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Fullerene Chemistry

$AlCl_3$-Mediated Mono-, Di-, and Trihydroarylation of [60]Fullerene**

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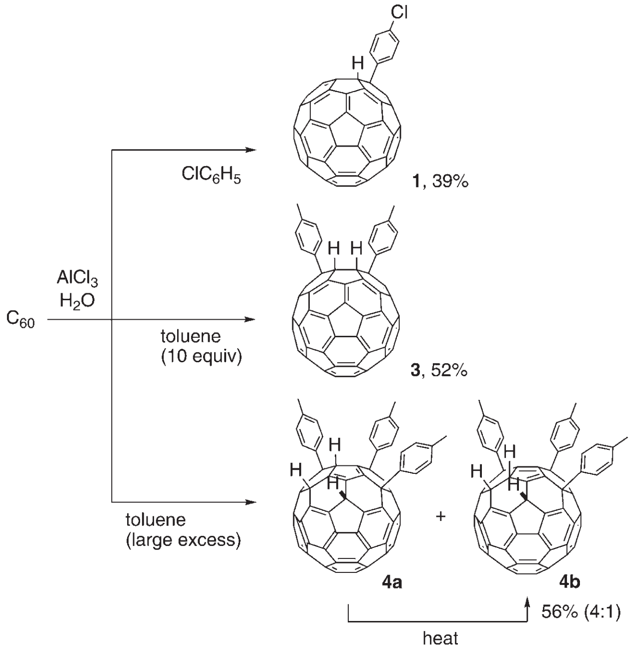
Reported over 10 years ago by Olah et al.,[1] the $AlCl_3$-mediated Friedel–Crafts-type hydroarylation reaction between [60]fullerene and benzene or toluene represents an early example of multifunctionalization reactions of fullerene molecules and still remains an intriguing reaction in several respects. First, as it requires only an aromatic solvent and $AlCl_3$, it is potentially a very inexpensive and convenient synthetic method. Second, the report described the formation of a mixture of many compounds formulated as $C_{60}Ar_nH_n$ (Ar = Ph, C_6H_4Me; $n = 1$–3, 6, 12, 16), suggested low product selectivity, and did not give any structure assignment. As a result, there have been no published reports[2] of attempts to utilize this reaction for the synthesis of useful materials despite the known utility of polyaryl-[3,4] and polyhydrofullerene[5,6] derivatives. We report herein that the Friedel–Crafts-type reaction as reported by Olah et al. produces mono-, di-, and trihydrofullerene derivatives in synthetically viable yields under the conditions most suitable for the synthesis of each class of compounds (Scheme 1). The reaction is applicable not only to intact fullerene but also to those that are already functionalized and is useful for the synthesis of new η^5-organometallic compounds.[7]



Scheme 1. $AlCl_3$-mediated hydroarylations of fullerene.

Careful reexamination of the reaction using a variety of conditions and substrates revealed that the reaction first produces mono- and dihydroarylation products and progressively gives higher hydroarylation products as the amount of toluene is increased and as a longer reaction time is employed. We noted that the hydroarylated products are air-sensitive under ambient light, which may have caused problems of structural identification in previous studies. For instance, the reaction of a mixture of [60]fullerene (30 mg) and $AlCl_3$ (30 mg, 5.4 equiv) in toluene (20 mL) at 25 °C for 32 h indeed formed a complex mixture of tri-, tetra-, penta-, and higher hydroarylated [60]fullerenes as determined by HPLC analysis and mass spectrometry. The presence of water, one equivalent to fullerene, is essential for a fast and reproducible reaction. Under strictly anhydrous conditions the reaction is very slow, and in the presence of a large amount of water the reaction does not proceed. The use of HCl gas without $AlCl_3$ was ineffective. We therefore consider that water produces HCl, which is further activated through removal of chloride anion by an Al^{III} species to form a very reactive proton source.[8]

When we use a less reactive benzene derivative, we can stop the reaction quite selectively at the monohydroarylation stage. For instance, the reaction of [60]fullerene in chlorobenzene in the presence of $AlCl_3$ afforded $C_{60}(4\text{-}ClC_6H_4)H$ (**1**) in 39 % yield with 50 % recovery of fullerene (Scheme 1; Table 1, entry 1). Anisole was less reactive and gave $C_{60}(4\text{-}OMeC_6H_4)H$ (**2**) only in 10 % yield with 80 % recovery of fullerene (Table 1, entry 2).[9] In both cases, the addition took place in a 1,2 manner as has been described for such reactions under basic conditions.[10] 1,2-Dichlorobenzene and trifluoromethylbenzene were unreactive.

When a more reactive arene was used, the reaction proceeded to the dihydroarylation stage. Thus, we obtained diaryl dihydro[60]fullerene $C_{60}(4\text{-}MeC_6H_4)_2H_2$ (**3**) in 52 % yield after flash chromatography (Scheme 1; Table 1, entry 3) when fullerene was treated with toluene (10 equiv), $AlCl_3$ (5 equiv), and water (1 equiv) in 1,2-dichlorobenzene for 30 min at 25 °C. The atmospheric-pressure chemical ionization time-of-flight (APCI-TOF) mass spectrum of the product exhibited a signal at m/z 903.11504 $[M-H^+]$, whereas the ^1H NMR spectrum exhibited only one set of ^1H NMR signals

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Table 1: Hydroarylation of [60]fullerene.[a]

Entry	Solvent	T [°C]	t [min]	Main product	Yield [%]
1	ClC_6H_5	25	120	$C_{60}(4\text{-}ClC_6H_4)H$ (**1**)	39
2	$MeOC_6H_5$[b]/1,2-$Cl_2C_6H_4$	80	1200	$C_{60}(4\text{-}OMeC_6H_4)H$ (**2**)	10
3	toluene[c]/1,2-$Cl_2C_6H_4$	25	480	$C_{60}(4\text{-}MeC_6H_4)_2H_2$ (**3**)	52
4	toluene	25	80	$C_{60}(4\text{-}MeC_6H_4)_3H_3$ (**4a**,**b**)	52
5	toluene/1,2-$Cl_2C_6H_4$ (4:1)	25	30	$C_{60}(4\text{-}MeC_6H_4)_3H_3$ (**4a**,**b**)	56
6	toluene/1,2-$Cl_2C_6H_4$ (4:1)	80	10	$C_{60}(4\text{-}MeC_6H_4)_3H_3$ (**4b**)	50
7[d]	benzene/1,2-$Cl_2C_6H_4$ (4:1)	25	30	$C_{60}Ph_3H_3$ (**7**)	51
8[d]	tBuC$_6$H$_5$/1,2-$Cl_2C_6H_4$ (4:1)	25	20	$C_{60}(4\text{-}t\mathrm{Bu}C_6H_4)_3H_3$ (**8**)	17
9[d]	o-xylene/1,2-$Cl_2C_6H_4$ (4:1)	25	25	$C_{60}(3,4\text{-}Me_2C_6H_3)_3H_3$ (**9**)	31
10	biphenyl[e]/1,2-$Cl_2C_6H_4$	25	20	$C_{60}(4\text{-}PhC_6H_4)_3H_3$ (**10**)	27

[a] General conditions: C_{60} (72.0 mg, 0.10 mmol) and $AlCl_3$ (66.7 mg, 0.50 mmol) were mixed in solvent (20 mL single solvent or 25 mL mixed-solvent system) containing water (0.10 mmol). [b] Anisole (10 equiv). [c] Toluene (10 equiv). [d] The reaction without 1,2-dichlorobenzene was slower because of insufficient solubility of fullerene, but the yield was almost the same. [e] Biphenyl (100 equiv).

corresponding to the *p*-tolyl moiety and one singlet signal at $\delta = 5.78$ ppm corresponding to two protons on the C_{60} skeleton which indicated C_s symmetry of the molecule. Neither *ortho*- nor *meta*-substituted isomers formed probably because of the steric effect of the bulky fullerene molecule. Unambiguous structure assignment of **3** was achieved by X-ray crystallographic analysis of a single crystal obtained by slow diffusion of hexane to a solution of **3** in 1,2-dichlorobenzene (Figure 1).[11] This is a rare example of crystallographic analysis obtained for a 1,2,3,4-tetrasubstituted adduct of [60]fullerene.[12]

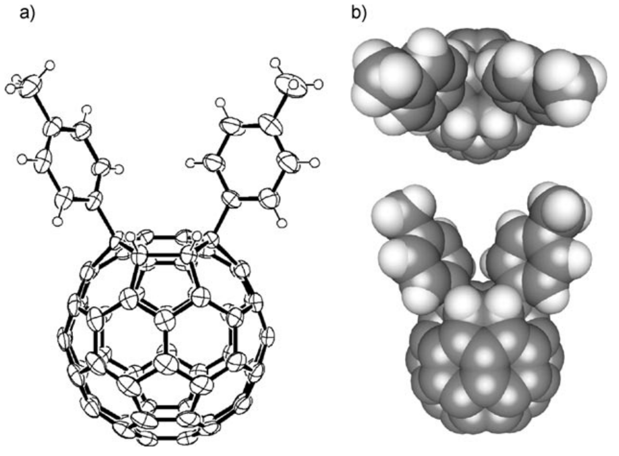
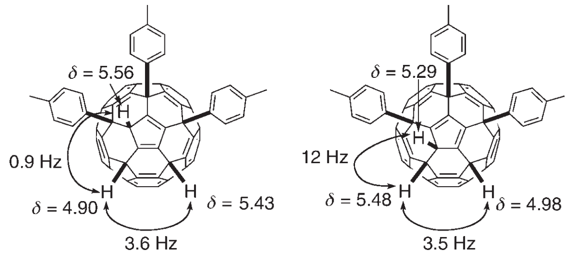


Figure 1. Molecular structure of **3**: a) ORTEP drawing with ellipsoids at the 30% probability level (C ellipsoids, H spheres); b) space-filling models of top and side views (C gray, H white).

When the reaction was carried out with a large excess of toluene, the reaction continued to the trihydroarylation stage to give triaryl trihydro[60]fullerene $C_{60}(4\text{-}MeC_6H_4)_3H_3$ (**4**) in 52% yield as a moderately air-sensitive compound under ambient light (Table 1, entry 4). This sensitivity is most likely attributed to photooxidation of the hydrogen atoms attached to the fullerene core. The product consisted of a mixture of regioisomers **4a** (80%) and **4b** (20%) that display similar polarity with respect to silica gel chromatography. The reaction proceeded faster when 1,2-dichlorobenzene was used as a cosolvent and gave the tris adduct **4** in 30 min (entry 5). Heating of the mixture **4a**,**b** at 80 °C afforded only **4b**, and when the hydroarylation reaction was carried out at 80 °C for 10 min in the presence of 20% 1,2-dichlorobenzene the reaction afforded only **4b** in 50% yield (Table 1, entry 6). The result strongly suggests that **4a** and **4b** are isomeric probably with respect to the position of the hydrogen atoms rather than the tolyl groups. The reaction could be performed easily on a 1-g scale (see Experimental Section). $AlBr_3$ and $GaCl_3$ similarly catalyzed the reaction but gave lower yields.

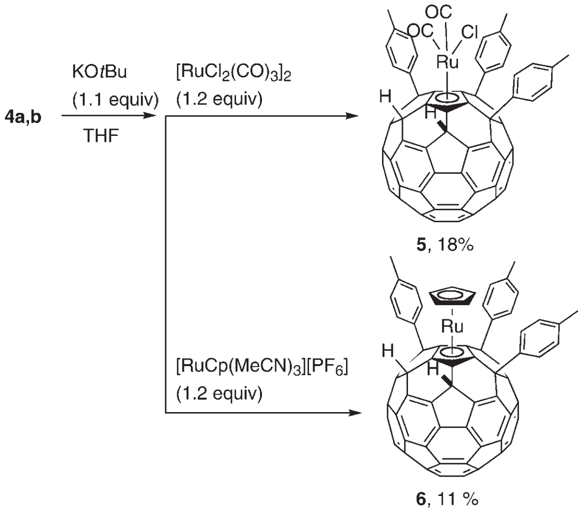
Compounds **4a** and **4b** were separated from each other by preparative HPLC (RP-FULLERENE, Nomura Chemical Co., toluene/acetonitrile = 4:6), and their structures were studied by ^1H and ^{13}C NMR, and UV/Vis spectroscopy, and high-resolution APCI-TOF mass spectrometry measurements. The UV/Vis spectra of **4a** and **4b** showed a characteristic absorption pattern ($\lambda_{max} = 350$ nm and 396 nm) as previously reported for penta(organo)hydro[60]fullerenes.[3] The ^1H NMR spectrum of **4a** exhibited signals at $\delta = 4.90$, 5.43, and 5.56 ppm assigned to the three hydrogen atoms directly attached to the fullerene core (Figure 2). The first two signals are coupled with each other with a small coupling constant $^5J_{H\text{-}H} = 3.6$ Hz characteristic of $^5J_{H\text{-}H}$ coupling between the protons on a hexagon in a dihydro[60]fullerene.[6] The first and the third signals also exhibited a small coupling constant $^4J_{H\text{-}H} = 0.9$ Hz, indicating that these two hydrogen atoms are neither in a 1,2 nor in a 1,4 relationship. In the ^1H NMR spectrum of **4b**, a large coupling constant between a pair of the 1,2-hydrogen atoms was observed ($^3J_{H\text{-}H} = 12$ Hz) while another pair of the hydrogen atoms exhibited $^5J_{H\text{-}H} = 3.5$ Hz. It is unclear at this time why **4b** is thermodynamically more stable than **4a**, and how this prototropy reaction takes place.



4a **4b**

Figure 2. The ^1H NMR chemical shifts [ppm] and coupling constants for the hydrogen atoms of **4a** and **4b**.

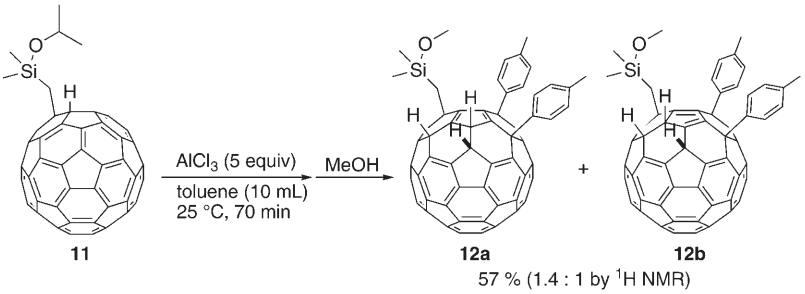
The mixture of the triaryl trihydrofullerenes **4a**,**b** was converted into a single η^5-organometallic complex,[7] which gave support to the above structural assignment. Thus, treatment of a mixture of **4a** and **4b** with KO*t*Bu in THF gave a dark red solution,[13] which upon treatment with $[RuCl_2(CO)_3]_2$ provided a ruthenium(II) complex $[Ru\{C_{60}(4\text{-}MeC_6H_4)_3H_2\}Cl(CO)_2]$ (**5**) in 18% yield as shown in Scheme 2. When treated with $[RuCp(MeCN)_3][PF_6]$ (Cp: cyclopentadienyl), it afforded a bucky ruthenocene $[Ru\{C_{60}(4\text{-}MeC_6H_4)_3H_2\}Cp]$ (**6**) in 11% yield. From the ^{1}H NMR spectra, compounds **5** and **6** displayed characteristic signals of C_s-symmetric structures which indicate that the metal is bonded in an η^5 fashion and hence supports the structural assignment of **4a**,**b**. On the basis of the reported reactivity of η^5-hydrofullerene metal complexes,[6] we expect that the two hydrogen atoms in **5** and **6** can be deprotonated and alkylated to provide access to further functionalized products.



Scheme 2. Synthesis of ruthenium fullerene complexes.

Table 1 illustrates the scope of the trihydroarylation reaction with several different benzene derivatives in 1,2-dichlorobenzene. The hydroarylation reactions took place with benzene as well as substituted benzenes, *tert*-butylbenzene, *o*-xylene, and biphenyl to afford the corresponding triaryl trihydrofullerenes $C_{60}Ph_3H_3$ (**7**), $C_{60}(4\text{-}t\text{Bu}C_6H_4)_3H_3$ (**8**), $C_{60}(3,4\text{-}Me_2C_6H_3)_3H_3$ (**9**), and $C_{60}(4\text{-}PhC_6H_4)_3H_3$ (**10**) in 51%, 17%, 31%, and 27% yields, respectively (Table 1, entries 7–10). In all cases, we isolated a single *para* regioisomer with respect to the substitution pattern of the benzene ring. We detected only a trace amount of dihydroarylated products but observed higher hydroarylated products, whose structures we could not assign with certainty.

The present procedure can be applied not only to intact [60]fullerene but also to a monoalkyl hydro[60]fullerene, which then affords monoalkyl diaryl trihydro[60]fullerenes. Treatment of $C_{60}(CH_2SiMe_2O\textit{i}Pr)H$ (**11**)[14] with five equivalents of $AlCl_3$ in toluene afforded a mixture of the dihydroarylated product $C_{60}(4\text{-}MeC_6H_4)_2(CH_2SiMe_2OMe)H_3$ (**12a**,**b**) in 57% yield (Scheme 3). The isopropyloxy group on the silicon atom was replaced by a methoxy group upon methanol workup. We expect that the flexibility of this synthetic approach will allow us to synthesize a variety of new types of organometallics and fullerene derivatives of interest in materials science.[15–17]



Scheme 3. Hydroarylation of an alkylhydro[60]fullerene.

Experimental Section

Synthesis of **4** as a mixture of **4a** and **4b**: Toluene (280 mL) containing water (25.0 μL, 1.39 mmol) was added to a mixture of C_{60} (1.00 g, 1.39 mmol) and aluminum(III) chloride (0.923 g, 6.94 mmol). The reaction mixture was stirred for 80 min at 25 °C before water (2 mL) was added. TLC analysis showed only one spot with $R_f = 0.52$ (CS_2/hexane = 2:1) while the rest of the product stayed near the baseline. Isolation of this product was carried out in the dark because of its moderate air-sensitivity under light. The dark brown reaction mixture was passed through a pad of silica gel (eluent: toluene), and the solvent from the eluate was removed by evaporation. This crude product was purified by column chromatography (6 cm(ID) × 25 cm, 350 g silica gel, CS_2/hexane = 2:1; $R_f = 0.52$). The first pale brown fraction (ca. 600 mL) contained a small amount of a mono and a bis adduct. The following 400-mL fraction contained the desired tris adducts, and the final 200-mL fraction contained a mixture of the desired tris adduct and polyarylated fullerenes. This last fraction was purified again on 70 g silica gel (3 cm(ID) × 20 cm, CS_2/hexane = 2:1). The first brown fraction (ca. 50 mL) was collected and combined with the second fraction from the first chromatography step. The combined fractions were concentrated under vacuum until a solid just began to appear on the inside wall of the flask. Methanol (200 mL) was added to precipitate the product. The title compound **4** (693 mg, 50%; 4:1 mixture of **4a**/**4b**) was obtained by filtration as a brown powder, which was over 95% pure according to ^{1}H NMR spectroscopic analysis. Spectroscopic data are described in the Supporting Information.

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Keywords: aluminum · Friedel–Crafts reaction · fullerenes · hydroarylation · ruthenium

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