Functionalization of Fullerene

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Regioselective Eightfold and Tenfold Additions of a Pyridine-Modified Organocopper Reagent to [60]Fullerene

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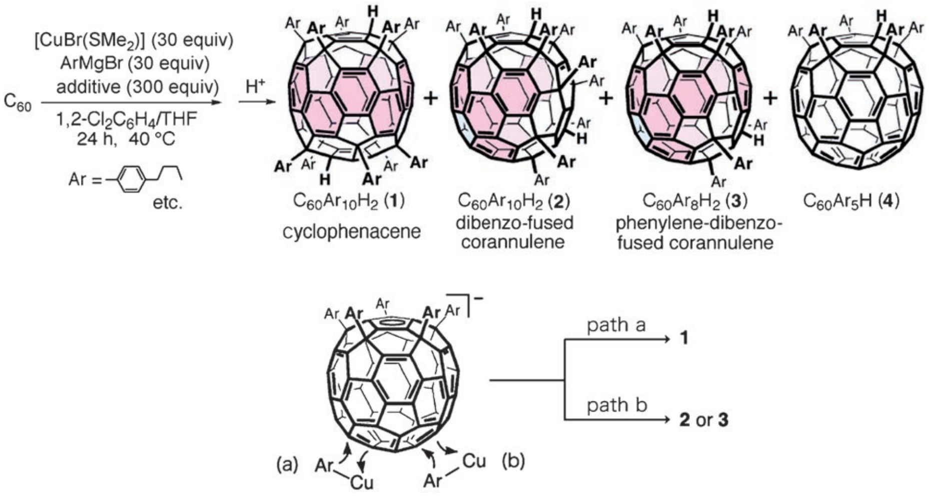
As the interests of chemists are shifting from single molecules to molecular arrays, the workspace of chemists has expanded from the Ångstrom scale to the nanometer scale. Because of its size, reactivity, and high degree of symmetry, [60]fullerene is an ideal structural unit for making larger structures. The high symmetry of this molecule, however, has posed serious synthetic problems, that is, chemical reactions may take place multiple times and at various places on this molecule.[1] The addition of an organocopper reagent to fullerenes that we reported some years ago is an exceptionally selective multiple-addition reaction that exclusively produces pentaadduct **4**.[2,3] We became intrigued by the possibility of achieving more than five additions, for instance, tenfold additions to synthesize tenfold-substituted [60]fullerenes **1** and **2**. These are interesting molecules not only for their radially expanding multisubstitution, but also for their luminescent hoop-shaped and curved conjugation systems (colored pink, Scheme 1)[4,5] and their ability to form metal complexes.[6] We report herein a one-step synthesis of these compounds by a new class of organocopper reagents. With appropriate choice of the substituent on the organic addend, the reaction also produces eightfold-substituted fullerenes **3** with very high selectivity. The reaction procedure is so simple that we can now consider the use of these compounds for further applications.



Scheme 1. Formation of octa- and decaadducts through two pathways.

A stoichiometric mixture of ArMgX and Cu^I in THF/1,2-$Cl_2C_6H_4$ reacts with [60]fullerene, and the addition completely stops when the pentaaddduct **4** forms as its cyclopentandienide anion. We reasoned that homoconjugation between the top cyclopentadienide moiety and the bottom 50π system causes deactivation of the latter.[2b] To alleviate such deactivation, we developed some time ago a multistep protection/deprotection synthetic strategy, and achieved the synthesis of decaadducts **1** and **2**.[4a] The overall yield was too poor (< 10 %) to be useful however. After extensive experimentation, we found that the desired tenfold addition of the organocopper reaction takes place selectively when an appropriately excessive amount of pyridine is present in the reaction mixture (Table 1). Thus, while the copper reagent prepared from equimolar amounts of 4-nBuC$_6$H$_4$MgBr and [CuBr(SMe$_2$)] (30 equiv to fullerene) in an approximately 4:1 mixture of THF and 1,2-$Cl_2C_6H_4$ exclusively gave the pentaadduct **4a** in 99 % yield (Table 1, entry 1, 4-*n*-butylphenyl derivatives are denoted in the compound numbers with "**a**"), a mixture of the same copper reagent (30 equiv) and 300 equivalents pyridine (ca. 1:2:1 pyridine/THF/1,2-$Cl_2C_6H_4$) nearly exclusively gave the decaadducts **1a** and **2a** in 92 % yield as an approximately 1:2 mixture together with trace amounts of the octaadduct **3a**. The reaction could be performed equally easily on a 50-mg or 1-g scale (see the Experimental Section). Since the two regioisomeric decaadducts **1a** and **2a** are structurally very different from each other, they could be separated rather easily by recrystallization and/or chromatography on silica gel.

The regioselectivity arises at the stage of the sixth addition of the ArCu reagent, which can take place either through path a or path b, as shown in Scheme 1. In path a the sixth to the tenth Ar groups are placed around the bottom pentagon to produce **1a**, and in path b these Ar groups are placed

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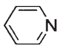
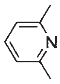
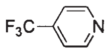
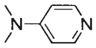
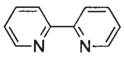
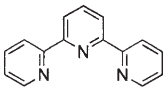
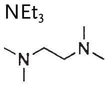
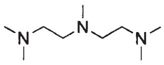
Table 1: Multiarylation of [60]fullerene in the presence of various additives (30 equiv 4-nBuC$_6$H$_4$MgBr and 300 equiv additive).[a]

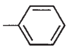
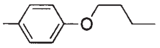
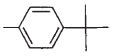
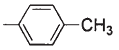
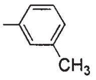
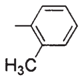
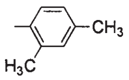
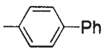
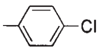
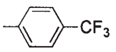
Entry	Additive	Yield [%][b]			
		1a	**2a**	**3a**	**4a**
1	none	0	0	0	99
2		32	60	2	5
3[c]		35	6	50	1
4		3	3	2	90
5		12	27	1	60
6		32	3	15	1
7		34	1	48	1
8		3	0	1	95
9	NEt$_3$	0	0	3	95
10		26	4	28	18
11		8	0	11	74
12		0	0	0	97
13	PPh$_3$	0	0	0	98

[a] The reaction conditions are those in Scheme 1 unless otherwise noted. The reaction was carried out on a 20-mg scale (C$_{60}$). All adducts comprise isomers owing to the relative positions of the hydrogen atoms of the cyclopentadiene moieties. [b] Yield was determined by HPLC with pyrene as an internal standard. [c] 60% v/v pyridine was used.

around one of the five side pentagons to produce **2a**. The experimental ratio was found to be about 1:2 regardless of which Ar groups were used (Table 2).

The octaadduct **3a** forms when the reaction leading to **2a** prematurely finishes after the addition of the eighth Ar group likely because of steric reasons. The use of a large excess of pyridine (60% v/v pyridine, 27% v/v THF, and 13% v/v 1,2-dichlorobenzene) is a synthetically viable procedure that afforded the decaadduct **1a** (35%) and an octaadduct **3a** (50%; Table 1, entry 3). Thus, we can stop the reaction by further tuning of the basic additive. The reaction with 4-dimethylaminopyridine (Table 1, entry 6), 2,2-bipyridine (entry 7), tetramethylethylenediamine (entry 10), or pentamethyldiethylenetriamine (entry 11) gave **3a** in preference to **2a**. Experiments on isolated adducts indicated that these additives slow down conversion of **3a** into **2a**. With hindered and less basic pyridines (Table 1, entries 4, 5, and 8) and monodentate triethylamine (entry 9), the reaction simply stopped after the fifth addition, which indicates that coordination of the nitrogen atom of pyridine to a metal atom is crucial for tenfold addition. 1,4-Dioxane, which binds to Mg^{II}, did not show any effects (Table 1, entry 12), and we surmise that the target atom is the copper atom, possibly the copper(III) intermediate, whose reductive elimination leading to C–C bond formation slows down upon coordination of a basic ligand.[7]

Table 2: Eightfold and tenfold arylation.[a]

Entry	Ar	t [h]	Yield [%][b] (compd)		
			1	**2**	**3**
1		24	24 (**1b**)	50 (**2b**)	0
2		16	24 (**1c**)	42 (**2c**)	0
3		40	20 (**1d**)	45 (**2d**)	0
4		45	24 (**1e**)	48 (**2e**)	0
5		48	17 (**1f**)	27 (**2f**)	0
6		48	3 (**1g**)	0	59 (**3g**)
7		48	3 (**1h**)	0	50 (**3h**)
8		69	21 (**1i**)	34 (**2i**)	0
9		30	2 (**1j**)	7 (**2j**)	0
10		30	2 (**1k**)	4 (**2k**)	0

[a] The reaction conditions are described in Scheme 1 unless otherwise noted. The reaction was carried out on a 50-mg scale (C$_{60}$). See also the Experimental Section. [b] Yield of isolated product.

The scope of this multiple-addition reaction is quite broad, as shown in Table 2. In all cases, [60]fullerene was completely consumed, and the pentaadduct **4** accounts for most of the rest of the product. Sterically unhindered phenyl groups (Table 2, entries 1–4) gave decaadducts **1** and **2** generally in a ratio of 1:2 in about 70% combined yield. Thus, the ten C–C bond-formation reactions took place in an average of 96.5% yield each time. A *meta*-methyl group on the Ar ring appears to exert some steric effects on the reaction to decrease the yield to 44% combined yield (Table 2, entry 5). Aryl copper reagents bearing an electron-withdrawing group that were previously found to be slow to undergo fivefold addition resisted undergoing either a tenfold- or eightfold-addition reaction (Table 2, entries 9 and 10). The reaction of MeMgBr under the same conditions stopped after the fifth addition and those of other alkyl Grignard reagents was not clean.

We also found that the regioselectivity of the multiple addition, that is, path a versus path b, can be controlled by installation of an *ortho*-methyl group to the incoming phenyl group. Thus, the *ortho*-methylphenylcopper reagent produced the octaadduct **3g** in 59% yield, very little of the D_5 decaadduct **1g**, and none of the C_2 decaadduct **2g** (Table 2, entry 6). The rest of the yield was largely a hexaadduct of unidentified structure. Similarly, an *ortho*,*para*-disubstituted phenyl copper reagent afforded predominantly the octaadduct **3h** (Table 2, entry 7). The *para*-methyl group may be used for further chemical modifications and chain extension. The regioselectivity between path a and path b was improved from 1:2 to 1:20. We consider that the steric interaction between the top five Ar groups and the incoming Ar group inhibits path a, while this problem does not exist in path b.

Double-decker ruthenocene was synthesized from **1a**. Treatment of a pale-yellow THF solution of **la** with KO*t*Bu (2 equiv) afforded a dark-brown dianion $[K^+(thf)_n]_2[C_{60}Ar_{10}]^{2-}$ (**5**), which reacted with $[RuCp(CH_3CN)_3]PF_6$ to give $[Ru_2(C_{60}Ar_{10})Cp_2]$ (**6**) in 11% yield of the isolated product. The crystal structure shown in Figure 1[8] illustrates the power of the new tenfold-addition reaction for construction of a well-defined nanostructure (ca. 3 nm along its long axis), which may serve as a useful scaffold for the synthesis of complex, functional molecular arrays. The crystal structure also indicated that the bond alternation pattern characteristic of the 40π [10]cyclophenacene moiety is retained in **6**.[4]

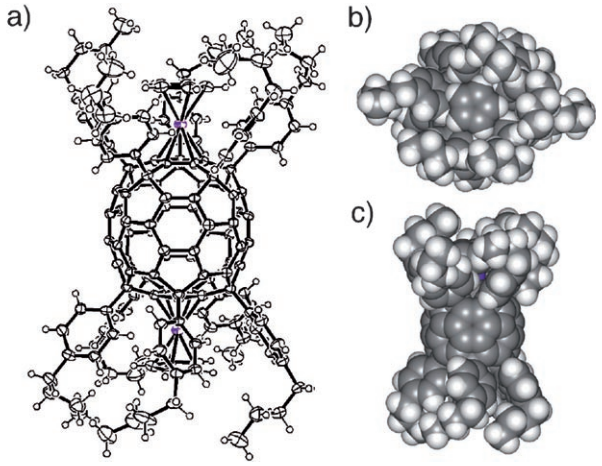


Figure 1. Crystal structure of **6**. a) ORTEP drawing with thermal ellipsoids at the 30% probability level. b) Top view of CPK model. c) Side view of CPK model.

The deca- and octaadducts **1**, **2**, and **3** are luminescent and emit yellow (**1a**: $\lambda_{max} = 562$ and 612 nm, bimodal), blue (**2a**: $\lambda_{max} = 463$ and 491 nm), and red (**3a**: $\lambda_{max} = 652$ and 715 nm) light (Figure 2). The luminescent quantum yields of **1a**, **2a**, and **3a** are $\Phi = 0.18$, 0.065, and 0.015, respectively. The value of the decaaryl compound **1a** is higher than those of an unsymmetrical decaadduct $C_{60}Me_5Ph_5H_2$ ($\Phi = 0.10$),[4a] and much higher than those of [60]fullerene ($\Phi = 0.00032$),[9] monoadducts ($\Phi = 0.0006$–0.0012),[10] and hexaadducts ($\Phi = 0.024$)[11] reported in the literature. The origin of the difference of the quantum efficiency as well as the emission wavelength will be an interesting subject of future photophysical studies.

In summary, we have developed a new pyridine-modified Grignard-based organocopper reagent that undergoes additions to [60]fullerene to the ultimate tenfold-addition stage through two regioisomeric pathways. The reaction may be stopped prematurely at the eightfold-addition stage by increasing the amount of pyridine or by the use of an *ortho*-methylated phenyl Grignard reagent. The one-step multiple functionalization of [60]fullerene can be carried out in a synthetically viable yield, and the products possess intriguing structures and physical properties. The results raise the hope that the reaction will be applicable to multifunctionalization of higher fullerenes and carbon nanotubes. We can envision the use of the reported compounds for host–guest complex formation[12] and for applications in the field of catalysis and materials research.

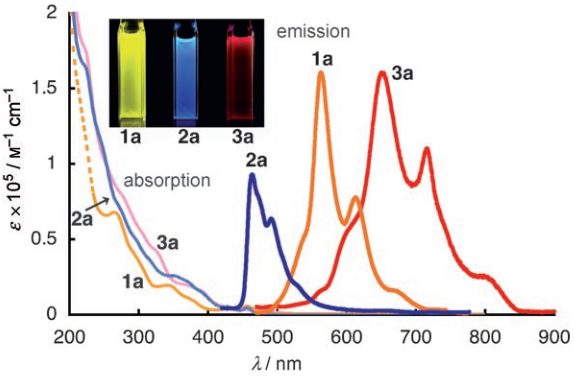


Figure 2. Absorption and emission (excited at $\lambda = 366$ nm) spectra of **1a**–**3a**. Intensities (arbitrary units) of emission spectra for **2a** and **3a** are magnified by factors of 3 and 5, respectively; inset: pictures of photoluminescence for **1a**–**3a**.

Experimental Section

1a and **2a** (1-g scale): Pyridine (34 mL) was added to a mixture of an organocopper reagent prepared from 4-*n*BuC_6H_4MgBr (0.95 M, 45 mL, 42 mmol) and $[CuBr(SMe_2)]$ (8.64 g, 42 mmol) in THF (44 mL) by syringe at 30°C. To this dark-green suspension was added a solution of C_{60} (1.0 g, 1.4 mmol) in 1,2-$Cl_2C_6H_4$ (40 mL). The resulting dark-brown suspension was gradually warmed to 40°C over 30 min. The reaction was monitored by HPLC (RPFullerene, Develosil; eluent: 1:1 toluene/acetonitrile), which indicated the formation of **1a** (retention time 6.5 min) and **2a** (retention time 9.2 min) after 40 h. The reaction was quenched with aqueous HCl (ca. 1 M, ca. 1 mL), and the solvent was removed under reduced pressure. The mixture was diluted with toluene (ca. 200 mL) and filtered through a pad of silica gel. An orange-colored eluent was evaporated to a solid, and the crude mixture was dissolved in the mixed solvent 1:1 toluene/acetonitrile (ca. 1000 mL). The yellow suspension was filtered and washed three times with the same mixed solvent to obtain **1a** (570 mg, 20%) as a yellow solid. The filtrate was evaporated to an orange solid and dissolved in 1:1 toluene/acetonitrile (ca. 100 mL), then subjected to treatment with preparative HPLC (RPFullerene, Develosil; eluent: 1:1 toluene/acetonitrile; flow rate: 20 mL min^{-1}). Compound **2a** was separated (retention time 19 min) and recrystallized with CS_2 and ethanol to obtain the desired product (1.1 g, 40%) as an orange solid.

Experimental details for compounds **1b**–**k**, **2b**–**f**, **2i**–**k**, **3a**, **3g**, **3h**, **5**, and **6** and X-ray data are supplied in the Supporting Information.

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[8] CCDC-629131 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request.cif.

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