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Addition of Tetrahydrofuran to [60]Fullerene through C–H Bond Activation Induced by Arylzinc Reagents

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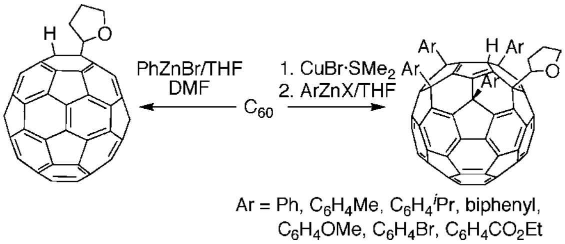
ABSTRACT



The reaction of [60]fullerene with an arylzinc halide in a mixture of THF and DMF produces a mono(2-tetrahydrofuranyl) adduct of [60]fullerene $C_{60}(C_4H_7O)H$ instead of the expected arylated fullerene. The reaction involves a C–H bond activation at the 2-position of THF that probably takes place through a radical mechanism. In the presence of a copper(I) complex, the reaction does not stop at the stage of mono-addition, with the aryl group of the zinc reagent adding four times regioselectively to the mono(2-tetrahydrofuranyl) adduct to produce a penta-adduct $C_{60}Ar_4(C_4H_7O)H$. This product can be converted further to the corresponding buckyferrocene $Fe[C_{60}Ar_4(C_4H_7O)]Cp$ and its derivatives.

Chemical reactions performed on fullerenes have created numerous fullerene derivatives. These compounds exhibit properties that are not found in fullerenes themselves and have found widespread use in chemical, biological, and materials sciences.[1] A wide variety of reactions have been employed for the fullerene functionalization, including cycloadditions,[2] nucleophilic additions,[3] organometallic reactions,[4] and radical reactions,[5] and others.[6] Among the reactions, the radical reactions appear to be less explored than the others, which may be due to the difficulty in controlling the reactivities of radical intermediates. We report herein that [60]fullerene can be selectively functionalized by way of carbon radicals generated by the reaction of tetrahydrofuran (THF) and an arylzinc halide, as contrasted to our recent work of sysnthesis of C_5-symmetric functionalized [60]fullerenes by copper-mediated 5-fold addition of alkylzinc reagents.[7] The reaction produces a mono(2-tetrahydrofuranyl) fullerene **1** in good yield, and when carried out in the presence of a copper(I) complex, the arylzinc

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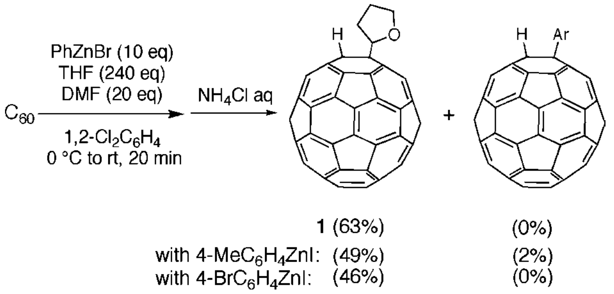
reagent takes part in the reaction to effect addition of four aryl groups to produce a mono(2-tetrahydrofuranyl) tetraaryl [60]fullerene **2** in good to excellent yield. The products can be further elaborated into a variety of new compounds (**3** and **4**) through organic and organometallic derivatization of the THF moiety and the cyclopentadienyl moiety.

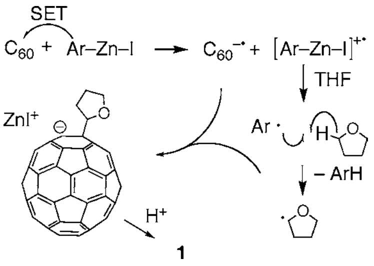
In the course of our systematic studies of the reactivities of organometallics with [60]fullerene, we made an intriguing observation; namely, when [60]fullerene was treated with phenylzinc bromide in a mixture of *N*,*N*-dimethylformamide (DMF) and THF, the reaction mixture became cloudy and dark gray and afforded, after careful optimization of the reaction conditions, mono(2-tetrahydrofuranyl) adduct $C_{60}(C_4H_7O)H$ (**1**) in 63% isolated yield (Scheme 1). As in the oxyamination of fullerenes that was shown to involve a single-electron transfer (SET) process,[8] the presence of DMF was essential for this reaction to take place smoothly and cleanly. Albini et al. recently reported a photochemical alkylation of electrophilic alkenes that was shown to involve a single-electron transfer (SET) process.[9] We also proposed that the reaction involves a C−H bond activation at the 2-position of THF that probably takes place through a radical mechanism. We could not detect the arylation product that we initially expected in any more than 2% yield under all conditions that we examined. 4-Methyl and 4-bromophenylzinc iodide also exhibited the same reactivity.

Scheme 1. Mono-THF Addition Reaction



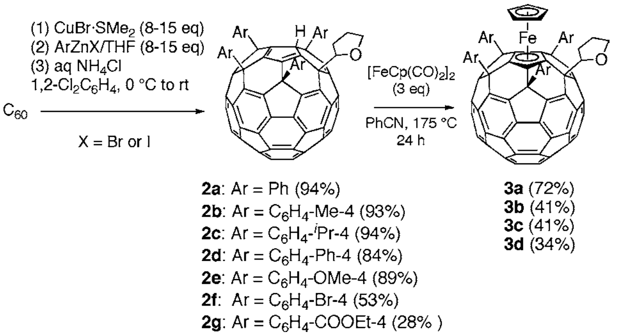
We consider that the reaction involves radical intermediates rather than carbanionic species because of the well-established base stability of THF under mildly basic conditions.[10] One possible pathway is shown in Scheme 2. We assume that the first step is a single-electron oxidation of the arylzinc reagent by fullerene that generates the corresponding aryl radical and a fullerene radical anion,[11] and the second step is hydrogen atom abstraction from the 2-position of THF by the aryl radical. Coupling of the 2-tetrahydrofuranyl radical with the fullerene radical anion produces the mono(2-tetrahydrofuranyl) fullerene anion $C_{60}(C_4H_7O)^-$ and ZnI^+.

Scheme 2. Suggested Pathway for the Mono-THF Addition Reaction



Being aware of the fact that a mono-addition product such as **1** can accept further addition of nucleophiles,[12] we considered that the reaction of an arylzinc reagent and [60]-fullerene in the presence of $CuBr{\cdot}SMe_2$ would give a mixed penta-addition product (Scheme 3). Indeed, the reaction of phenylzinc bromide in THF gave, in one pot, the expected compound $C_{60}Ph_4(C_4H_7O)H$ (**2a**) in 94% yield. The product was obtained as a mixture of five diastereomers because of the diastereoisomerism resulting from the positions of the cyclopentadienyl hydrogen and the chiral center on the THF moiety. The use of the DMF additive was unnecessary for this reaction. The cyclopentadiene **2a** can be converted as previously described[13] to the corresponding bucky ferrocene derivative **3a** in good yield and as a single diastereomer (the crystal structure is discussed below).

Scheme 3. Synthesis of the Mono(2-tetrahydrofuranyl) Tetraaryl Addition Product **2** and Conversion to the Buckyferrocene **3**



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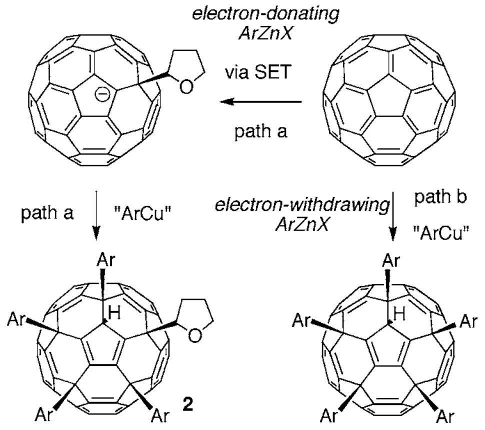
Scheme 3 shows other examples of the synthesis of the mono(2-tetrahydrofuranyl) tetraaryl fullerene derivatives **2b−g** and their buckyferrocene derivatives **3a−d**. In the top five entries **2a−e**, the multiple addition reaction exclusively produced the mono(2-tetrahydrofuranyl) tetraaryl fullerenes (path a, Scheme 4), but in the bottom two entries, where the aryl group bears an electron-withdrawing group, the reaction also produced pentaarylated fullerenes $C_{60}Ar_5H$ in 42 and 59% yield, respectively (path b) in addition to **2f** and **2g**. The difference in the reactivity between 4-methylphenyl and 4-bromophenylzinc iodide is interesting, because both afforded the mono(2-tetrahydrofuranyl) adduct **1** in similar yields under the DMF/THF conditions described in Scheme 1. This result suggests that either path a or path b is sensitive to the electronic effect in the arylzinc or copper intermediate. In the course of the reaction, we did not observed di- or more 2-tetrahydrofuranyl adducts at all. This strongly supports the stepwise reaction pathway, path a (Scheme 4) via the mono(2-tetrahydrofuranyl) adduct.

Scheme 4. Reaction Pathways of the Mono(2-tetrahydrofuranyl) Tetraaryl Addition Product (Path a) and the Pentaarylation Product (Path b) in the Copper-Mediated Penta-Addition Reactions in Scheme 3[a]



[a] SET process may involve either the arylzinc reagent as shown in Scheme 1 or a copper intermediate derived from the arylzinc reagent.

The structure of the 2-tetrahydrofuranyl adduct was unambiguously determined by X-ray analysis of the buckyferrocene Fe[$C_{60}(C_6H_4{}^iPr)_4(C_4H_7O)$]Cp (**3c**). Dark-red single crystals containing a 1:1 mixture of the buckyferrocene and 1,2-$Cl_2C_6H_4$ were obtained and the crystal structure is shown in Figure 1. The Cp ring is tilted by 3.2° against the cyclopentadienide moiety of the fullerene core because of the 2-tetrahydrofuranyl group. The average bond length between the iron atom and the carbon atoms of the Cp ring is 2.055 Å and that between the iron atom and the carbon atoms of the fullerene cyclopentadienide is 2.082 Å, values comparable to those found for the C_{5v}-symmetric buckyferrocene Fe($C_{60}Ph_5$)Cp.[12b,c]

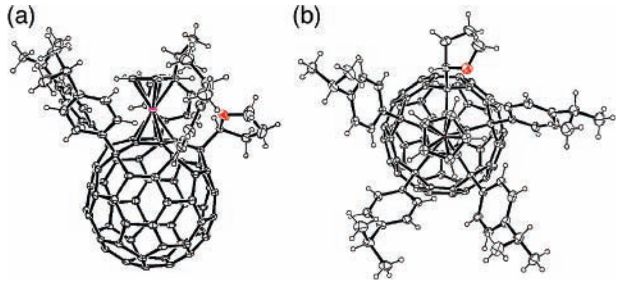
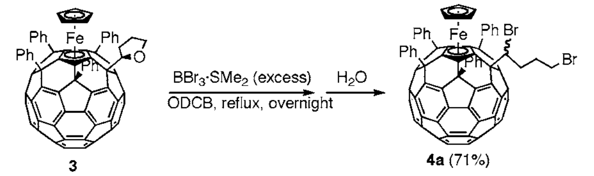


Figure 1. Crystal structure of the buckyferrocene **3c**·(1,2-$Cl_2C_6H_4$). Solvent molecules are omitted for clarity. (a) Side view. (b) Top view.

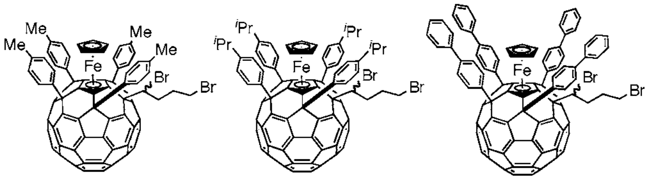
The 2-tetrahydrofuranyl group can be transformed into other functional groups that have been thus far unavailable by other synthetic methods. For instance, treatment of Fe[$C_{60}Ar_4(C_4H_7O)$]Cp with excess BBr_3·SMe_2 resulted in cleavage of the THF ring to give a dibromide Fe[$C_{60}Ar_4(C_4H_7Br_2)$]Cp (**4**) in good yield, as shown in Scheme 5.

Scheme 5. Conversion of the 2-Tetrahydrofuranyl Group Compound **3** to the Dibromide **4**



3

4a (71%)



4b (79%) **4c** (68%) **4d** (75%)

Recrystallization of Fe[$C_{60}(C_6H_4{}^iPr)_4(C_4H_7Br_2)$]Cp (**4c**) from $CHCl_3$/ethanol afforded dark-red crystals composed of a 1:3 mixture of the buckyferrocene and $CHCl_3$, and its structure was determined by X-ray crystallography (Figure 2).

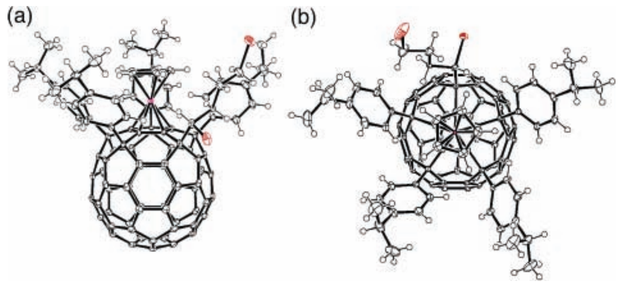


Figure 2. Crystal structure of the dibromide **4c**·$(CHCl_3)_3$. Solvent molecules are omitted for clarity. (a) Side view. (b) Top view.

In summary, we have found an intriguing new reaction of [60]fullerene with THF in the presence of an arylzinc reagent and a copper complex. The reaction mechanism is intriguing because it appears to involve a complex set of reactions that start with an electron-transfer reaction from the zinc reagent to fullerene followed by C−H bond activation by an aryl radical intermediate. The overall yield of the reaction is quite respectable, and the product serves as a useful starting material for further synthetic elaborations.

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Supporting Information Available: Experimental section for procedures to obtain new compounds and CIF files including lists of positional parameters, thermal displacement parameters, bond lengths, and bond angles for **3c** and **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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