.20—5.45 ppm. The ^{13}C NMR spectrum of compound **2** contains groups of signals for the carbon atoms of the ethyl substituents centered at 17.64 (CH_3) and 30.33 ppm (CH_2). We were unable to identify signals corresponding to the sp^2-hybridized carbons incorporated in the fullerene fragment, because of appreciable splitting.

Thus, catalytic cyclometallation of C_{60} fullerene with $AlEt_3$ gives rise to a mixture of organometallic clusters **1** containing 1 to 12 aluminacyclopentane fragments, which are quantitatively converted into compounds **2** upon hydrolysis. The mechanism of this reaction can be suggested to be similar to the mechanism that we proposed for the transformation of α-olefins and alkynes.[8—10] Cycloalumination of C_{60} fullerene might involve as well the intermediate formation of Zr- and Al-containing bimetallic species.[11—13]

Experimental

The HPLC analysis of the hydrolysis and deuterolysis products was carried out on a Beckman chromatograph (model 153) with UV detection at λ = 254 nm. The separation was performed in a 250×3 mm metallic column packed with Diasorb 130 modified with cyanodecyl groups (grain size 8 μm). Hexane at a flow rate of 0.2 mL min^{-1} was used as the mobile phase. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300 (300 and 75 MHz) and Jeol FX 90Q (90 and 22.5 MHz) spectrometers. Deuterated toluene C_7D_8 and a 10 : 1 CS_2—C_6D_6 mixture were used as the solvents. The negative- and positive-ion mass spectra were run on a modified MI-1201 mass spectrometer.[14] The substances to be analyzed were injected into the mass spectrometer through a

direct-introduction tube. The pressure outside the collision chamber was no more than 10^{-6}—10^{-7} mbar, which corresponds to the conditions of single collisions. In the ionization chamber, the molecular beam crossed at a right angle a computer-controlled monokineticized electron beam, generated by a trochoidal monochromator and having an energy in the $E_e \approx 0$—80 eV range. The energy distribution of the electron beam measured at its half-height was $\Delta\varepsilon \approx 200$—300 meV for an electron current of 300—500 nA during the whole experiment. The low resolution in energy and, correspondingly, the great electron current were due to the low intensity of signals. The calibration and checking of linearity of the electron scale E_e were performed by recording the curves of the effective yields for SF_6^-/SF_6 and NH_2^-/NH_3.

Cyclometallation of C_{60} with $AlEt_3$ and Cp_2ZrCl_2 (general procedure). The catalyst Cp_2ZrCl_2 (0.0876 g, 0.3 mmol) and $AlEt_3$ (1.71 g, 15 mmol) were added to C_{60} (0.036 g, 0.05 mmol) in 40 mL of toluene under dry Ar, and the mixture was stirred for 36 h at 22—23 °C and treated with 5% HCl or DCl. The organic layer was dried with $MgSO_4$ and the solvent was removed on a rotary evaporator. The residue was purified by column chromatography using a graphite powder as the sorbent and toluene as the eluent. The solvent was evaporated and the residue was analyzed.

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