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Review

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Selective Multiaddition of Organocopper Reagents to Fullerenes

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Contents

1. Introduction

As soon as a macroscopic quantity of fullerenes was synthesized and isolated from the soot produced by the arc-discharge method in 1990,[1,2] chemists started to study their reactivity toward organometallics such as alkyl, allyl, and aryl Grignard and organolithium reagents.[3–5] In retrospect, it is not surprising that nucleophilic addition reactions took place readily because of the high electrophilic reactivity of fullerenes. It was, however, rather unexpected that the reaction stopped at the monoaddition stage and did not take place further to the di- and multiaddition stages, giving the desired monoaddition product at best in moderate yield. It is notable that C_{60} was always recovered while the multi-addition side reactions took place.

One can consider two possible reasons for this complication (Scheme 1). The simplest hypothesis would be that the

second equivalent of the RLi or RMgX reagent added to the initial product a monoalkyl[60]fullerene anion, RC_{60}^-. However, this hypothesis may be too simple to account for the addition of more than three R anionic groups, because such reactions would generate $R_nC_{60}^{n-}$ intermediates, which may be energetically too unfavorable. Another hypothesis would assume a single-electron transfer (SET) reaction between RC_{60}^- and C_{60}. This process oxidizes RC_{60}^- to $RC_{60}^{\bullet}$ and generates a C_{60} radical anion. The neutral radical $RC_{60}^{\bullet}$ can then react with another equivalent of the R anion. Repetition of the SET and the monoaddition processes produces multiadducts and C_{60} anions. The latter regenerates C_{60} upon quenching of the reaction with water at the end of the reaction.

The necessary presence of an oxidant to promote the multiadditions was proven by a recent finding that molecular oxygen promotes the diaddition of Grignard reagents, which makes this reaction a reaction of considerable synthetic utility.[6–9] Thus, one can consider that molecular oxygen oxidized $C_{60}R^-$ in situ to the monoalkyl[60]fullerene radical $C_{60}R^{\bullet}$, to which the second equivalent of the Grignard reagents added (eq 1).

$$C_{60} + 2\ RMgBr + O_2 \longrightarrow \qquad (1)$$

R = CH$_2$SiMe$_3$, etc.
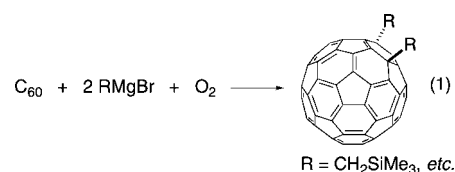
Multiaddition products are no less useful than the monoadducts if they can be synthesized selectively and in high yield, because richly functionalized fullerenes show interesting properties such as biochemical activities (e.g., DNA cleavage, etc.)[10–15] and photoelectrochemical functions (e.g., photo-voltaics, etc.).[16,17] To achieve selective multiaddition of organometallic reagents to fullerenes, one needs to control not only the number of organic groups to be added but also the regioselectivity of the addition, and the yield on each step must be very high to achieve high overall yield of the multiple reaction.

In 1996, one of us reported that a phenylcopper reagent derived from a Grignard reagent and a copper(I) halide adds five times and with complete regioselectivity to [60]fullerene in quantitative yield to produce 1,4,11,15,30-pentaaryl-2-hydro[60]fullerenes {abbreviated as penta(aryl)[60]fullerenes, $C_{60}Ar_5H$, in this review}.[18,19] When applied to [70]fullerene, the reaction selectively produced a triaddition product instead of the penta-addition product. When the copper reagent was modified by addition of pyridine, it added to [60]fullerene eight or 10 times. All of these reactions took place frequently in quantitative yield and with complete

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Eiichi Nakamura received degrees from the Tokyo Institute of Technology (B.S. and Ph.D. in chemistry). After postdoctoral work at Columbia, he came back to his alma mater and was promoted to the rank of professor. In 1995, he moved to the University of Tokyo. He has been honored with The Chemical Society of Japan Award for Young Chemists (1984), The Japan IBM Prize (1993), The Nagoya Medal for Organic Chemistry (2001), The Chemical Society of Japan Award (2003), and The Humboldt Research Award (2006). He is an Elected Fellow of the American Association for the Advancement of Science (1998), a Fellow of the Royal Society of Chemistry (2005), and a Foreign Honorary Member of the American Academy of Arts and Sciences (2008). His interests cover the field of physical organic, synthetic, organometallic, bioorganic, computational/theoretical chemistry, and electron microscopy, all of which focus on reactive intermediates.

regioselectivity and allowed the introduction of organic functionalities such as hydroxyl, thiol, ester, and carboxylic acid groups that are useful for further derivatization. In the past decade, the penta-addition and related multiple addition reactions of organocopper reagents to fullerenes were developed into a synthetic reaction of wide scope and with wide utility. This review reports on the chemistry of the multiaddition of organocopper reagents to [60]fullerene and [70]fullerene, as well as on some representative uses of the products.

**Scheme 1. Possible Pathways for Multiaddition of RLi and RMgX to C_{60}**
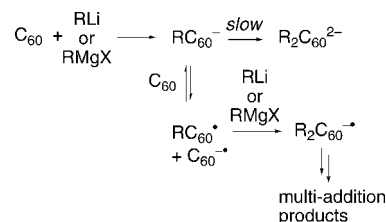
2. Multiple Addition of the Organocopper Reagents to [60]Fullerene

2.1. Penta-Additions of Aryl Groups

2.1.1. The Reaction, Its Synthetic Scope, and the Utility of the Products

The reaction of [60]fullerene and PhMgBr in the presence of a copper(I) halide was discovered serendipitously.[20] The yield of the pentaphenyl-adduct $C_{60}Ph_5H$ in the first experiment was a few percent but was quickly improved to over 90%. Under the optimized conditions, the reaction employing an excess amount of organocopper reagent prepared from PhMgBr (16 equiv) and $CuBr \cdot SMe_2$ (16 equiv) at room temperature, followed by acid quenching, gave the pentaphenyl-adduct $C_{60}Ph_5H$ (**1**) as an orange powder in almost quantitative yield (eq 2 and Table 1, entry 1). This reaction has been conducted up to the 100 g scale. The five phenyl groups are introduced around one pentagon of the fullerene molecule, which was converted to a cyclopentadiene. The phenyl groups surround the cyclopentadiene moiety and form an interesting cavity structure.

1: Ar = Ph
2: Ar = 4-$CF_3C_6H_4$
3: Ar = 4-$MeOC_6H_4$
4: Ar = 4-ClC_6H_4
5: Ar = 4-PhC_6H_4
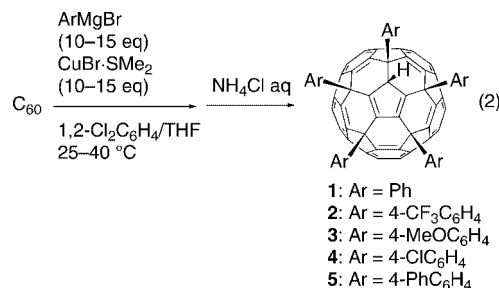
Monitoring of the reaction by high-performance liquid chromatography (HPLC) indicated the conversion of C_{60} directly to **1** without formation of mono- to tetra-adducts in detectable quantities and quenching of the reaction with acidic D_2O quantitatively produced $C_{60}Ph_5D$ with 96% deuterium incorporation. On the basis of our previous study on the reactivity of mono, di-, and triaddition products,[21] one can consider that the reaction takes place sequentially, as shown in Scheme 2. Thus, the first addition of one molecule of Ph_2Cu^- produces a mono(aryl)[60]fullerene anion A, and this is the slowest step in the whole reaction scheme. This anion is oxidized by the copper(I) salt to form a mono(aryl)[60]fullerene radical B, which undergoes a further addition reaction to give a diaryl[60]fullerene radical anion C. Oxidation of C gives a neutral 1,4-bis-adduct D. This intermediate D is probably more strained and more reactive than [60]fullerene. The same addition/oxidation reactions occur for D to produce the fulvene E.

The fifth phenyl group adds to the reactive fulvene moiety of **E** to produce a cyclopentadienide **F**. Formation of metallic copper in this reaction attests to the role of the copper(I)

Table 1. Multiaddition Reactions to Fullerenes Using Organocopper Reagents Prepared from CuBr·SMe$_2$ and RM

entry	fullerene	R	M	additives	products	yield(%)[a]	ref
addition of aryl and vinyl groups							
1	C$_{60}$	Ph	MgBr		C$_{60}$R$_5$H (**1**)	99	19
2	C$_{60}$	4-CF$_3$C$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**2**)	99	21
3	C$_{60}$	4-MeOC$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**3**)	99	21
4	C$_{60}$	4-ClC$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**4**)	99	21
5	C$_{60}$	4-PhC$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**5**)	99	21
6	C$_{60}$	(E)-1-propenyl[b]	Li		C$_{60}$R$_5$H (**6**)	85	22
7	C$_{60}$	(Z)-1-propenyl[b]	Li		C$_{60}$R$_5$H (**7**)	77	22
8	C$_{60}$	(E)-2-phenylethenyl[b]	Li		C$_{60}$R$_5$H (**8**)	83	22
9	H$_2$@C$_{60}$	Ph	MgBr		H$_2$@C$_{60}$R$_5$H (**9**)	92	39
10	C$_{60}$	4-(THPO)C$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**21**)	92	40
11	C$_{60}$	4-(THPS)C$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**27**)	~90	42
addition of alkyl groups							
12	C$_{60}$	Me	MgBr	DMI	C$_{60}$R$_5$H (**33**)	93	48
13	C$_{60}$	PhMe$_2$SiCH$_2$	MgCl	DMI	C$_{60}$R$_5$H (**44**)	25[b]	61
14	C$_{60}$	(4-PhC$_6$H$_4$)Me$_2$SiCH$_2$	MgCl	DMI	C$_{60}$R$_5$H (**45**)	16[b]	61
15	C$_{60}$	{4-(THPO)C$_6$H$_4$}Me$_2$SiCH$_2$	MgCl	DMI	C$_{60}$R$_5$H (**46**)	12[b]	61
addition of functional groups: aryl groups							
16	C$_{60}$	4-(EtO$_2$C)C$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**53**)	93	63
17	C$_{60}$	3-(EtO$_2$C)C$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**54**)	90	63
18	C$_{60}$	4-BrC$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**55**)	96	63
19	C$_{60}$	3-BrC$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**56**)	90	63
20	C$_{60}$	4-(piperidylcarbonyl)C$_6$H$_4$	MgBr	NMP[c]	C$_{60}$R$_5$H (**57**)	66	63
21	C$_{60}$	4-(MeC$_6$H$_4$O$_2$C)C$_6$H$_4$	MgBr		C$_{60}$R$_5$H (**58**)	45	63
22	C$_{60}$	4-(Me$_3$SiCC)C$_6$H$_4$	MgBr		C$_{60}$R$_5$Me (**61**)[d]	95	67
23	C$_{60}$	4-(^{n}BuMe$_2$SiCC)C$_6$H$_4$	MgBr		C$_{60}$R$_5$Me (**62**)	89	67
24	C$_{60}$	4-(n-C$_8$H$_{17}$Me$_2$SiCC)C$_6$H$_4$	MgBr		C$_{60}$R$_5$Me (**63**)	92	67
25	C$_{60}$	4-(n-C$_{10}$H$_{21}$Me$_2$SiCC)C$_6$H$_4$	MgBr		C$_{60}$R$_5$Me (**64**)	86	67
26	C$_{60}$	4-(n-C$_{12}$H$_{25}$Me$_2$SiCC)C$_6$H$_4$	MgBr		C$_{60}$R$_5$Me (**65**)	93	67
27	C$_{60}$	4-(n-C$_{14}$H$_{29}$Me$_2$SiCC)C$_6$H$_4$	MgBr		C$_{60}$R$_5$Me (**66**)	90	67
addition of functional groups: alkyl groups							
28	C$_{60}$	EtO$_2$CCH$_2$	ZnBr	DMI	C$_{60}$R$_5$H (**68**)	92	70
29	C$_{60}$	n-C$_6$H$_{13}$O$_2$CCH$_2$	ZnBr	DMI	C$_{60}$R$_5$H (**69**)	91	70
30	C$_{60}$	PhCH$_2$O$_2$CCH$_2$	ZnBr	DMI	C$_{60}$R$_5$H (**70**)	89	70
31	C$_{60}$	^{t}BuO$_2$CCH$_2$	ZnBr	DMI	C$_{60}$R$_5$H (**71**)	19[b]	70
32	C$_{60}$	1-adamantylO$_2$CCH$_2$	ZnBr	DMI	C$_{60}$R$_5$H (**72**)	30[b]	70
33	C$_{60}$	CF$_3$CH$_2$O$_2$CCH$_2$	ZnBr	DMI	C$_{60}$R$_5$H (**73**)	91	70
34	C$_{60}$	H(CH$_2$CH$_2$O)$_3$OCCH$_2$	ZnBr	DMI	C$_{60}$R$_5$H (**74**)	29[b]	70
35	C$_{60}$	Me$_3$SiCC(CH$_2$)$_2$O$_2$CCH$_2$	ZnBr	DMI	C$_{60}$R$_5$H (**75**)	31[b]	70
36	C$_{60}$	((-)-menthyl)O$_2$CCH$_2$	ZnBr	DMI	C$_{60}$R$_5$H (**76**)	92	70
addition of functional groups: a tetrahydrofuranyl group							
37	C$_{60}$	Ph	ZnBr	THF	C$_{60}$R$_4$(THF)H (**77**)	94	71
38	C$_{60}$	4-MeOC$_6$H$_4$	ZnI	THF	C$_{60}$R$_4$(THF)H (**78**)	93	71
39	C$_{60}$	4-^{i}PrC$_6$H$_4$	ZnI	THF	C$_{60}$R$_4$(THF)H (**79**)	94	71
40	C$_{60}$	4-PhC$_6$H$_4$	ZnI	THF	C$_{60}$R$_4$(THF)H (**80**)	84	71
41	C$_{60}$	4-MeC$_6$H$_4$	ZnI	THF	C$_{60}$R$_4$(THF)H (**81**)	89	71
42	C$_{60}$	4-BrC$_6$H$_4$	ZnI	THF	C$_{60}$R$_4$(THF)H (**82**)	53	71
43	C$_{60}$	4-(EtO$_2$C)C$_6$H$_4$	ZnI	THF	C$_{60}$R$_4$(THF)H (**83**)	28	71
octa- and deca-additions							
44	C$_{60}$	4-^{n}BuC$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_{10}$H$_2$-A (**93**)/B (**94**)[f]	32/60	77
45	C$_{60}$	4-^{n}BuC$_6$H$_4$	MgBr	pyridine[g]	C$_{60}$R$_{10}$H$_2$-A (**93**)/C$_{60}$R$_8$H$_2$ (**92**)	35/50	77
46	C$_{60}$	Ph	MgBr	pyridine[e]	C$_{60}$R$_{10}$H$_2$-A (**95**)/B (**96**)	24/50	77
47	C$_{60}$	4-^{n}BuOC$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_{10}$H$_2$-A (**97**)/B (**98**)	24/42	77
48	C$_{60}$	4-^{t}BuC$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_{10}$H$_2$-A (**99**)/B (**100**)	20/45	77
49	C$_{60}$	4-PhC$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_{10}$H$_2$-A (**101**)/B (**102**)	21/34	77
50	C$_{60}$	4-MeC$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_{10}$H$_2$-A (**103**)/B (**104**)	24/48	77
51	C$_{60}$	3-MeC$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_{10}$H$_2$-A (**105**)/B (**106**)	17/27	77
52	C$_{60}$	2-MeC$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_8$H$_2$ (**107**)	59	77
53	C$_{60}$	2,4-Me$_2$C$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_8$H$_2$ (**108**)	50	77
54	C$_{60}$	4-ClC$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_{10}$H$_2$-A (**109**)/B (**110**)	2/7	77
55	C$_{60}$	4-CF$_3$C$_6$H$_4$	MgBr	pyridine[e]	C$_{60}$R$_{10}$H$_2$-A (**111**)/B (**112**)	2/4	77
addition to fullerene derivatives							
56	C$_{60}$Bn$_2$	Ph	MgBr		C$_{60}$Bn$_2$Ph$_3$H (**115**)	86	21
57	CpFeC$_{60}$Me$_5$	Me	MgBr	pyridine[h]	CpFeC$_{60}$Me$_{10}$H (**116**)	~10	83
58	C$_{60}$Me$_5$Ph$_3$H$_2$	Ph	MgBr	DAD[i]	C$_{60}$Me$_5$Ph$_5$H−B (**118**)	90	75
addition to [70]fullerene							
59	C$_{70}$	Ph	MgBr		C$_{70}$R$_3$H (**119**)	93	89
60	C$_{70}$	4-CF$_3$C$_6$H$_4$	MgBr		C$_{70}$R$_3$H (**120**)	94	88
61	C$_{70}$	4-ClC$_6$H$_4$	MgBr		C$_{70}$R$_3$H (**121**)	94	89
62	C$_{70}$	4-PhC$_6$H$_4$	MgBr		C$_{70}$R$_3$H (**122**)	99	89
63	C$_{70}$	1-naphthyl	MgBr		C$_{70}$R$_3$H (**123**)	95	89
64	C$_{70}$	Me	MgBr		C$_{70}$R$_3$H (**124**)	90	89

[a] Yields are based on an isolated product that shows an HPLC purity better than 90%. [b] Isolated yield of 100% pure compounds after thorough purification by preparative HPLC. [c] N-Methyl-2-pyrrolidone was added to increase the solubility of the organomagnesium reagent. [d] The reactions were terminated with methyl iodide. [e] Pyridine/THF/1,2-Cl$_2$C$_6$H$_4$ = 1/2/1. [f] In the table, suffixes A and B are used to indicate the cyclophenacene type deca-adduct (**93**) and its isomer (**94**). [g] Pyridine/THF/1,2-Cl$_2$C$_6$H$_4$ = 35/20/45. [h] Pyridine/THF/1,2-Cl$_2$C$_6$H$_4$ = 13/27/60. [i] A stoichiometric amount of an α-diimine compound, 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene, was used.

atom as an oxidizing agent, as well as the carrier of the aryl group. The cyclopentadienide part of the product **F** donates

electrons to the bottom 50π-system through endohedral homoconjugation,[22] and this must be the reason that the

Scheme 2. Plausible Reaction Mechanism for the Penta-Addition of Five Phenyl Groups onto [60]Fullerene[a]
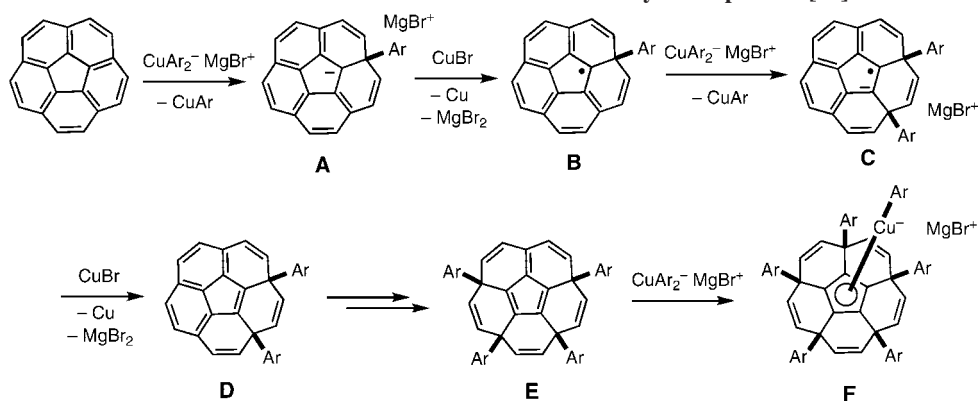
[a] Only a part of the structure of the fullerene core is shown in this scheme.

reaction stops at the penta-addition stage even when a large excess of the organocopper reagent was used. Note, however, that octa- and deca-additions take place when excess pyridine is present in the reaction mixture (vide supra).

This reaction can introduce five organic groups of considerable variety into [60]fullerene. Various aromatic groups with different electronic and steric properties (compounds **2**–**5**, eq 2) can be introduced in excellent yields essentially under one standard set of conditions (Table 1, entries 2–5).[23] Vinyl groups are also introduced by the use of 1-lithioalkene and a copper(I) halide in moderate to good yield (eq 3 and Table 1, entries 6–8).[24] A cuprate type (R$_2$CuLi) stoichiometry was employed for this reaction, and the E and Z isomers of the alkenyllithium reagents react with retention of the stereochemistry to give the corresponding E and Z adducts **6**–**8**.
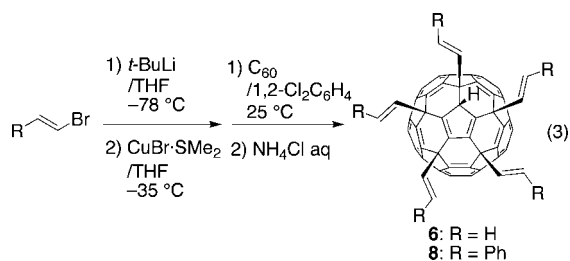
The electrochemistry of the penta-adduct C$_{60}$Ph$_5$H has been investigated in detail.[22] On the reduction side, an electron is accepted to the fullerene part and immediately transferred to the top cyclopentadienyl part to generate a cyclopentadienyl anion **9** with expulsion of H[•] (Scheme 3). This process took place more slowly at lower temperatures. A theoretical study of the penta-adduct suggested homoconjugation between the top cyclopentadiene moiety and the bottom 50π-moiety.[25] The cyclopentadienyl anion **9** was further reduced by reaction with potassium/mercury amalgam and potassium metal, producing a radical dianion **10** and trianion **11**, which are useful for obtaining fullerene dimers and hepta-adducts.[26] The anion **9** undergoes one-electron oxidation in the electrochemical process to form radical **12**.

The pentaaryl[60]fullerene anions C$_{60}$Ar$_5^-$·K$^+$ are soluble in water[27] and form spherical bilayer vesicles (Figure 1).[28] The fullerene bilayer was found to be unusually watertight, over a thousand times more watertight than lipid vesicles, the water permeation being controlled by the activation entropy.[29] X-ray crystallographic studies for the potassium complexes of the pentaaryl[60]fullerene anion K(C$_{60}$Ph$_5$)-

Scheme 3. Mono-, Di-, and Trianions of Pentaphenyl[60]fullerene
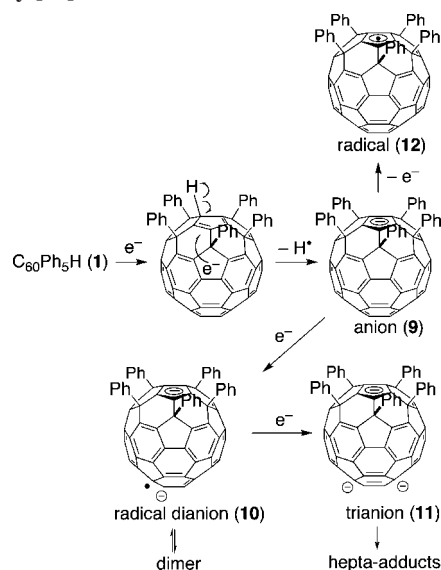
(thf)$_3$ (**13**), [K(thf)$_6$][C$_{60}$Ph$_5$] (**14**), and [K(18-crown-6)(DMF)]-[C$_{60}$Ph$_5$] (**15**) were performed (Figure 2).[30] The potassium ions were found to be solvated by polar ligands such as THF.

One of the most interesting features of the penta-adduct **1** is the cyclopentadienyl part, which can be used as a cyclopentadiene ligand for metal complexation. As in conventional cyclopentadienyl chemistry, the cyclopentadienyl moiety can be derivatized to a variety of pentahapto metal complexes. One striking application is the synthesis of sandwich type metal-η^5-fullerene complexes, buckyferrocenes[31–35] and buckyruthenocenes,[36–38] M(η^5-C$_{60}$R$_5$)(η^5-
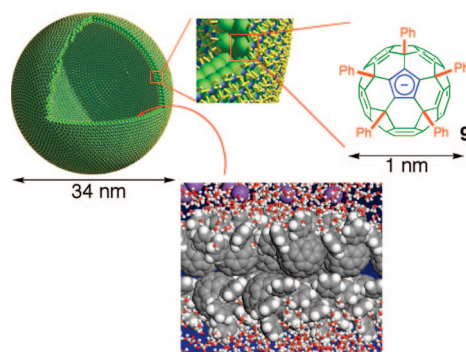
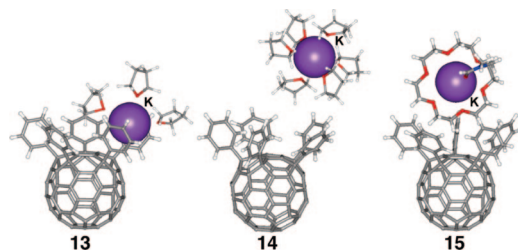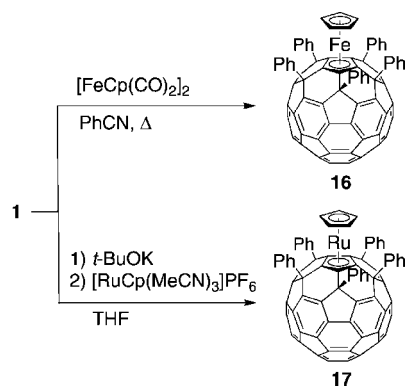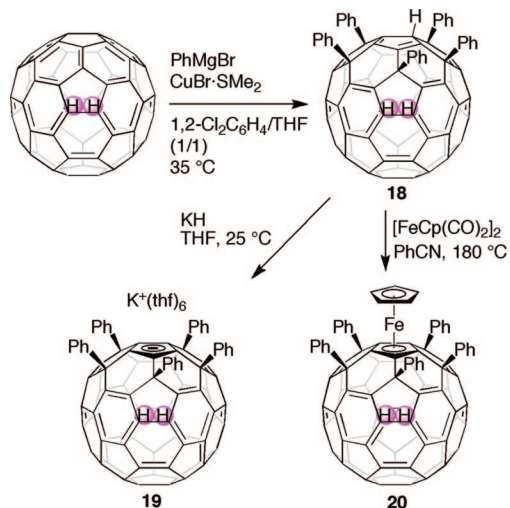

Figure 1. Watertight spherical bilayer vesicles.

Figure 2. X-ray crystallographic structures of the potassium complexes of $C_{60}Ph_5$.

**Scheme 4. Synthesis of Buckyferrocene and Buckyruthenocene**

Scheme 5. Synthesis of the Dihydrogen Encapsulated Penta-Adduct and Its Potassium and Iron Complexes

Cp) (M = Fe (**16**) and Ru (**17**); R = various organic groups; Cp = C_5H_5) (Scheme 4). These compounds were found to be extremely stable: They do not decompose even at temperatures above 300 °C and, upon cyclic voltammetric analysis, undergo reversible oxidation at the metal atoms and reversible reduction at the fullerene part.

The penta-addition of phenylcopper reagent onto dihydrogen encapsulated [60]fullerene, $H_2@C_{60}$, also proceeds regioselectively, and produces a dihydrogen encapsulated penta-adduct, $H_2@C_{60}Ph_5H$ (**18**) in quantitative yield (Scheme 5 and Table 1, entry 9).[39] Potassium and iron complexes, $[K(thf)_6][H_2@C_{60}Ph_5]$ (**19**) and $Fe(H_2@C_{60}Ph_5)Cp$ (**20**) were synthesized and crystallographically characterized to investigate susceptibility of the encapsulated molecular hydrogen to the magnetic environment of inside as well as outside of the fullerene cage.

Scheme 6. Synthesis of Shuttlecock-Shaped Molecules through Protection and Deprotection

23: R = $C_{12}H_{25}$
24: R = $C_{14}H_{29}$
25: R = $C_{16}H_{33}$
26: R = $C_{18}H_{37}$
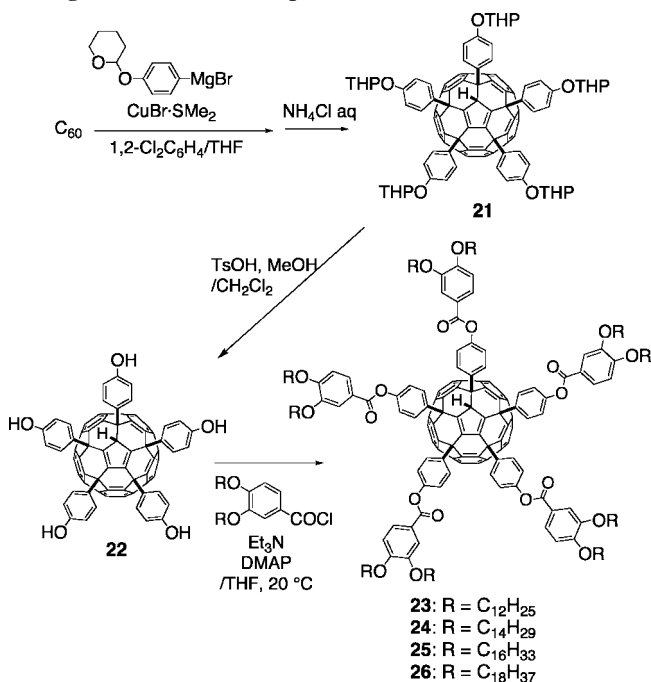
2.1.2. Penta(hydroxyphenyl)[60]fullerenes

The mild conditions of the penta-addition allow us to introduce a variety of functional groups onto the fullerene core. In this section, the introduction of substituted phenyl groups is described. For instance, the phenol group in 4-bromophenol is first protected with a tetrahydropyranyl (THP) ether, converted into the corresponding copper reagent and added to fullerene, and the THP group is then removed (Scheme 6).[40] Thus, the penta-addition of the copper reagent prepared from 4-(THPO)C_6H_4MgBr and CuBr·SMe$_2$ to [60]fullerene gave the protected compound **21**, which was subjected to deprotection by acid hydrolysis of the THP group producing the penta(4-hydroxyphenyl)[60]fullerene **22** in 92% yield (Table 1, entry 10). Acylation of the five hydroxyl groups with an appropriate acid chloride gave penta(ester) derivatives **23–26**. One conspicuous structural characteristic of these molecules is their conical shape. It was found that they form a columnar stack in crystalline and liquid crystalline states, because molecules can stack with each other in a head-to-tail manner. This molecular design led to the development of conical columnar liquid crystals from metallomesogens that have multistep redox active properties (Figure 3).[41]

2.1.3. Penta(mercaptophenyl)[60]fullerenes

The thiolate anion is a powerful nucleophile and serves to covalently connect the penta-adduct to electrophiles bearing a complex functionality. An example is the synthesis of fullerene glycoconjugates by a thiolate/alkyl halide coupling reaction in aqueous media (Scheme 7).[42] The precursor, **27**, was obtained by the penta-addition of the copper reagent prepared from a THP-protected 4-mercaptophenyl Grignard reagent and CuBr·SMe$_2$ (Table 1, entry 11). It is interesting to note that the sulfide groups did not interfere with the organocopper reaction. Deprotection of the THP groups was achieved by the use of trifluoroacetic acid and 2-mercaptoethanol[43,44] to obtain the penta(mercaptophenyl)[60]fullerene **28**. The reaction of **28** with glycoside
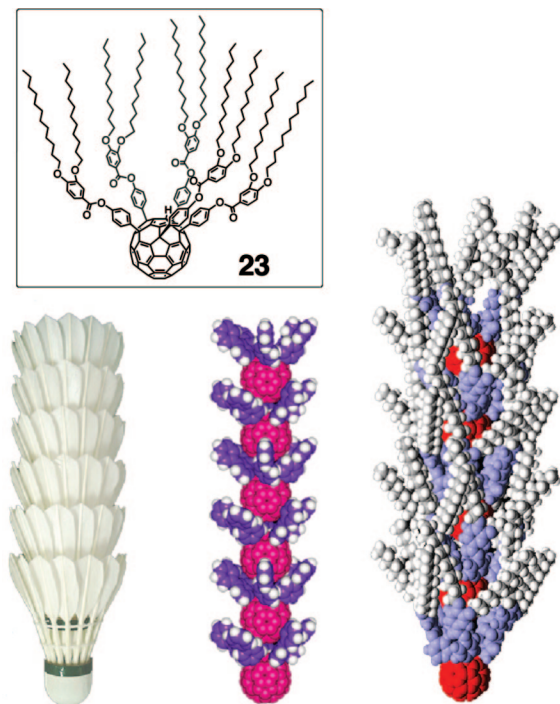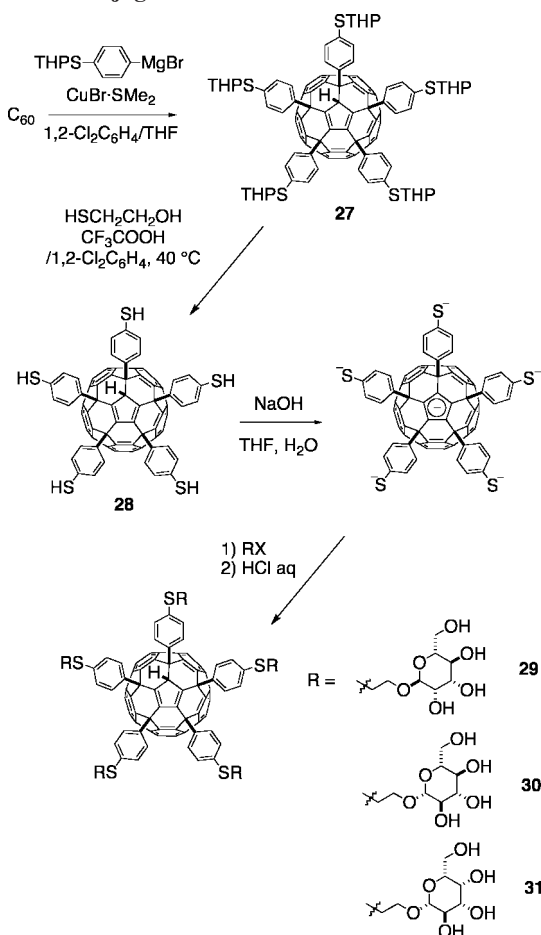
Figure 3. Columnar structure of crystalline and liquid crystalline fullerene derivatives.

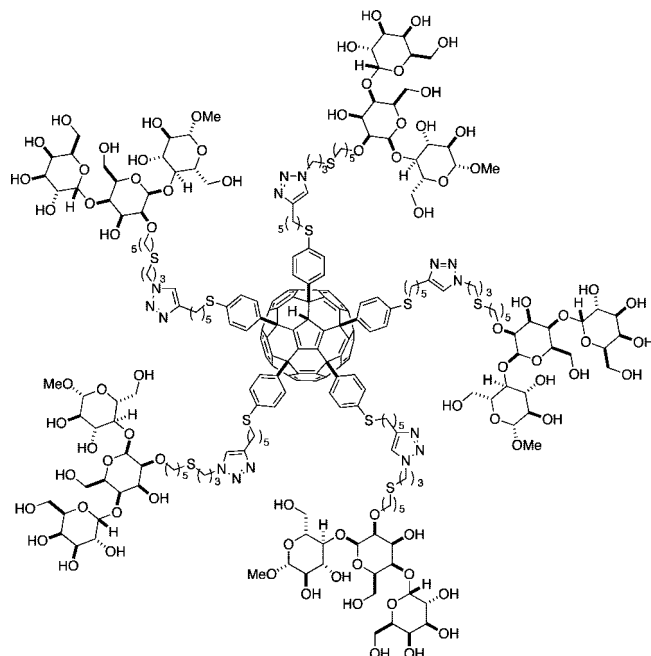**Scheme 7. Synthesis of α-D-Manno-, β-D-Gluco-, and β-D-Galactoconjugates**

Figure 4. Fullerene derivative **32** bearing five trisaccharides.
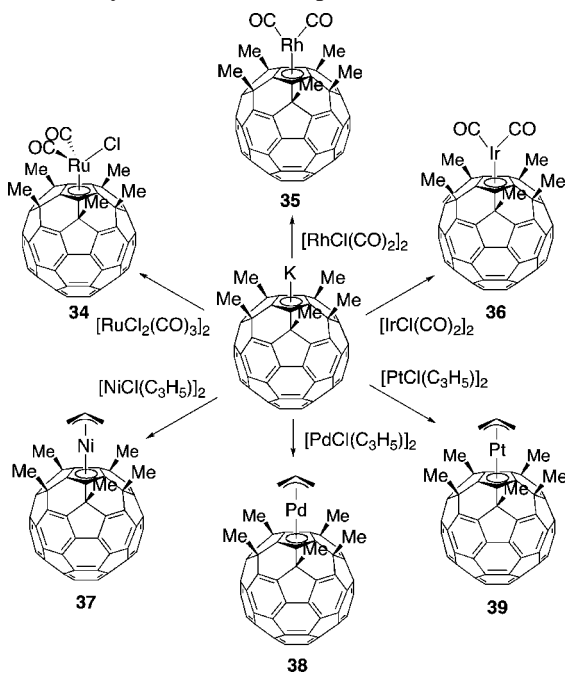
coupled with the fullerene part so that problematic deprotection procedures are unnecessary in the last stage of the synthesis. These amphiphilic glycoconjugates are expected to be useful in multivalent saccharide displays.[45] Much more complex glycoconjugates (**32**) (Figure 4) were also synthesized by the combined use of this method and the Click chemistry, a copper-catalyzed Huisgen cycloaddition reaction.[46]

## 2.2. Penta-Additions of Alkyl Groups

2.2.1. Penta(methyl)[60]fullerenes

In the preceding section, we described the penta-addition of aryl groups. This section describes the addition of alkyl groups. The pentaaryl[60]fullerenes $C_{60}Ar_5H$ are useful compounds, but the five aryl groups are not particularly suitable for some applications. It was found that addition of a methylcopper reagent and a silylmethylcopper reagent take place as smoothly as that of arylcopper reagents. It has, however, so far not been achieved to perform addition of higher alkyl groups, probably because of premature decomposition of the corresponding organocopper reagents through the β-hydrogen elimination. Thus, a penta-adduct bearing the methyl group, 1,4,11,15,30-pentamethyl-2-hydro[60]-fullerene, $C_{60}Me_5H$ (**33**), was synthesized[47] and serves as a better ligand for the formation of the transition metal complexes than the $C_{60}Ar_5H$ compounds. A detailed procedure for the large-scale synthesis of **33** is available in the literature.[48]
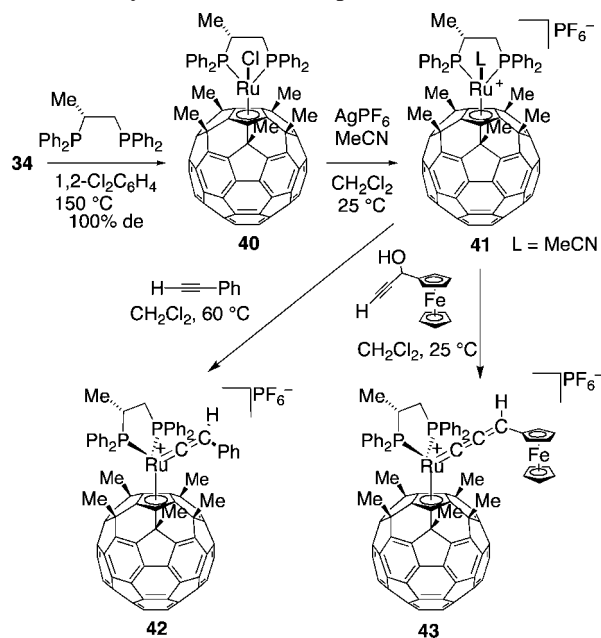
The synthesis of **33** was achieved in a manner similar to that employed for **1**, but it was necessary to use 1,3-dimethyl-2-imidazolidinone (DMI) as an additive. In addition, care must be taken to consider the high susceptibility of **33** and, particularly, its anionic form, to air oxidation. The pentamethylation of [60]fullerene with 12 equiv each of MeMgBr, CuBr·SMe₂, and DMI in 1,2-dichlorobenzene/THF at 35 °C was completed within 40 min, and after aqueous workup, **33** was obtained as a red microcrystalline solid in 93% isolated yield (eq 4 and Table 1, entry 12). The origin of the favorable effects of DMI is uncertain at this time, but it may

in the presence of sodium hydroxide (6 equiv) in THF/H₂O (2/1) produced the glycoconjugates **29**–**31** in 73–87% yield. This synthetic route allowed an unprotected sugar to be

Scheme 8. Synthesis of Transition Metal η^5-Pentamethyl[60]fullerene Complexes

Scheme 9. Derivatization of the Half-Sandwich Ruthenium η^5-Pentamethyl[60]fullerene Complexes

stabilize the organocopper reagent. In the absence of DMI, the copper reagent is consumed rapidly, which results in the recovery of a considerable amount of [60]fullerene. The product is quite stable in air as a solid but decomposes in solution in air, resulting in a decrease of the purity from 100 to 80% in 24 h.
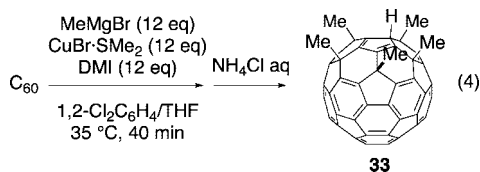
Because of smaller steric hindrance of the $C_{60}Me_5$ moiety of **33** than the $C_{60}Ar_5$ moiety in **1**, not only sandwich complexes, buckymetallocenes, but also half-sandwich type complexes[49–53] were obtained by the use of the $C_{60}Me_5$ ligand. Late transition metal complexes, for instance, $Ru(\eta^5$-$C_{60}Me_5)Cl(CO)_2$ (**34**), $Rh(\eta^5$-$C_{60}Me_5)(CO)_2$ (**35**), $Ir(\eta^5$-$C_{60}Me_5)$-$(CO)_2$ (**36**), and $M(\eta^5$-$C_{60}Me_5)(\eta^3$-allyl) (**37–39**; M = Ni, Pd, and Pt), have been synthesized (Scheme 8). These complexes are useful starting materials for investigations of the organometallic chemistry of the metal−fullerene complexes. A variety of ligand exchange reactions involving the carbonyl and the chloro ligands took place on the metal center without cleavage of the metal−fullerene bond. Note that such ligand exchange reactions in the η^2-fullerene metal complexes[54,55] are known to result in the loss of the η^2-fullerene ligand during the reaction. The ruthenium chloro dicarbonyl complex **34** has been derivatized to chiral complex $Ru(\eta^5$-$C_{60}Me_5)((R)$-prophos)Cl (**40**),[56] cationic complex $[Ru(\eta^5$-$C_{60}Me_5)((R)$-prophos)(MeCN)][PF_6]$ (**41**), carbene complex $[Ru(\eta^5$-$C_{60}Me_5)((R)$-prophos)(=C=CH-Ph)][PF_6]$ (**42**), allenylidene complex $[Ru(\eta^5$-$C_{60}Me_5)((R)$-prophos){=C=C=CH(ferrocenyl)}][PF_6]$ (**43**),[57] and so on (Scheme 9).[58]

Scheme 10. Synthesis of the Pentaalkyl Adducts That Form a Columnar Liquid Crystalline Structure
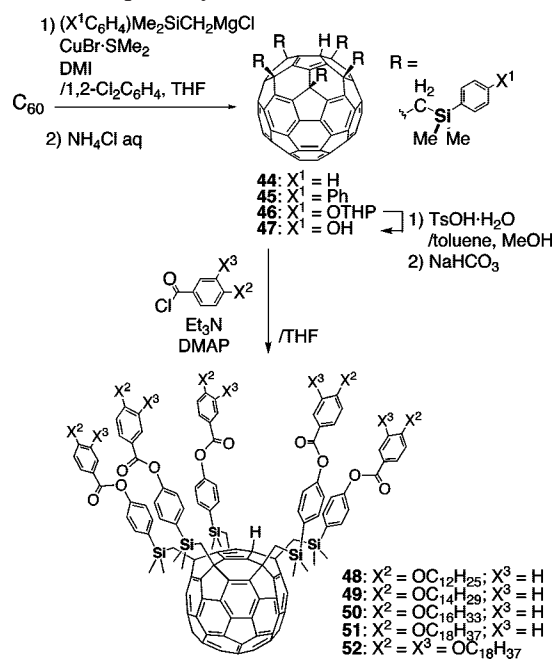
2.2.2. Penta(silylmethyl)[60]fullerenes

Organocopper-mediated penta-addition reactions to [60]-fullerene were also performed with tri(organo)silylmethyl groups. Because these alkyl groups have no β-hydrogen atoms, the organocopper reagents are easily prepared without decomposition resulting from β-elimination on the copper atom. For example, a trimethylsilylmethylcopper reagent is stable and soluble in common organic solvents, and its single crystals are characterized by X-ray analysis as a tetramer, $[Cu(CH_2SiMe_3)]_4$.[59,60] Penta-addition of aryldimethylsilyl-methyl magnesium chloride in the presence of a copper(I) salt to [60]fullerene takes place to produce the desired penta-adducts, $C_{60}(CH_2SiMe_2Ar)_5H$ (**44−46**; Ar = Ph, 4-PhC$_6$H$_4$, and 4-THPOC$_6$H$_4$) (Scheme 10 and Table 1, entries
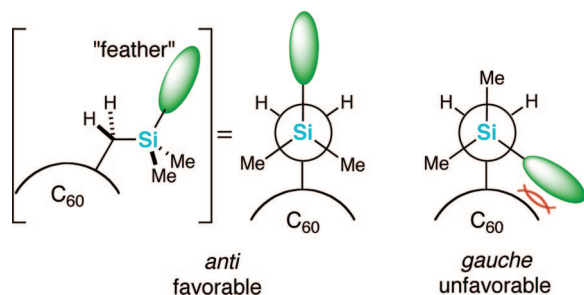
Figure 5. Schematic drawing for the anti conformation that creates a cap-shaped cavity on a fullerene core.

13−15).[61] These products are highly soluble in toluene, THF, chloroform, and dichloromethane but insoluble in ethanol and water.
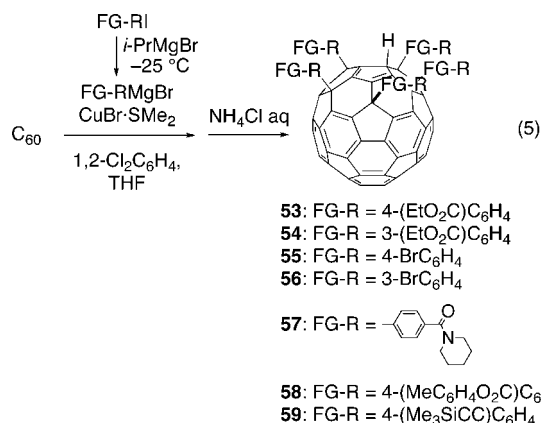
These penta(aryldimethylsilylmethyl)[60]fullerenes form better mesogenic structures **48**−**52**. The cavity created by these groups on the fullerene core is wider than the cavity created by five aryl groups (Figure 3) and has the shape of a cup rather than a cone. This structural feature is due to the rather long Si−C bond (1.89 Å) and a conformational characteristic peculiar to the CH$_2$Si(Me$_2$)C system (Figure 5). As a result of the larger cavity size, the fullerene moiety of the next molecule in a columnar stack can be fitted more deeply and with a shorter fullerene−fullerene distance than a fullerene in the column created by the penta-aryl molecules (compare Figure 6 with Figure 3 and **44/45** with **5** in Figure 6). With such second-generation shuttlecock mesogens, the resulting columnar liquid crystals exhibit higher transition temperatures (ca. 180 vs 140 °C) than those for the first-generation mesogens.

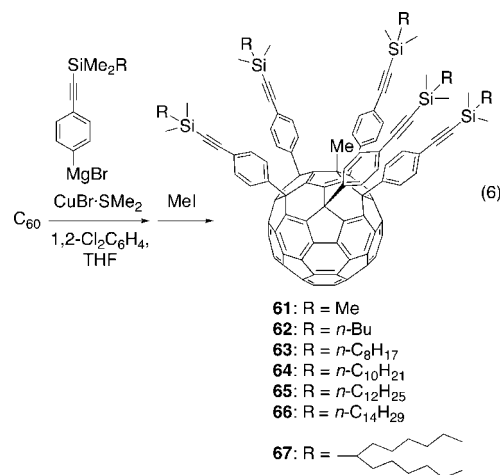## 2.3. Additions of Functionalized Organocopper Reagents

2.3.1. Synthesis Using Organocopper Reagents with Mg/I Exchange

In sections 2.1.2 and 2.1.3, we described the postfunctionalization of fullerene penta-adducts. It would, however, be much more convenient and more pleasing if one could introduce a functional group directly by the penta-addition reaction. Introduction of ester groups is a good example, because the ester linkage is a useful tool for connection of two or more chemical structures under very mild conditions.[62] Thus, 5-fold introduction of alkoxycarbonylphenyl groups was achieved by the use of functionalized organocopper reagents (eq 5)[63] with the aid of a mild iodine/magnesium exchange procedure pioneered by Knochel.[64–66] A transmetalation reaction between the functionalized aryl iodide and the ^{i}PrMgBr is employed to prepare the functionalized Grignard reagents, which are then transmetallated in situ to the corresponding copper reagents by reaction with CuBr·SMe$_2$. The aryl iodides are treated with ^{i}PrMgBr at −25 °C for 1 h and then with CuBr·SMe$_2$ at the same temperature. Orange organocopper reagents are generated and are warmed to 25 °C, and then, a solution of C$_{60}$ is added at the same temperature. In this manner, functionalized adducts **53**−**59** were prepared in high yields (Table 1, entries 16−22). In particular, an ethyl benzoate ester compound **53** is amenable to further modifications through elaboration of the functional groups. Hydrolysis of the five ester groups yields the pentacarboxylic acid derivative C$_{60}$(C$_6$H$_4$COOH)$_5$H (**60**). This compound is highly soluble in THF, DMF, ethanol,

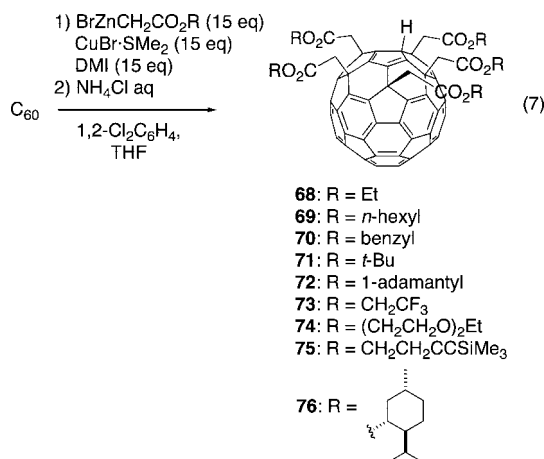methanol, and alkaline water and will be useful for engineering applications.

53: FG-R = 4-(EtO$_2$C)C$_6$H$_4$
54: FG-R = 3-(EtO$_2$C)C$_6$H$_4$
55: FG-R = 4-BrC$_6$H$_4$
56: FG-R = 3-BrC$_6$H$_4$

57: FG-R =

58: FG-R = 4-(MeC$_6$H$_4$O$_2$C)C$_6$H$_4$
59: FG-R = 4-(Me$_3$SiCC)C$_6$H$_4$

The 4-(silylethynyl)phenyl motif was used to obtain new mesogenic structures. A related compound, C$_{60}$(C$_6$H$_4$CC-SiMe$_3$)Me (**61**), was obtained in 90% yield[67] by the penta-addition followed by in situ methylation[68,69] of the cyclopentadienide intermediate with iodomethane. Similarly, a homologous series of compounds **62**−**67** bearing linear long alkyl chains was obtained with an isolated yield of better than 85% (eq 6 and Table 1, entries 22−27). Interestingly, these pentakis[4-(alkyldimethylsilylalkynyl)phenyl] compounds **61**−**66** form a layered structure in crystals and in liquid crystals (Figure 7), rather than columnar stacks. Molecules **62**−**64** possessing longer alkyl chains show a smectic liquid crystalline phase over the temperature range 10−220 °C.

61: R = Me
62: R = n-Bu
63: R = n-C$_8$H$_{17}$
64: R = n-C$_{10}$H$_{21}$
65: R = n-C$_{12}$H$_{25}$
66: R = n-C$_{14}$H$_{29}$

67: R =

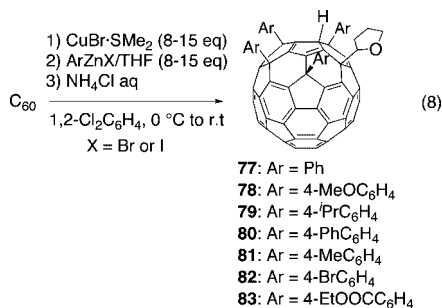### 2.3.2. Organocopper Reagents from the Reformatsky Reagent

Another way to install polar functional groups is through the use of organozinc reagents. Reformatsky reagents, ester-stabilized organozinc reagents, have high functional group tolerance and provide a synthetic method complementary to the iodine/magnesium exchange method in the previous section. Penta-additions of the Reformatsky reagents in the presence of a stoichiometric amount of CuBr·SMe$_2$ to [60]fullerene gave the expected penta-adducts, C$_{60}$(CH$_2$-CO$_2$R)$_5$H (**68**−**75**; R = Et, n-hexyl, benzyl, t-Bu, 1-adamantyl, CH$_2$CF$_3$, (CH$_2$CH$_2$O)$_2$Et, and CH$_2$CH$_2$CCSiMe$_3$) (eq 7 and Table 1, entries 28−35).[70] These penta-adducts can be derivatized to the corresponding buckyferrocenes and

buckyruthenocenes. The (−)-menthyl group was also introduced, producing a homochiral C_5 symmetric compound (Table 1, entry 36).

68: R = Et
69: R = n-hexyl
70: R = benzyl
71: R = t-Bu
72: R = 1-adamantyl
73: R = CH_2CF_3
74: R = $(CH_2CH_2O)_2Et$
75: R = $CH_2CH_2CCSiMe_3$

76: R =

2.3.3. Addition of 2-Tetrahydrofuranyl Groups by C−H Bond Activation

An interesting reaction was discovered recently when arylzinc reagents were used under the copper-mediated conditions.[71] The reaction of [60]fullerene with PhZnBr reagent (8 equiv) in the presence of CuBr·SMe$_2$ (8 equiv) and THF (420 equiv) in 1,2-dichlorobenzene produces a mono-2-tetrahydrofuranyl tetraaryl adduct, $C_{60}Ph_4(C_4H_7O)H$ (**77**) in 94% yield (eq 8 and Table 1, entry 37). Other arylzinc reagents may also be used for the synthesis of the 2-tetrahydrofuranyl adducts **78**−**83** in 28−94% yield. Electron-donating zinc reagents give higher chemical yields (Table 1, entry 38−41) than electron-withdrawing zinc reagents, $4\text{-}BrC_6H_4ZnX$ and $4\text{-}(EtO_2C)C_6H_4ZnX$ (28−53%) (Table 1, entries 42 and 43). The normal pentaaryl-adduct, $C_{60}Ar_5H$ (42−59%), formed when an arylzinc reagent bearing an electron-withdrawing group was employed.

77: Ar = Ph
78: Ar = 4-MeOC$_6$H$_4$
79: Ar = 4-^{i}PrC$_6$H$_4$
80: Ar = 4-PhC$_6$H$_4$
81: Ar = 4-MeC$_6$H$_4$
82: Ar = 4-BrC$_6$H$_4$
83: Ar = 4-EtOOCC$_6$H$_4$

One possible reaction mechanism involves a SET process[72] from the arylzinc reagent to [60]fullerene (Scheme 11). The resulting radical cation of the arylzinc reagent generates a 2-tetrahydrofuranyl radical, which is coupled with the [60]fullerene radical anion to produce an anion of the mono-2-tetrahydrofuranyl adduct, $C_{60}(C_4H_7O)^-$. In the presence of a copper salt, a further addition reaction of the aryl groups takes place to give $C_{60}Ar_4(C_4H_7O)^-$, which is protonated to produce the products. The electron-rich arylzinc reagent undergoes a fast SET process to give the mono-2-tetrahydrofuranyl tetraaryl adducts in good yield, while the electron-deficient reagents yield both 2-tetrahydrofuranyl adducts and pentaaryl-adducts with a slow SET process.

The cyclopentadiene parts of the THF-added products can be converted to the corresponding buckyferrocene derivatives
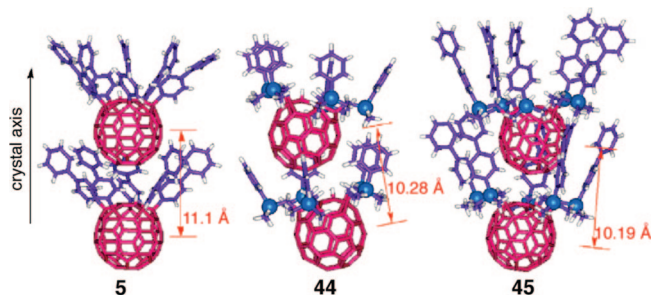

Figure 6. Closer distance between the fullerene cores in the penta(dimethylsilylmethyl)[60]fullerenes **44** and **45** than in the penta-biphenyl fullerene **5**.
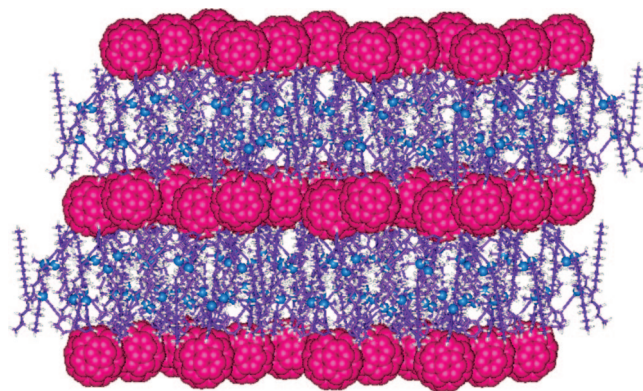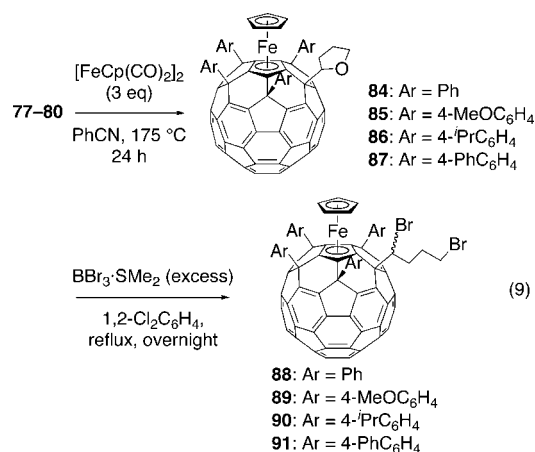

**Figure 7.** Lamellar assembly of the penta-adduct **64**.

$Fe[C_{60}Ar_4(C_4H_7O)]Cp$ (**84**−**87**) in good yields (eq 9). The 2-tetrahydrofuranyl group can be transformed into other functional groups that have been unavailable thus far by other synthetic methods. For instance, treatment of $Fe[C_{60}Ar_4\text{-}(C_4H_7O)]Cp$ with excess BBr$_3$·SMe$_2$ resulted in cleavage of the THF ring to give a dibromide $Fe[C_{60}Ar_4(C_4H_7Br_2)]Cp$ (**88**−**91**) in good yield, as shown in eq 2.4.

84: Ar = Ph
85: Ar = 4-MeOC$_6$H$_4$
86: Ar = 4-^{i}PrC$_6$H$_4$
87: Ar = 4-PhC$_6$H$_4$

88: Ar = Ph
89: Ar = 4-MeOC$_6$H$_4$
90: Ar = 4-^{i}PrC$_6$H$_4$
91: Ar = 4-PhC$_6$H$_4$

2.4. Octa- and Deca-Additions

Addition of more than five organic groups by the copper methodology once appeared to be impossible because the reaction stopped so perfectly at the penta-addition stage. It was found recently, however, that when excess pyridine was added to the reaction mixture, one can achieve octa- and deca-addition of arylcopper reagents to obtain $C_{60}Ar_8H_2$ (**92**; Ar = 4-n-BuC$_6$H$_4$) and $C_{60}Ar_{10}H_2$ (**93** and **94**; Ar = 4-n-BuC$_6$H$_4$) (Scheme 12).[73–78] The deca-adducts consisted of two regioisomers **93** and **94** because of the structural isomerism resulting from the location of the aryl groups.

Scheme 11. Plausible Reaction Pathway Containing a SET from the Arylzinc Reagent to [60]Fullerene Generating the 2-Tetrahydrofuranyl Radical
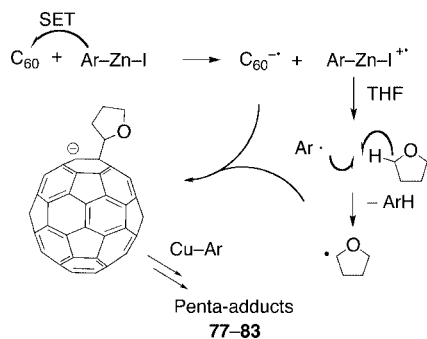
Scheme 12. One-Step Deca-Addition of the Aryl Groups to [60]Fullerene[a]
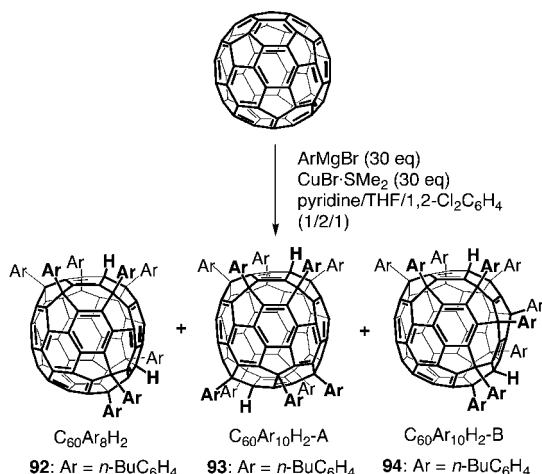
[a] Isomers always form with respect to the relative location of the hydrogen atom in the pentagon surrounded by five aryl groups. Only one isomer is shown in this figure.

When the first penta-addition took place on the pentagon at the top (i.e., North Pole) of fullerene, the second penta-addition can take place either on the pentagon at the bottom (South Pole) to give **93** or on the one at the side bottom (Australia) to give **94**. Because of steric effects of the five aryl groups at the top, the side bottom path may stop prematurely at an octa-addition stage to give **92**. The bottom addition product is C_5 symmetric, and the side bottom adduct is C_{2v} symmetric (n.b., here, we neglect the cyclopentadienyl hydrogen groups that cause the formation of many diastereomers). To differentiate these two isomers, we use a suffix A for the C_{2v} type isomer and a suffix B for the C_5 type isomer.

The reaction of [60]fullerene with an organocopper reagent prepared from a stoichiometric mixture of n-BuC$_6$H$_4$MgBr and CuBr·SMe$_2$ in 1,2-Cl$_2$C$_6$H$_4$/THF in the presence of excess pyridine (ca. 1:2:1, pyridine/THF/1,2-Cl$_2$C$_6$H$_4$) gives a 1:2 mixture of the deca-adducts **93** and **94** in a combined yield of 92% together with a trace amount of the octa-adduct **92** (Table 1, entry 44). The reaction procedure is as simple as the penta-addition and can be executed easily on a 1 g scale. Separation of the two structurally different deca-adducts **93** and **94** can often be achieved easily by recrystallization and/or chromatography on silica gel. It has been suggested that weak coordination of pyridine to the copper atom in a possible intermediate, Cu–C$_{60}$Ar$_5$, is responsible for the success of the second penta-addition.[79]
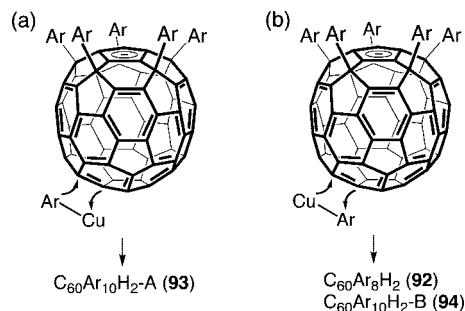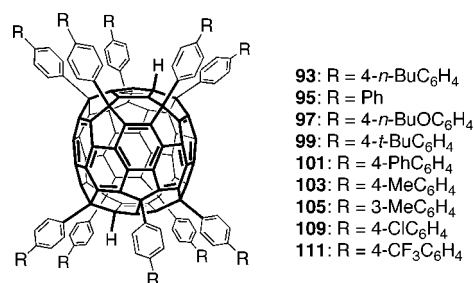

Figure 8. Selectivity of the bottom functionalization. (a) The reaction producing **93**. (b) The reaction producing **92** and **94**.

The observed bifurcation of the reaction pathways must have occurred when the sixth aryl group was added to the penta-adduct, as shown in Figure 8. In path a, the sixth Ar group reacts with the carbon atom next to the bottom pentagon, and the seventh to the tenth Ar groups are placed around the bottom pentagon to produce C$_{60}$Ar$_{10}$H$_2$-A (**93**). Path b is an alternative mode of addition and produces, in the end, C$_{60}$Ar$_8$H$_2$ (**92**) and C$_{60}$Ar$_{10}$H$_2$–B (**94**). Assuming equal reactivities of the pentagons, one can expect that the **93**:**94** ratio should be 1:5. The experimental ratio, however, is 1:2.

The octa-adduct **92** forms when the reaction leading to **94** prematurely finishes after the addition of the eighth Ar group, probably as a result 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-Cl$_2$C$_6$H$_4$) is a synthetically viable procedure that produced the deca-adduct **93** (35%) and the octa-adduct **92** (50%; Table 1, entry 45). The octa-adduct C$_{60}$Ar$_8$H$_2$ can be converted into the deca-adduct-B as described in section 2.5.

The scope of this octa- and deca-addition reaction is quite broad, as shown in Table 1, entries 46−55 (compounds **95**−**112**). In all cases, [60]fullerene was completely consumed, and the penta-adduct C$_{60}$Ar$_5$H accounts for most of the rest of the product other than the octa- and deca-adducts. Phenyl groups free of steric effects (Table 1, entries 46−50) yield the deca-adducts in about 70% combined yield (A and B generally in a ratio of 1:2). Thus, the 10 carbon−carbon bond formation reactions take place in an average of 96.5% yield each time. A *meta*-methyl group on the aryl addend appears to exert some steric effects on the reaction to decrease the yield to 44% combined yield (Table 1, entry 51). An *ortho*-substituted arylcopper reagent selectively produces the octa-adduct (Table 1, entries 52 and 53). Aryl copper reagents bearing an electron-withdrawing group undergo the 10-fold addition, but reaction is very slow (Table 1, entries 54 and 55).

93: R = 4-n-BuC$_6$H$_4$
95: R = Ph
97: R = 4-n-BuOC$_6$H$_4$
99: R = 4-t-BuC$_6$H$_4$
101: R = 4-PhC$_6$H$_4$
103: R = 4-MeC$_6$H$_4$
105: R = 3-MeC$_6$H$_4$
109: R = 4-ClC$_6$H$_4$
111: R = 4-CF$_3$C$_6$H$_4$

The octa- and deca-addition reactions to [60]fullerene offer not only a powerful methodology for the preparation of
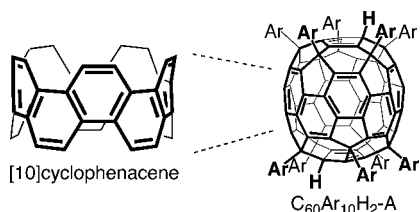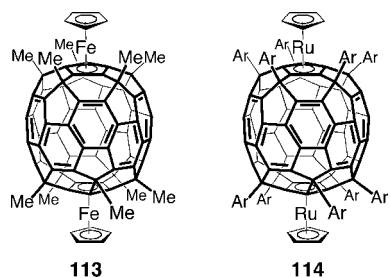
Figure 9. Cyclic benzenoid system, [10]cyclophenacene.

Figure 10. Double-decker buckymetallocenes.

nanometer-scale molecules in one step but also a unique tool for selective destruction of the spherical π-conjugation system of the [60]fullerene, leading to the construction of a hoop-shaped cyclic π-electron-conjugated benzenoid system (Figure 9). These compounds belong to the long sought class of [10]cyclophenacenes, which can be formally generated by rolling a phenacene ribbon into a ring. Such π-systems have attracted the interest of chemists and physicists for more than 50 years, ever since Heilbronner's prediction,[80] and the cyclophenacenes are predicted to be stable by theoretical calculations.[81,82] The [10]cyclophenacene part of the deca-adduct was found to be luminescent with maximum emission at 562 and 612 nm, with a quantum yield ϕ from 0.1 to 0.18. Note that [60]fullerene itself is known not to be fluorescent ($\phi = 0.00032$).

Another interesting feature of the deca-adducts is that the compounds provide a scaffold for the synthesis of dinuclear metal complexes because there are two cyclopentadiene parts on the top and bottom of [60]fullerene.[83] Di-iron and diruthenium [60]fullerene complexes, $(CpM)_2(C_{60}R_{10})$ (**113**,

116   **113**
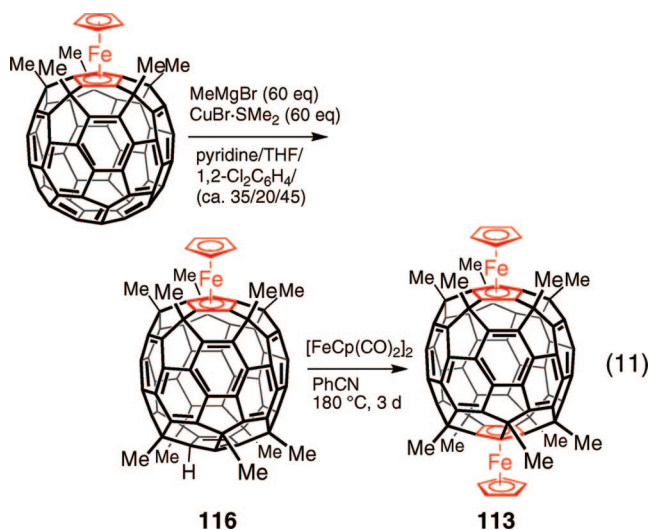
$M = Fe; R = Me;$ **114**, $M = Ru; R =$ aryl groups), have two metallocene moieties attached to both poles of [60]fullerene (Figure 10). These bis-metallocene compounds may be called double-decker buckyferrocenes and -ruthenocenes. Electronic interaction between two iron atoms through the [10]cyclo-

phenacene part with endohedral homoconjugation was found by electrochemical studies; that is, the two iron atoms in **113** are electrochemically nonequivalent (a pair of oxidation waves at 0.06 and 0.17 V vs Fc/Fc^+) despite the fact that they are structurally equivalent. This 110 mV difference in the two oxidation potentials (ΔE) is comparable to those observed previously for phenylene-linked diferrocenes (ΔE = 131, 90, and 104 mV for o-, m-, and p-C_6H_4) and larger than that of a biphenylene-linked diferrocene ($\Delta E = 70$ mV).[84,85] Hence, the fullerene cage of **113** is still a good π-electron bridge despite the interruption of the sp^2 conjugation by the 10 sp^3 carbon atoms. This suggests that multimetal fullerene complexes have potential as a molecular semiconductor on a single molecule basis.

2.5. Additions to [60]Fullerene Derivatives

It has been reported that the copper-mediated multiple addition reaction to [60]fullerene derivatives also takes place under the same conditions.[21] When a dibenzyl[60]fullerene $C_{60}(CH_2Ph)_2$[86] ($C_{60}Bn_2$) was treated with the phenylcopper reagent, addition of three phenyl groups took place to give a mixed penta-addition product, $C_{60}Bn_2Ph_3H$ (**115**), in 86% yield (eq 10 and Table 1, entry 56). The corresponding metal complexes have been reported.[87] These products provide an unsymmetrical environment to the symmetric fullerene core and provide us further opportunities that are unavailable for the symmetric penta-addition products.
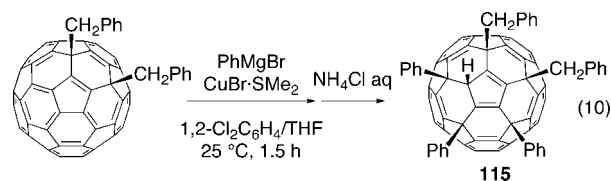

The buckyferrocene, $Fe(C_{60}Me_5)Cp$, undergoes a further penta-addition reaction under the "pyridine" condition (eq 11 and Table 1, entry 57).[83] A solution of $Fe(C_{60}Me_5)Cp$ in 1,2-dichlorobenzene was added to a pyridine-modified methylcopper reagent that was prepared from $CuBr \cdot SMe_2$ and MeMgBr in pyridine, and the reaction produced an air-sensitive deca-adduct $(CpFe)(C_{60}Me_{10})H$ (**116**). Heating **116** and $[FeCp(CO)_2]_2$ together in benzonitrile at 180 °C for 3 days produced the double-decker buckyferrocene, $(CpFe)_2(C_{60}Me_{10})$ (**113**). This very stable compound **113** adds to the repertoire of three-layered metal/C_{60}/metal molecules discussed in a previous section.

An octa-adduct was smoothly converted into the deca-adduct **B** with the aid of an α-diimine additive (eq 12). The reaction of $C_{60}Me_5Ph_3H_2$ (**117**) with an organocopper reagent derived from PhMgBr (30 equiv) and $CuBr \cdot SMe_2$ (30 equiv) in the presence of 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (30 equiv) in o-dichlorobenzene/THF (1/1) produced $C_{60}Me_5Ph_5H_2$–B (**118**) in 90% yield (Table 1, entry 58). The reaction mechanism is unclear, but interaction between the Cu atom and this α-diimine ligand may favorably affect the use of pyridine.

3. Tri-Addition of the Organocopper Reagents to [70]Fullerene

The reactions of [70]fullerene with organocopper reagents are reported (eq 13 and Table 1, entries 59−64).[88,89] Unlike the reactions of [60]fullerene, the products are triadducts
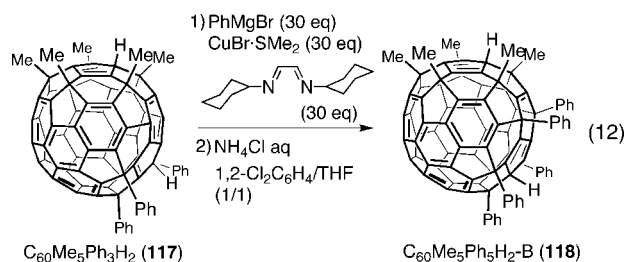
$C_{70}R_3H$ (**119**–**124**). Thus, the addition reaction takes place 100% selectively on the side top region of the football-shaped [70]fullerene rather than at the pointed end of the molecule and stopped precisely after triaddition. The triadducts **119**–**124** have an indene part structure embedded on the large [70]fullerene π-electron conjugated system.
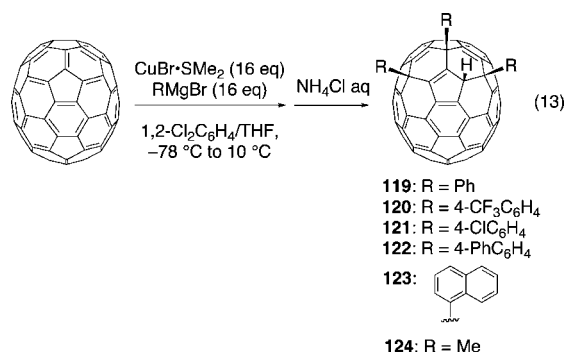
The triadduct **120** can be deprotonated with thallium ethoxide to obtain the corresponding pentahapto [70]fullerene complex $Tl[\eta^5\text{-}C_{70}(C_6H_4CF_3)_3]$ (**125**).[89] The trimethylated compound $C_{70}Me_3H$ (**124**) gives a buckyferrocene $Fe(\eta^5\text{-}C_{70}Me_3)(\eta^5\text{-}Cp)$ (**126**) by the reaction of **124** with [FeCp-$(CO)_2]_2$ in benzonitrile at high temperature (160 °C). The X-ray crystal structures of both complexes **125** and **126** show a pentahapto indenyl structure that is directly connected to the large π-system of the [70]fullerene (Figure 11). This iron complex can be regarded as a "superindenyl" ferrocene with a new π-d system incorporated into a graphitic structure.
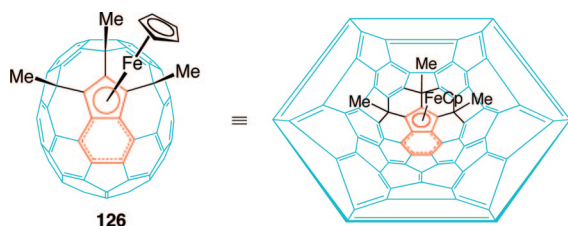

Figure 11. Buckyferrocene of trimethyl[70]fullerene and the large π-electron conjugated system.

4. Concluding Remarks

Multiple addition reactions of organocopper reagents to fullerenes are by far the most effective tools for one-step multiple functionalization of fullerenes reported in the literature. Most functionalized organofullerenes described in this review were obtained in good to excellent yield and provide a number of useful and unique fullerene-based materials such as pentahapto fullerene−metal complexes, watertight vesicles, liquid crystals, and molecular device motifs. These derivatives show electron affinity and photo-responsive properties[90,91] similar to those known for the starting fullerene molecules and have already found useful applications. Given the ability of the method to construct

stereochemically defined nanostructures, these molecules hold the promise of a number of applications to the development of a new class of functional materials and biologically useful molecules.

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