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Regioselective synthesis of [60]fullerene η^5-indenide $R_3C_{60}^-$ and η^5-cyclopentadienide $R_5C_{60}^-$ bearing different R groups

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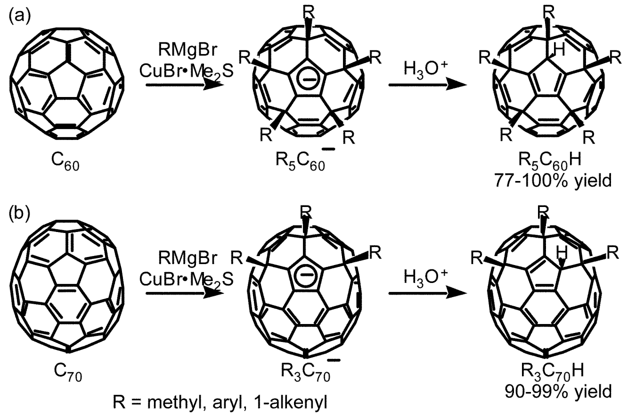
Treatment of a 1,7-diorgano[60]fullerene with Grignard reagents or organocopper reagents affords a [60]fullerene indenide or a [60]fullerene cyclopentadienide regioselectively in good to excellent yields. These reactions gave an insight into the reaction mechanism of the organocopper penta-addition reaction of [60]fullerene, giving [60]fullerene cyclopentadienide in quantitative yield.

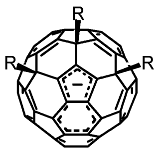
Introduction

An organocopper compound prepared from a Grignard reagent and CuBr·SMe$_2$ adds five times to [60]fullerene to give a fullerene cyclopentadienide $R_5C_{60}^-$, which upon protonation gives the corresponding cyclopentadiene $R_5C_{60}H$ in quantitative yield without giving any regioisomers (Scheme 1a).[1] When the same reaction conditions were applied to [70]fullerene, a tri-addition reaction takes place to afford a fullerene indenide $R_3C_{70}^-$, which then affords the corresponding indene derivative $R_3C_{70}H$ (Scheme 1b).[2] These two reactions are apparently related to each other. The latter reaction stops after the third addition reaction, however, since the two sp^2 carbon atoms expected to receive the fourth and the fifth addition are in a relatively flat "equatorial belt region" and hence resist rehybridization to sp^3 centres. These reactions, taking place in quantitative yield, are unique among a variety of polyaddition reactions of fullerenes,[3,4] which rarely achieve 100%-yield based on the fullerene molecule used for the reaction.[5] Besides the remarkable regioselectivity and the high product yield, the products of those organocopper reactions have been found to open new areas of research. Thus, $Me_5C_{60}H$ was converted to a hybrid of fullerene and ferrocene $Fe(Me_5C_{60})(C_5H_5)$[6] and formed molecular epitaxial films on H–Si(111) and MoS$_2$(0001) surfaces.[7] $Ph_5C_{60}^-$ has been dissolved in water to form small-size bilayer vesicles,[8] and $Ar_5C_{60}H$ bearing long aliphatic side chains on the Ar groups was found to give one-dimensional stacks of shuttlecock-shaped molecules.[9]

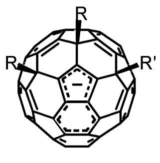


Scheme 1 Organocopper reactions of [60]fullerene and [70]fullerene.

With such growing interest in the fullerene polyadducts, we felt it necessary to address some important issues; that is, the synthesis of a symmetrical [60]fullerene indenide (**A**), unsymmetrical indenides $R_2R'C_{60}^-$ (**B**, **C**), and unsymmetrical cyclopentadienides such as $R_xR'_yR''_zC_{60}^-$ ($x + y + z = 5$, *e.g.*, **D**, **E**, **F**).[10] In this article, we describe the synthesis of such compounds, and also shed light on the reaction pathway of the organocopper penta-addition reaction to [60]fullerene.



A



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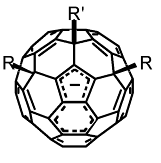

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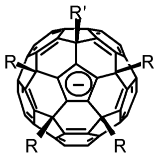

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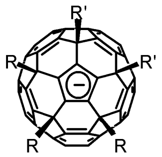

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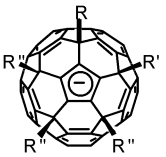

F

Results and discussion

1 Synthesis of fullerene indenides

One remarkable feature of the penta-addition reactions is that the reactions almost always give only the penta-addition product (and the starting material, if any). Only under rare exceptional conditions was the mono-adduct $RC_{60}H$ detected in a trace amount, but no other intermediary adducts have been detected. This observation suggests that, once the first addition occurs, the subsequent additions take place extremely quickly. Besides the organic products, $R_5C_{60}H$ and R–R (detected as biphenyl when R is phenyl), metallic copper forms partly as a black solid and partly as a copper mirror.

These observations, combined with the knowledge on organocopper mechanisms,[11]polyalkylation reactions of fullerenes,[12,13,14] and the experiments described in this article led us to consider the reaction pathway shown in Scheme 2. One may consider that a diorganocuprate R_2Cu^- first undergoes addition to [60]fullerene and subsequent one-electron oxidation of the

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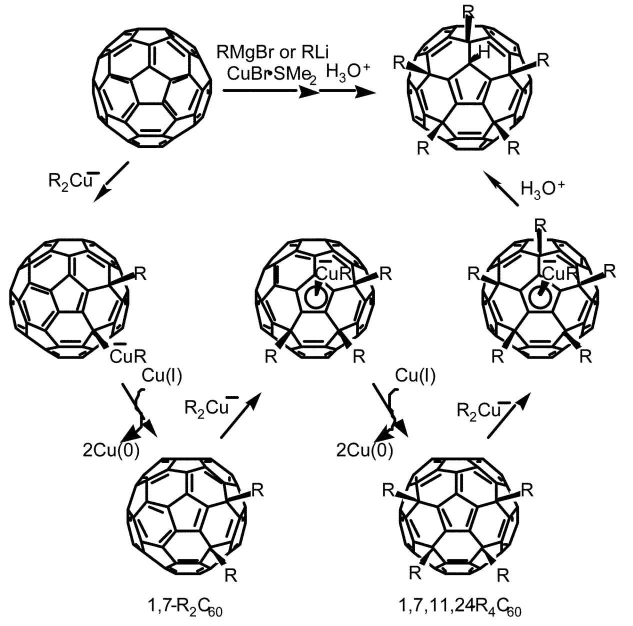


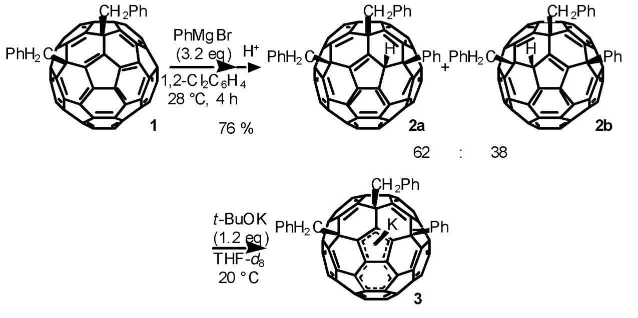
Scheme 2 A likely reaction course of the penta-addition reaction of [60]fullerene.

organocopper(I) intermediate by a Cu(I) salt would give 1,7-R_2C_{60} and Cu(0). The same sequence of reactions takes place on this initial product to give the 1,7,11,24-R_4C_{60} product. This type of product has previously been isolated when R was a bulky fluorenyl group.[15] This tetra-adduct contains a fulvene part structure and therefore readily accepts the fifth R group. According to this reaction mechanism, we considered that addition of an organometallic reagent R′M to the postulated intermediate 1,7-R_2C_{60} would afford unsymmetrical fullerene η^5-indenide $R_2R'C_{60}^-$ as well as fullerene η^5-cyclopentadienide $R_2R'_3C_{60}^-$, regioselectively.[16]

1.1 Reaction of 1,7-$(PhCh_2)_2C_{60}$ with PhMgBr.

A Grignard reagent reacts with C_{60} in a "1,2-addition" across a double bond.[17] Hence we conjectured that the reaction of 1,7-R_2C_{60} with a Grignard reagent will take place only once to give a fullerene tri-adduct. We have chosen 1,7-$(PhCH_2)_2C_{60}$ (**1**) as a starting compound for the present studies because it is available in one step from [60]fullerene and shows reasonably high solubility in common organic solvents.[14]

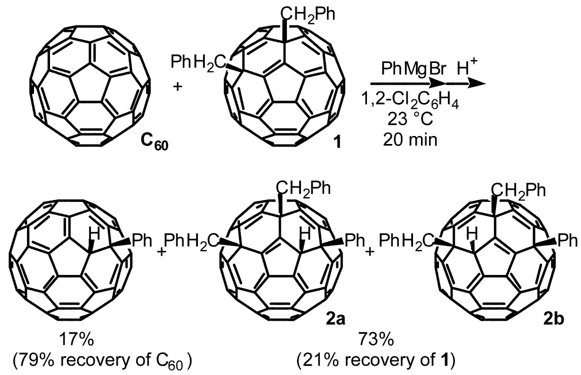
Thus **1** was treated with PhMgBr (3.2 equiv.) in 1,2-dichlorobenzene at 28 °C to give, after hydrolysis with aqueous NH_4Cl and preparative HPLC (high pressure liquid chromatography) purification, $(PhCH_2)_2PhC_{60}H$ in 76% yield as a mixture of two isomers (**2a**–**2b** = 62 : 38). They differ from each other only in the position of the hydrogen atom attached directly to the fullerene core (Scheme 3). The mass spectrum of the isolated product indicated that the reaction stopped after the addition of only one phenyl group [atmospheric pressure chemical ionization (APCI), $M^+ = 981$]. The ^1H NMR of the isomeric mixture shows a pair of singlets (**2a**: δ 5.65 ppm, **2b**: δ 5.22 ppm) due to the protons attached to the fullerene core, eight distinct doublets due to the methylene groups of the benzyl addends, and a multiplet in the aromatic region in an integration ratio of 1 : 4 : 15. These NMR data are fully consistent with the assigned molecular formula of **2a**/**2b** and their molecular symmetry (C_1).



Scheme 3 Synthesis and structural determination of **2**.

The position of the phenyl group and the hydrogen atom of **2a**/**2b** was deduced from a deprotonation experiment with *t*-BuOK (Scheme 3, bottom). Treatment of a solution of the isomeric mixture of **2a**/**2b** in THF with *t*-BuOK (1.2 equiv.) at 20 °C caused immediate colour change from dark brown to dark green. The ^1H NMR spectrum in THF-d_8 showed that the isomeric mixture converged into a single product $K^+[(PhCH_2)_2PhC_{60}]^-$ (**3**) with C_1 symmetry. This result indicates that the isomerism in **2a**/**2b** arises from the positional isomers of the hydrogen atom, and therefore that the phenyl group was regioselectively installed.[18] The reactions of **1** with other phenylmetal reagents (PhLi, Ph_2Mg) also gave the same product but in much lower yields.

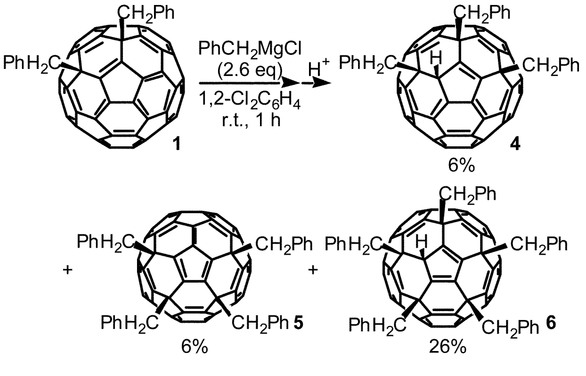
We found that the di-adduct **1** is more reactive than the parent [60]fullerene toward PhMgBr (Scheme 4), which is consistent with the fact that we never detected the formation of a di-adduct during the organocopper penta-addition reaction. Thus, when an equimolar mixture of C_{60} and **1** was treated with an excess amount of PhMgBr in a molar ratio of 1 : 1 : 6 at 23 °C for 20 min, only 21% of C_{60} was consumed to give a mono-adduct $PhC_{60}H$ (17% yield), while **1** was converted to **2** in 73% yield.



Scheme 4 Comparison of the reactivity between C_{60} and **1**.

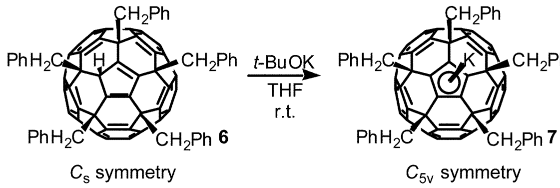
1.2 Reaction of 1,7-$(PhCh_2)_2C_{60}$ with $PhCH_2MgCl$.

When we treated 1,7-$(PhCH_2)_2C_{60}$ (**1**) with 2.6 equiv of $PhCH_2MgCl$ rather than with PhMgBr, we observed the formation of not only the expected mono-adduct $(PhCH_2)_3C_{60}H$ (**4**, 6% yield) but also a double addition product $(PhCH_2)_4C_{60}$ (**5**, 6% yield) and a triple addition product $(PhCH_2)_5C_{60}H$ (**6**, 26% yield) as shown in eqn. (1). Such a mixture invariably formed under a variety of reaction conditions (reaction temperature, control of ambient light, concentration, and amount of reagents). Similarly, a mixture of higher adducts $[(PhCH_2)_2R_2C_{60}$ and $(PhCH_2)_2R_3C_{60}H]$ formed when MeMgBr and BuMgBr were used (data not shown).



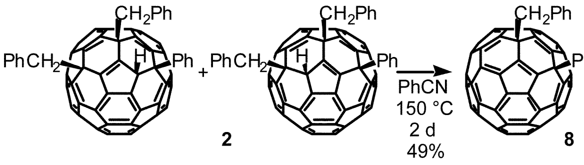
(1)

Structures of the products were determined by spectroscopic methods as described for the previous compounds (and in the Experimental Section). The penta-benzylated compound **6** was converted to the corresponding C_{5v} symmetric cyclopentadienide $K^+[(PhCH_2)_5C_{60}]^-$ (**7**) by deprotonation with *t*-BuOK in THF-d_8 (eqn. (2)). The deprotonation markedly simplified the ^1H NMR spectrum, in which the methylene signal of the five benzyl addends appears as a singlet (δ 3.40 ppm). The ^{13}C NMR spectrum exhibits only eight signals for the fullerene carbon atoms (one signal for the cyclopentadienyl carbon atoms, one signal for the sp^3 carbon atoms and six signals for the other sp^2 carbon atoms) and five signals for the five equivalent benzyl addends.



(2)

1.3. Addition–elimination synthesis of fullerene indenides. Owing to the lack of a synthetic route to 1,7-diaryl[60]fullerene,[12–14] the above synthetic approaches did not allow us to prepare tri-arylated compounds such as **14**. The synthesis of **14** was achieved by a rather intriguing arylation–debenzylation route. Thus we heated **2** in PhCN at 150 °C for 2 d to obtain the dehydrobenzylation product 1-($PhCH_2$)-7-PhC_{60} (**8**) in 49% yield (eqn. (3)). The mass (APCI, $M^- = 888$), ^1H and ^{13}C NMR spectra (63 signals) are consistent with the assigned C_1 structure.[19] The thermal degradation reaction is facilitated by a trace amount of water contained in PhCN, and there is proton exchange between water and **2**. Thus, when $(PhCH_2)_2$-$PhC_{60}H$ (**2**) was heated in D_2O-saturated PhCN at 100 °C for 2 h, $(PhCH_2)_2PhC_{60}D$ (**2**-*d*) was obtained in 84% deuterium incorporation with >95% recovery of the starting material (H/D mixture).

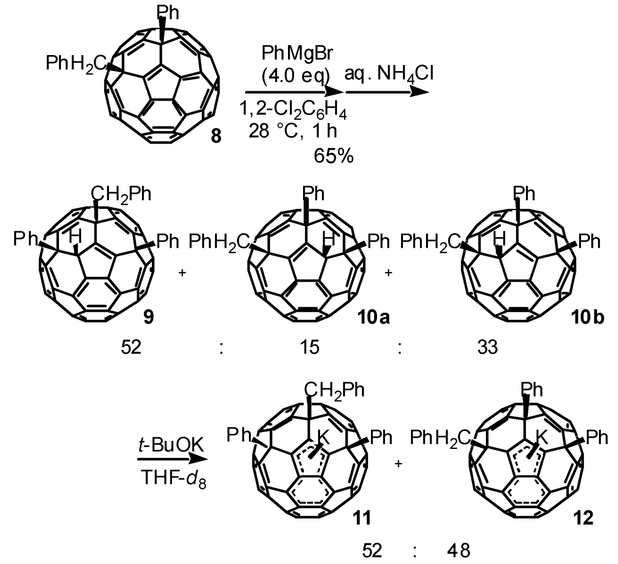


(3)

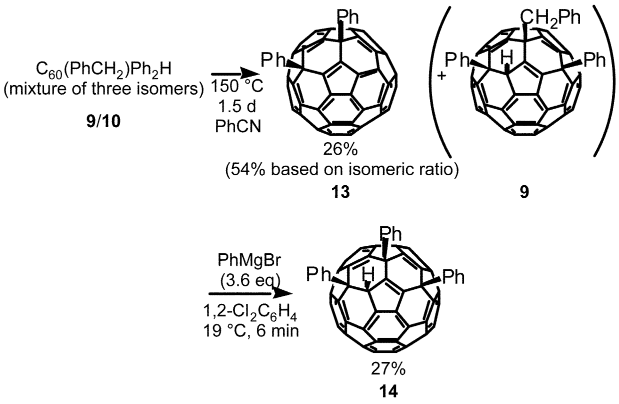
The synthesis of **8** can be achieved in a single pot from **1**. Thus, **1** in 1,2-dichlorobenzene was treated first with PhMgBr and the mixture was quenched with aq. HCl. The crude product obtained by removal of the solvent was heated in PhCN to obtain **8** in 44% yield after HPLC purification (*cf.* 37% yield by the multi-pot synthesis).

Next, we examined the reaction of **8** with PhMgBr to obtain $(PhCH_2)Ph_2C_{60}H$ (**9/10**) in 65% yield as a mixture of three isomers; namely, one C_1 symmetric compound (**9**) and two C_1 symmetric compounds (**10a/10b**) which differ only in the position of the hydrogen atom. The isomeric ratio was determined by deprotonation experiments, in which the **9/10** mixture converged into a mixture of two compounds, a C_s symmetric compound **11** and a C_1 symmetric compound **12** (Scheme 5, also see Experimental Section).

Through another dehydrobenzylation–carbometalation cycle, a symmetric tri-adduct $Ph_3C_{60}H$ (**14**) was synthesized (Scheme 6). Thus, when the mixture of **9** and **10** was heated in PhCN, 1,7-Ph_2C_{60} (**13**) was obtained in 26% yield (54% yield based on the isomer content; **9** remained unchanged). The mass analysis gave the correct molecular weight (APCI, $M^- = 874$) and the ^1H NMR spectrum is identical with the authentic one.[20] The reaction of **13** with PhMgBr proceeded smoothly to obtain **14** in 27% yield as a single isomer. While it is low-yielding, this synthetic sequence provided the tri-arylated compound for the first time.



Scheme 5 Synthesis and structural determination of a mixture of **9** and **10**.



Scheme 6 Synthesis of the tri-arylated fullerene **14**.

2 Structures and electronic states of metal fullerene η^5-indenides

None of the compounds reported in this study afforded single crystals suitable for X-ray analysis. To obtain information on the nature of the η^5-indenyl metal complex, we optimized the structure of a C_s symmetric model compound $K(H_3C_{60})$ at the HF/3-21G$^{(*)}$ level (Fig. 1a).[21] The optimized structure shares some important features with the X-ray structure of $Tl(Ar_3C_{70})$ ($Ar = 4\text{-}CF_3C_6H_4$).[2] Thus, the fully delocalized 10-π indenyl framework attached to the metal atom is electronically distributed in the whole 58-π electron system as noted by the seven surrounding C–C bonds of rather long bond lengths (1.47–1.52 Å),[22] and the HOMO surface of $K(H_3C_{60})$ is localized on the indenyl substructure as shown in Fig. 1b (resembling that of $K(H_3C_{70})$).[2] Such an effective π-electron delocalization within the indenyl framework of $K(H_3C_{60})$ is rather surprising in view of the non-planarity of the bicyclo[4.3.0] ring.[23]

3 Synthesis of unsymmetrical fullerene cyclopentadienide

The stage is now set to describe the synthesis of unsymmetrical fullerene cyclopentadienides. Starting with 1,7-$(PhCH_2)_2C_{60}$ (**1**), we first synthesized $(PhCH_2)_2Ph_3C_{60}H$ (**15**). The reaction of **1** (1,2-dichlorobenzene–THF, 25 °C, 1.5 h) with 15 equiv. of an organocopper reagent prepared from PhMgBr and $CuBr{\cdot}SMe_2$ gave, after quenching with aqueous NH_4Cl, **15a**–**c** in quantitative yield (86% yield after HPLC purification; Scheme 7).

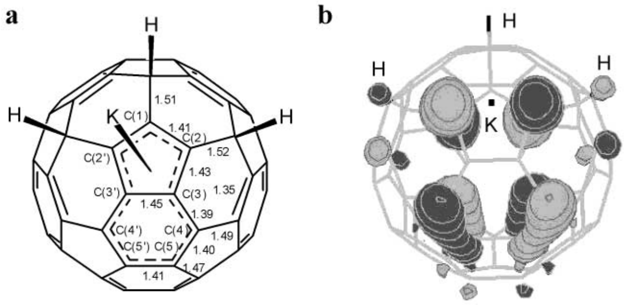
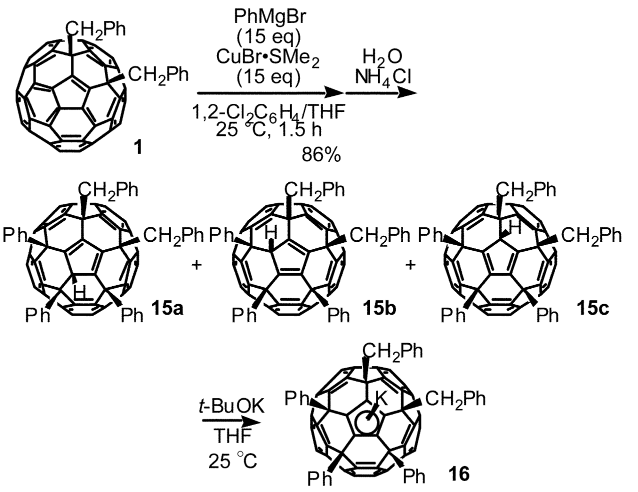
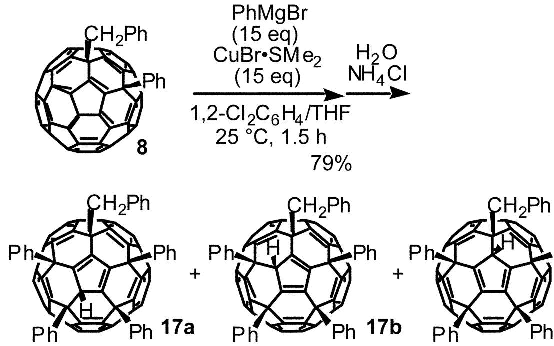


Fig. 1 Calculated molecular structure and the HOMO of $K(H_3C_{60})$ at the HF/3-21G(*) level. (a) The structure of the indenyl moiety. C–C bond lengths (Å) are shown next to the respective bonds. K–C bond lengths (Å): K–C(1), 3.08; K–C(2), 2.98; K–C(3), 2.93. (b) HOMO surface. Total energy = −2857.00417344 hartree.



Scheme 7 Synthesis and deprotonation of $(PhCH_2)_2Ph_3C_{60}H$ (**15**).

Treatment of **15** in THF with *t*-BuOK (1.2 equiv.) at 20 °C gave a single cyclopentadienide $K^+[(PhCH_2)_2Ph_3C_{60}]^-$ (**16**) of C_s symmetry. Similarly, $(PhCH_2)Ph_4C_{60}H$ (**17**) was synthesized from 1-$(PhCH_2)$-7-PhC_{60} (**8**) in 79% yield (eqn. (4)).



(4)

4 Mechanism of polyaddition to [60]fullerene

Several lines of new mechanistic information surfaced during the present synthetic studies: first, the di-adduct is more reactive than the parent [60]fullerene and must lie along the pathway to the penta-adduct as an important intermediate. Second, the formation of this di-adduct is probably the slowest step in the organocopper penta-addition reaction, since we did not see any side products other than the mono-adduct under all reaction conditions ever examined. Third, an aliphatic Grignard reagent (*e.g.* $PhCH_2MgCl$) reacts with 1,7-R_2C_{60} to produce a mixture of multiadducts. It is most likely that the Grignard reagent is oxidized by a fullerene compound to afford an organo radical species which produces a mixture of polyadducts (Scheme 8a).[4,24] The carbometallation reaction would compete with the oxidation reaction, which may account for the difficulty in controlling the reaction with $PhCH_2MgCl$. Exclusive formation of the mono-addition product **2** in the reaction of **1** with PhMgBr can be attributed to the straightforward anionic mono-addition, as it is more difficult to oxidize a phenyl anion to a phenyl radical than to oxidize a benzyl anion to a benzyl radical (Scheme 8b).

(a)

$$(PhCH_2)_2C_{60} \xrightarrow{PhCH_2MgCl} (PhCH_2)_3C_{60}^{-}MgCl^{+} \xrightarrow{H_3O^+} \underline{(PhCH_2)_3C_{60}H}$$

$$(PhCH_2)_2C_{60} \xrightarrow{PhCH_2MgCl} (PhCH_2)_2C_{60}^{\bullet-}MgCl^{+} + PhCH_2^{\bullet}$$

$$(PhCH_2)_2C_{60} \xrightarrow{PhCH_2^{\bullet}} (PhCH_2)_3C_{60}^{\bullet} \xrightarrow{H^{\bullet}} \underline{(PhCH_2)_3C_{60}H}$$

$$(PhCH_2)_3C_{60}^{\bullet} \xrightarrow{PhCH_2^{\bullet}} \underline{(PhCH_2)_4C_{60}}$$

$$(PhCH_2)_4C_{60} \xrightarrow{PhCH_2^{\bullet}} (PhCH_2)_5C_{60}^{\bullet} \xrightarrow{H^{\bullet}} \underline{(PhCH_2)_5C_{60}H}$$

(b)

$$(PhCH_2)_2C_{60} \xrightarrow{PhMgBr} (PhCH_2)_2PhC_{60}^{-}MgBr^{+} \xrightarrow{H_3O^+} \underline{(PhCH_2)_2PhC_{60}H}$$

$$(PhCH_2)_2C_{60} \overset{PhMgBr}{\not\longrightarrow} (PhCH_2)_2C_{60}^{\bullet-}MgBr^{+} + Ph^{\bullet}$$

Scheme 8 Possible pathways of reaction of $(PhCH_2)_2C_{60}$ (**1**) with phenyl and benzyl Grignard reagents. Experimentally observed products are underlined. (a) Benzyl Grignard reagent. (b) Phenyl Grignard reagent.

Taking the above considerations into account, we can draw the overall stoichiometry of the penta-addition of an organocopper reagent to [60]fullerene as the one shown in Scheme 9a, and a stepwise sequential addition–oxidation mechanism of the penta-addition reaction as in Scheme 9b. All compounds in the boxes have been isolated and independently subjected to the reaction conditions,[15] which gave support to the feasibility of this pathway. Note that oxidation of [60]fullerene radical anion by a Cu(I) salt is highly exothermic (−21.0 kcal mol^{-1}, calculated from their redox potential, Scheme 9c),[25] indicating that the Cu(I) salt can receive an electron from the anionic intermediates such as $(PhCH_2)_2PhC_{60}^{-}$.

In conclusion we developed the stepwise methods for the regioselective synthesis of unsymmetrical fullerene indenides and cyclopentadienides. The studies on the stepwise synthesis

(a)

$$C_{60} + 5RMgBr + 5CuBr \longrightarrow R_5C_{60}Cu + 4Cu(0) + 5MgBr_2$$

(b)

$$C_{60} + R^{-} \longrightarrow RC_{60}^{-} \dashrightarrow \boxed{RC_{60}H}$$

$$RC_{60}^{-} + Cu(I) \longrightarrow RC_{60}^{\bullet} + Cu(0)$$

$$RC_{60}^{\bullet} + R^{-} \longrightarrow R_2C_{60}^{-\bullet}$$

$$R_2C_{60}^{-\bullet} + Cu(I) \longrightarrow \boxed{R_2C_{60}} + Cu(0)$$

$$R_2C_{60} + R^{-} \longrightarrow R_3C_{60}^{-} \dashrightarrow \boxed{R_3C_{60}H}$$

$$R_3C_{60}^{-} + Cu(I) \longrightarrow R_3C_{60}^{\bullet} + Cu(0)$$

$$R_3C_{60}^{\bullet} + R^{-} \longrightarrow R_4C_{60}^{-\bullet}$$

$$R_4C_{60}^{-\bullet} + Cu(I) \longrightarrow \boxed{R_4C_{60}} + Cu(0)$$

$$R_4C_{60} + R^{-} \longrightarrow R_5C_{60}^{-} \dashrightarrow \boxed{R_5C_{60}H}$$

(c)

$$C_{60}^{-\bullet} + Cu(I) \xrightarrow{-21.0\ kcal/mol} C_{60} + Cu(0)$$

Scheme 9 Cu(I)-mediated penta-addition reaction of a Grignard reagent to C_{60}. (a) Overall stoichiometry. (b) Stepwise addition–oxidation route. (c) Oxidation of fullerene radical anion by a Cu(I) salt.

also gave valuable information about the mechanism of the organocopper penta-addition reaction. The synthetic protocols presented here will allow us to obtain a wide variety of fullerene ligands, which would play useful roles in organometallic chemistry, catalysis and nano-sciences.

Experimental

General

All reactions were carried out in an oven-dried reaction vessel under argon or nitrogen and were analyzed by HPLC (column: Buckyprep, 4.6 × 250 mm, Nacalai tesque; flow rate: 1.0 ml min^{-1}; eluent: toluene–2-propanol = 7 : 3; detector: SPD-M10Avp, Shimadzu). Common organic solvents as well as aqueous solutions used for work up procedure were deoxygenated by freeze–thaw cycles (over 3 times), by bubbling nitrogen (over 30 min) or by pumping at 0 °C (over 30 min). All ^{1}H NMR spectra were taken at 400 MHz (JEOL EX-400), and ^{13}C NMR spectra at 100 MHz. Spectra are reported in part per million from internal tetramethylsilane or the residual protons of the deuterated solvent for the ^{1}H NMR spectra, and from the deuterated solvent for the ^{13}C NMR spectra. IR spectra were recorded on Applied. Systems. Inc., REACT IR 1000 as powders on a diamond probe; absorptions are reported in cm^{-1}. Mass spectra were measured with Shimadzu LCMS-QP8000 (APCI mode) equipped with Buckyprep column or JEOL JMS SX102 (FAB mode). Preparative HPLC was performed on a Buckyprep column (20 × 250 mm) using toluene–2-propanol = 7 : 3 as eluent (flow rate 12 to 20 ml min^{-1}, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). Recycle preparative gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 machine equipped with JAIGEL 1H/2H column and an RI detector RI-5HC ($CHCl_3$ as eluent, flow rate: 3.5 ml min^{-1}).

Solvents and materials

All commercially available reagents were distilled or recrystallized before use unless otherwise noted. THF was purchased from KANTO KAGAKU and stored over molecular sieves 4 Å under nitrogen. 1,2-$Cl_2C_6H_4$ was distilled under reduced pressure from CaH_2 and dried over molecular sieves 4 Å. PhCN was distilled under reduced pressure from P_2O_5 and dried over molecular sieves 4 Å. The water content of the solvent was determined with a Karl-Fisher Moisture Titrator (MK-210, Kyoto Electronics Company) to be less than 30 ppm. CuBr·SMe_2 was freshly prepared from CuBr and precipitated twice from Me_2S–pentane. A solution of *t*-BuOK in THF (1 M) was purchased from Sigma Aldrich Japan K. K. and used as received.

Structural determination

The compounds that differ only about the position of the hydrogen atom were identified on the assumption that the signal for the hydrogen atom directly attached to the fullerene sphere is highly affected by the addend on the neighboring sp^3 carbon atom; the hydrogen with an aryl (*e.g.* phenyl) addend on the neighboring sp^3 carbon shows lower field shift than that with an alkyl (*e.g.* benzyl) addend. All NMR data are so far consistent with this assumption. In addition, molecular symmetry sometime helps identification of the compounds.

Preparation of 1,7-dibenzyl-1,7-dihydro(C_{60}-I_h)[5,6]fullerene. (1,7-$(PhCH_2)_2C_{60}$ (1)). Both a solution of trimethylhydroquinone (1.14 g, 7.49 mmol, 5.4 equiv.) in 1300 ml of benzonitrile and a suspension of C_{60} (1.00 g, 1.39 mmol, 1.0 equiv.) in 700 ml of benzonitrile were degassed under reduced pressure over 30 min. Tetrabutylammonium hydroxide (1 M in methanol, 15.3 ml, 11.0 equiv.) was added to a solution of trimethylhydroquinone at 26 °C. The color of the solution changed immediately from colorless to red. After stirring for 30 min at this temperature, the resulting red solution was transferred to the purple suspension of C_{60} in benzonitrile *via* a cannula over 30 min and stirred for a further 30 min, giving a dark solution. To this solution was added benzyl bromide (16.6 ml, 139 mmol, 100 equiv.) and the solution was stirred further for 16 h at 26 °C. Then the reaction mixture was treated with 5 ml of aq. HCl (*ca.* 1 M), dried over anhydrous $MgSO_4$ and filtered through a pad of silica gel (eluted with toluene). The filtrate was concentrated under reduced pressure and the residue was subjected to preparative HPLC purification. The fractions containing **1** were concentrated to a small volume under reduced pressure and precipitated with methanol. The precipitates were washed thoroughly with methanol and dried under reduced pressure to give **1** in 65% yield (819 mg, 0.907 mmol) as a brown solid.

Synthesis of a mixture of 6,18-dibenzyl-9-phenyl-1,6,9,18-tetrahydro(C_{60}-I_h)[5,6]fullerene (2a) and 6,9-dibenzyl-18-phenyl-1,6,9,18-tetrahydro(C_{60}-I_h)[5,6]fullerene (2b). ($(PhCH_2)_2PhC_{60}H$ (2)). A brown solution of **1** (1.01 g, 1.12 mmol, 1.0 equiv.) in 300 ml of 1,2-$Cl_2C_6H_4$ was degassed under reduced pressure over 30 min. To this solution was added PhMgBr in THF (0.93 M, 3.87 ml, 3.60 mmol, 3.2 equiv) at 28 °C. The mixture was stirred for 4 h at this temperature. The colour of the solution gradually changed from brown to dark green. HPLC analysis indicated full consumption of the starting material after 4 h. The major peak appeared in an 84% area ratio and the rest 16% was composed of many tiny peaks. After quenching with 1.0 ml of a degassed saturated NH_4Cl aqueous solution, the mixture was filtered through a pad of silica gel (eluted with toluene) and concentrated to dryness under reduced pressure. The residue was subjected to HPLC purification. Fractions containing **2** were collected and concentrated to a small volume under reduced pressure. Addition of methanol caused precipitation of the product. The precipitates were collected by filtration, washed with methanol and dried under reduced pressure to give 840 mg (76%) of **2** as a brown solid. The ratio of **2a**–**2b** is determined by ^{1}H NMR analysis to be 62 : 38, which was estimated from an integrated area ratio of signals for the protons attached to the fullerene cage (5.22 ppm for **2b** and 5.65 ppm for **2a**). Analytically pure material was obtained by GPC purification.

IR (powder) 3025 (w), 2912 (w), 1602 (w), 1493 (m), 1453 (w), 1030 (w), 739 (m), 729 (w), 697 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.20 (d, J = 13.2 Hz, 1H, PhCH*H*, **2b**), 3.28 (d, J = 13.2 Hz, 1H, PhCH*H*, **2b**), 3.29 (d, J = 13.2 Hz, 1H, PhCH*H*, **2a**), 3.32 (d, J = 13.2 Hz, 1H, PhCH*H*, **2a**), 3.48 (d, J = 13.2 Hz, 1H, PhCH*H*, **2a**), 3.69 (d, J = 13.2 Hz, 1H, PhCH*H*, **2b**), 3.77 (d, J = 13.2 Hz, 1H, PhCH*H*, **2b**), 3.85 (d, J = 13.2 Hz, 1H, PhCH*H*, **2a**), 5.22 (s, 1H, C_{60}H, **2b**), 5.65 (s, 1H, C_{60}H, **2a**), 7.13–7.64 (m, 13H + 13H, Ph, **2a** + **2b**), 8.04–8.08 (m, 2H, Ph, **2a**), 8.11–8.14 (m, 2H, Ph, **2b**); APCI-MS *m*/*z* 981 (M^+); Anal. Calcd for $C_{80}H_{20}$, C 97.95; H, 2.05. Found: C 97.66; H, 2.34%.

Preparation of potassium 6,9-dibenzyl-12-phenyl-9,12-dihydro(C_{60}-I_h)[5,6]fullerene-1(*6H*)-ide (K[$(PhCH_2)_2PhC_{60}$] (3)). A solution of *t*-BuOK in THF (1.0 M, 7.0 µl, 7.0 µmol) was added to a solution of **3** (5.2 mg, 5.3 µmol) in 0.55 ml of degassed THF-d_8 under an argon atmosphere in an NMR tube. The colour of the solution changed immediately from dark brown to dark green, indicating the formation of indenyl anion. Then the NMR tube was sealed and used in NMR analysis. Since the fullerene indenide **2** slowly decomposed at ambient temperature, ^{13}C NMR measurement has so far not been achieved. ^{1}H NMR (THF-d_8, 400 MHz) δ 3.73 (d, J = 12.6 Hz, 1H, PhCH*H*), 4.10 (d, J = 12.6 Hz, 1H, PhCH*H*), 7.05–7.32 (m, 7H, Ph), 7.41–7.50 (m, 4H, Ph), 7.52–7.56 (m, 2H, Ph), 8.29–8.34 (m, 2H, Ph). Signals for two methylene protons overlapped with those of THF.

Synthesis of 6,9,18-tribenzyl-1,6,9,18-tetrahydro(C_{60}-I_h)[5,6]-fullerene (4), 1,7,11,24-tetrabenzyl-1,7,11,24-tetrahydro(C_{60}-I_h)-[5,6]fullerene (5), and 6,9,12,15,18-pentabenzyl-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene (6) (($PhCH_2)_3C_{60}H$ (4), ($PhCH_2)_4C_{60}$ (5), and ($PhCH_2)_5C_{60}H$ (6)). $PhCH_2MgCl$ (0.98 M in Et_2O, 0.020 ml, 0.022 µmol) was added to a degassed solution of **1** (30.6 mg, 0.0339 µmol) in 25 ml of 1,2-dichlorobenzene in four portions at 5 min intervals at ambient temperature. After stirring for 1.5 h, the reaction mixture was quenched with 0.5 ml of sat. aq. NH_4Cl and dried over anhydrous Na_2SO_4. The supernatant was passed through a pad of silica gel (eluted with toluene) and concentrated to dryness under reduced pressure. The residue was purified by GPC to give **4** (2.1 mg, 6.2%), **5** (2.6 mg, 6.1%), and **6** (10.3 mg, 26%). Structural assignments of **4**, **5** and **6** came from the mass and the ^1H NMR data. The mass spectra are fully consisted with assigned structures (see below). The ^1H NMR spectrum ($CDCl_3$–CS_2 = 1 : 1) of **4** shows a singlet assignable to the proton directly attached to the C_{60} cage at δ 4.35 ppm, six distinct doublets assigned to the three methylene groups of the benzyl addends at δ 3.00, 3.17, 3.19, 3.26, 3.38, 3.48 ppm and a multiplet in the aromatic region in an integration ratio of 1 : 6 : 15. The ^1H NMR spectra ($CDCl_3$–CS_2 = 1 : 1) of **5** and **6** indicate that these compounds are C_s symmetric. In the ^1H NMR spectrum of **5**, four doublets due to the two methylene groups of the benzyl addends appears at δ 2.89, 2.98, 3.23, 3.32 ppm. The spectrum of **6** shows a singlet assignable to the proton attached to the C_{60} cage at δ 4.35 ppm, a singlet due to the methylene group of the benzyl addend at δ 2.39 ppm, four doublets due to the remaining four benzyl addends at δ 2.66, 2.71, 2.75, 2.94 ppm, and a multiplet in the aromatic region with an integration ratio of 1 : 2 : 8 : 25.

4: ^1H NMR (CS_2–$CDCl_3$ = 1 : 1) δ 3.00 (d, J = 13.2 Hz, 1H), 3.17 (d, J = 13.2 Hz, 1H), 3.19 (d, J = 13.2 Hz, 1H), 3.26 (d, J = 13.2 Hz, 1H), 3.38 (d, J = 13.2 Hz, 1H), 3.48 (d, J = 13.2 Hz, 1H), 4.35 (s, 1H), 7.25–7.51 (m, 15H); FAB-MS *m*/*z* 995 (MH^+); **5**:^1H NMR (CS_2–$CDCl_3$ = 1 : 1) δ 2.89 (d, J = 13.2 Hz, 2H), 2.98 (d, J = 13.2 Hz, 2H), 3.23 (d, J = 13.2 Hz, 2H), 3.32 (d, J = 13.2 Hz, 2H), 7.14–7.41 (m, 20H); FAB-MS *m*/*z* 1085 (MH^+); **6**: ^1H NMR (CS_2–$CDCl_3$ = 1 : 1) δ 2.39 (s, 2H), 2.66 (d, J = 13.2 Hz, 2H), 2.71 (d, J = 13.2 Hz, 2H), 2.75 (d, J = 13.2 Hz, 2H), 2.94 (d, J = 13.2 Hz, 2H), 4.35 (s, 1H), 7.01–7.41 (m, 25H); FAB-MS *m*/*z* 1177 (MH^+).

Preparation of potassium 6,9,12,15,18-pentabenzyl-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(6*H*)-ide (K[($PhCH_2)_5C_{60}$] (7)). A solution of *t*-BuOK in THF (1.0 M, 10 µl, 10 µmol) was added to a solution of **6** (4.8 mg, 4.1 µmol) in 1 ml of degassed THF at ambient temperature and stirred for 3 min at this temperature. The resulting dark green solution was concentrated under reduced pressure. The residue was rinsed into an NMR tube with 0.7 ml of THF-d_8 to measure the ^1H and ^{13}C NMR spectra.

^1H NMR (400 MHz, THF-d_8) δ 3.40 (s, 10H, CH_2), 7.04 (t, J = 7.2 Hz, 5H, *p*-Ph), 7.23 (t, J = 8.4 Hz, 10H, *m*-Ph), 7.41 (d, J = 8.0 Hz, 10H, *o*-Ph); ^{13}C NMR (100 MHz, THF-d_8) δ 26.44 (5C), 31.76 (5C), 126.18 (5C), 128.07 (10C), 131.39 (5C), 131.87 (10C), 141.49 (10C), 142.58 (10C), 146.13 (5C), 146.94 (10C + 5C), 148.70 (5C), 148.89 (10C).

Synthesis of 1-benzyl-7-phenyl-1,7-dihydro(C_{60}-I_h)[5,6]fullerene (1-($PhCH_2$)-7-PhC_{60} (8)). A solution of **2** (203 mg, 207 µmol) in PhCN (200 ml) was degassed under reduced pressure over 30 min and was heated at 150 °C for 2 d. HPLC analysis indicated the full consumption of the starting material after 2 d. Then the reaction mixture was concentrated to dryness under reduced pressure and the resulting crude product was purified by preparative HPLC. The fractions containing **8** were concentrated and precipitated with methanol. The precipitates were collected by filtration, washed with methanol and dried under reduced pressure to give **8** as a brown solid (91.0 mg, 49% yield).

IR (powder) 3058 (w), 3026 (w), 1493 (m), 1430 (m), 1188 (m), 1081 (m), 1031 (m), 731 (s), 694 (s); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.18 (d, J = 13.2 Hz, 1H), 4.30 (d, J = 13.2 Hz, 1H), 7.23–7.28 (m, 1H), 7.31–7.36 (m, 2H), 7.48–7.53 (m, 2H), 7.54–7.59 (m, 1H), 7.66–7.72 (m, 2H), 8.34–8.38 (m, 2H); ^{13}C NMR (CS_2, 100 MHz) δ 48.20, 59.95, 61.33, 126.77 (2C), 127.11, 127.97, 128.01 (2C), 129.39 (2C), 130.21 (2C), 134.91, 136.70, 138.30, 138.32, 138.67, 140.55, 140.58, 141.59, 141.61, 141.84, 142.05, 142.09, 142.17, 142.30 (1C + 1C), 142.60, 142.74, 142.77 (1C + 1C), 142.79 (1C + 1C), 143.34, 143.38, 143.56, 143.58 (1C + 1C), 143.68, 143.77, 143.84, 143.94 (1C + 1C), 143.95, 144.00, 144.01, 144.13, 144.33, 144.44, 144.46, 144.52, 144.69 (1C + 1C), 145.11, 145.16, 145.86, 146.30, 146.46, 146.49, 146.52, 146.57, 146.65, 146.78, 147.02, 148.15, 148.19, 148.21, 148.23, 150.41, 150.92, 155.64, 156.83; APCI-MS *m*/*z* 888 (M^-).

Synthesis of a mixture of 6-benzyl-9,18-diphenyl-1,6,9,18-tetrahydro(C_{60}-I_h)[5,6]fullerene (9), 18-benzyl-6,9-diphenyl-1,6,9,18-tetrahydro(C_{60}-I_h)[5,6]fullerene (10a) and 9-benzyl-6,18-diphenyl-1,6,9,18-tetrahydro(C_{60}-I_h)[5,6]fullerene (10b) (($PhCH_2$)-$Ph_2C_{60}H$ (9/10)). These compounds were synthesized in the same manner as **2**. Starting from 49.7 mg of **8** (55.9 µmol), 35.0 mg of a mixture of **9** and **10a/b** was obtained as a brown solid (36.2 µmol, 65% yield); namely, one C_1 symmetric compound (**9**) and two C_1 symmetric compounds (**10a/10b**) which differ only in the position of the hydrogen atom. An isomeric ratio was determined by the deprotonation experiment (*vide infra*). Treatment of a mixture of ($PhCH_2)Ph_2C_{60}H$ (**9/10**) with a THF solution of *t*-BuOK gave K[$C_{60}(PhCH_2)Ph_2$] as a mixture of a C_s symmetric compound **11** and a C_1 symmetric compound **12**. In the ^1H NMR spectrum, three singlet signals (δ 5.78, 5.94, 5.99 ppm) assignable to the hydrogen atoms directly attached to the C_{60} cage disappeared and signal pattern became simple. Three doublet peaks were observed at δ 8.06, 8.29, 8.46 ppm in an integrated ratio of 24 : 52 : 24, which were assigned to protons *ortho* to phenyl groups (not the benzyl groups). From the integration ratio of these three peaks, the ratio of **11** : **12** was determined to be 52 : 48. Subsequently, the ratio of **9** : **10a** : **10b** was determined to be 52 : 15 : 33 from peak intensities for the three singlet peaks assigned to the hydrogen atoms attached to the fullerene cage in the ^1H NMR spectrum of ($PhCH_2)Ph_2C_{60}H$ (**9/10**).

IR (powder) 3059 (w), 3027 (w), 1493 (m), 1446 (m), 1030 (m), 911 (m), 736 (s), 693 (s); ^1H NMR (THF-d_8, 400 MHz) δ 3.94–4.14 (m, 2H + 2H + 2H, PhCH_2, **9** + **10**), 5.78 (s, 1H, $C_{60}H$, 10b), 5.94 (s, 1H, $C_{60}H$, **9**), 5.99 (s, 1H, $C_{60}H$, **10a**), 7.07–7.69 (m, 11H + 11H + 11H, Ph, **9** + **10**), 7.82 (d, J = 7.2 Hz, 2H, Ph, **10**), 7.98 (d, J = 8.0 Hz, 2H + 2H, Ph, **10**), 8.10 (d, J = 8.0 Hz, 2H, Ph, **9**), 8.16 (d, J = 8.0 Hz, 2H, Ph, **9**), 8.34 (d, J = 7.2 Hz, Ph, 2H, **10**); ^{13}C NMR (CS_2–$CDCl_3$ = 5 : 1, 100 MHz) (**9**, recovered in the dehydrobenzylation reaction described below.) δ 46.44, 59.29, 61.62, 63.58, 126.60 (2C), 126.64 (2C), 127.09, 127.24, 127.62, 128.07 (2C), 129.09 (2C), 129.18 (2C), 130.01 (2C), 132.85, 133.62, 134.61, 135.04, 136.97, 140.39, 140.48, 140.62, 141.38, 141.57, 141.86, 142.27, 142.40, 143.13, 143.37, 143.47, 143.64, 143.66, 144.02, 144.05, 144.13, 144.17, 144.21, 144.25, 144.50, 144.54, 144.59, 144.60, 144.94, 144.96, 145.04, 145.05, 145.27, 145.30, 145.42, 145.45, 145.63, 146.06, 146.09, 146.10, 146.13, 146.22, 146.27, 146.33, 146.35, 146.36, 146.37, 147.01, 147.26, 147.37, 148.33, 148.76 (1C + 1C), 149.04, 149.63, 150.86, 153.47, 153.54, 154.57, 155.36, 159.48; APCI-MS *m*/*z* 966 (M^-).

Preparation of a mixture of potassium 9-benzyl-6,12-diphenyl-9,12-dihydro(C_{60}-I_h)[5,6]fullerene-1(6*H*)-ide (11) and potassium 6-benzyl-9,12-diphenyl-9,12-dihydro(C_{60}-I_h)[5,6]fullerene-1(6*H*)-ide (12) (K[($PhCH_2)Ph_2C_{60}$] (11/12)). This was prepared in the same manner as **3**. Since the fullerene indenide **11/12** was slowly decomposed even at ambient temperature, ^{13}C NMR measurement was so far unsuccessful. ^{1}H NMR (THF-d_8, 400 MHz) δ 4.35 (s, 2H, PhCH_2, **11** or **12**), 6.97–7.45 (m, 11H + 11H, Ph, **11** + **12**), 8.06 (d, J = 8.0 Hz, 2H, *o*-Ph, **12**), 8.29 (d, J = 8.0 Hz, 4H, *o*-Ph, **11**), 8.46 (d, J = 8.0 Hz, 2H, *o*-Ph, **12**), Signals due to the two methylene protons were overlapped with that of THF.

Synthesis of 1,7-diphenyl-1,7-dihydro(C_{60}-I_h)[5,6]fullerene (1,7-Ph_2C_{60} (13)). A solution of a mixture of $(PhCH_2)Ph_2C_{60}H$ (**9/10**, 13.0 mg, 13.4 µmol) in 13 ml of benzonitrile was degassed under reduced pressure at ambient temperature over 30 min. This solution was heated at 150 °C for 1.5 d and then concentrated under reduced pressure to give a crude product. The crude product was subjected to preparative HPLC purification. The fractions containing **13** were concentrated and dried under reduced pressure to give **13** (3.0 mg, 26% yield) as a dark brown solid.

IR (powder) 3056 (w), 3029 (w), 1493 (m), 1492 (m), 1446 (m), 1432 (m), 1188 (m), 1032 (m), 735 (s), 692 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43–7.51 (m, 6H, Ph), 8.06–8.09 (m, 4H, Ph); APCI-MS *m*/*z* 874 (M^-).

Synthesis of 6,9,18-triphenyl-1,6,9,18-tetrahydro(C_{60}-I_h)[5,6]-fullerene ($Ph_3C_{60}H$ (14)). A solution of PhMgBr in THF (1.35 M, 15.0 µl, 20.3 µmol, 3.73 equiv.) was added to a degassed solution of **13** (4.75 mg, 5.43 µmol) in 1.50 ml of 1,2-dichlorobenzene at 19 °C and the resulting mixture was stirred for 6 min at this temperature. After quenching with 10 µl of 10% HCl aqueous solution, the crude mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was subjected to HPLC purification. Fractions containing **14** were collected and concentrated to a small volume. Precipitation by addition of methanol afforded **14** (27%) as a brown solid.

IR (powder) 3058 (w), 3029 (w), 2924 (w), 1492 (m), 1446 (m), 1031 (m), 736 (s), 693 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.69 (s, 1H), 7.34–7.43 (m, 9H), 7.81 (d, J = 7.2 Hz, 2H), 7.96–7.97 (m, 4H); ^{13}C NMR (CS_2–$CDCl_3$ = 1 : 1, 100 MHz) δ 29.90, 62.18, 63.69 (1C + 1C), 127.09 (2C), 127.32 (1C + 1C), 127.35, 127.53 (2C), 127.83 (2C), 128.95 (2C), 129.04 (2C), 129.11 (2C), 133.89, 133.99, 135.47, 136.94, 137.18, 139.85, 140.06, 140.70, 140.76, 141.55, 141.83, 142.12, 142.51, 142.67, 143.63 (1C + 1C), 143.82, 144.00, 144.26, 144.29, 144.35, 144.39, 144.46, 144.71 (1C + 1C), 144.75, 144.78, 144.91, 145.03, 145.16, 145.24, 145.58, 145.59, 145.62, 146.10, 146.12, 146.23, 146.33, 146.35, 146.40, 146.55, 146.64, 146.66, 146.83, 147.26, 147.43, 147.50, 148.53, 149.04 (1C + 1C), 149.33, 149.92, 152.59, 152.85, 152.92, 153.87, 154.52, 155.55, 157.74; APCI-MS *m*/*z* 952 (M^-).

Synthesis of a mixture of 15,18-dibenzyl-6,9,12-triphenyl-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene (15a), 6,18-dibenzyl-9,12,15-triphenyl-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene (15b) and 6,9-dibenzyl-12,15,18-triphenyl-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene (15c) ($(PhCH_2)_2Ph_3C_{60}H$ (15)). A solution of PhMgBr in THF (0.89 M, 0.951 ml, 847 µmol, 15 equiv.) was added to a suspension of $CuBr{\cdot}SMe_2$ (176 mg, 847 µmol, 15 equiv.) in 5 ml of degassed THF at 23 °C. To this suspension was added a degassed solution of **1** (51.0 mg 56.5 mmol) in 5 ml of 1,2-$Cl_2C_6H_4$, and the mixture was stirred for 1.5 h at 23 °C. HPLC analysis indicated full consumption of the starting material. The reaction mixture (brownish-green suspension) was quenched with 0.2 ml of degassed saturated NH_4Cl solution. The resulting brown suspension was filtered through a pad of silica gel and concentrated to dryness under reduced pressure. The residue was subjected to HPLC purification. Fractions containing **15** were concentrated to a small volume under reduced pressure and precipitated by addition of methanol. The precipitates were collected and washed with methanol to afford 53.7 mg (86%) of **15** as an orange solid. The ^{1}H NMR analysis indicated a ratio of **15a** : **15b** : **15c** was 10 : 25 : 65, which was determined from an integrated area ratio of the signals due to the protons directly attached to the fullerene core. Analytically pure material was obtained by GPC purification.

IR (powder) 3060 (w), 3027 (w), 1600 (w), 1493 (m), 1455 (w), 1077 (w), 1030 (w), 735 (m), 695 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (d, J = 13.0 Hz, 1H, PhCH*H*, **15c**), 2.89 (d, J = 13.2 Hz, 1H, PhCH*H*, **15b**), 2.96 (d, J = 13.0 Hz, 1H, PhCH*H*, **15c**), 3.10 (d, J = 13.2 Hz, 1H, PhCH*H*, **15b**), 3.23 (d, J = 13.2 Hz, 2H, PhCH*H*, **15a**), 3.40 (d, J = 13.2 Hz, 1H, PhCH*H*, **15c**), 3.48 (d, J = 13.2 Hz, 1H + 2H, PhCH*H*, **15a** + **15b**), 3.50 (d, J = 13.2 Hz, 1H, PhCH*H*, **15b**), 3.55 (d, J = 13.0 Hz, 1H, PhCH*H*, **15c**), 4.66 (s, 1H, $C_{60}H$, **15c**), 5.14 (s, 1H, $C_{60}H$, **15b**), 5.24 (s, 1H, $C_{60}H$, **15a**), 7.00–7.68 and 7.83–8.05 (m, 25H + 25H + 25H, Ph, **15a** + **15b** + **15c**); Anal. Calcd for $(PhCH_2)_2Ph_3HC_{60}{\cdot}(CHCl_3)_{0.9}$ ($C_{92.9}H_{30.9}Cl_{2.7}$): C, 89.79; H, 2.78. Found: C, 90.05; H, 3.08.

Preparation of potassium 6,9-dibenzyl-12,15,18-triphenyl-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(6*H*)-ide (K[$C_{60}(PhCH_2)_2Ph_3$] (16)). This compound was prepared in the same manner as **3**.

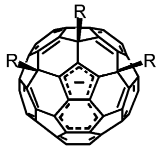
^{1}H NMR (THF-d_8, 400 MHz) δ 3.34 (d, 2H, J = 13.1 Hz, PhCH*H*), 3.66 (d, 2H, J = 13.1 Hz, PhCH*H*), 6.98 (t, J = 7.3 Hz, 2H, Ph), 7.03 (deformed d, J = 5.1 Hz, 3H, Ph), 7.11 (t, J = 7.6 Hz, 4H, Ph), 7.17 (t, J = 7.7 Hz, 2H, Ph), 7.28 (deformed t, 8H, Ph), 7.84–7.88 (m, 2H, Ph), 8.25 (deformed d, J = 7.7 Hz, 4H, Ph); ^{13}C NMR (THF-d_8, 100 MHz) δ 50.74 (2C), 60.66 (2C), 62.09 (2C), 62.42, 125.80, 126.14 (2C), 126.16 (2C), 127.84 (2C), 127.96 (2C), 127.98 (4C), 128.27 (4C), 128.99, 129.13 (4C), 129.22 (2C), 129.95 (2C), 131.52 (4C), 140.96 (3C), 142.68 (2C), 142.71 (2C), 142.84 (4C), 142.92 (2C), 146.19 (2C), 146.24, 146.37 (2C), 146.74, 146.87 (2C), 146.88 (2C), 146.89 (2C), 147.09 (4C), 147.19 (2C), 148.82 (2C), 148.83 (2C), 148.98 (2C), 149.02 (2C), 149.25 (2C), 149.29 (2C), 149.59 (2C), 159.26 (2C), 159.61 (2C), 159.75 (2C), 160.29 (2C), 160.31 (2C).

Synthesis of a mixture of 9-benzyl-6,12,15,18-tetraphenyl-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene (17a), 6-benzyl-9,12,15,18-tetraphenyl-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]-fullerene (17b) and 15-benzyl-6,9,12,18-tetraphenyl-1,6,9,12,15,18-hexahydro(C_{60}-I_h)[5,6]fullerene (17c) ($(PhCH_2)Ph_4C_{60}H$ (17)). These compounds were synthesized in the same manner as **15**. Starting from 20.5 mg of **8** (23.1 µmol), 20.5 mg of **17** was obtained as near 1 : 1 : 1 mixture of three isomers (an orange solid, 18.2 µmol, 79% yield). The isomeric ratio remains ambiguous due to the difficulty in distinguishing between **17b** and **17c**.

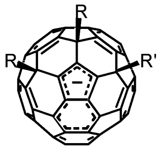
IR (powder) 3059 (w), 3028 (w), 1599 (m), 1493 (m), 1447 (m), 1077 (w), 1031 (m), 741 (m), 735 (m), 694 (s), 684 (s); ^{1}H NMR (THF-d_8, 400 MHz) δ 3.63 (d, J = 13.2 Hz, PhCH*H*, 1H, **17b** or **17c**), 3.72 (s, PhCH_2, 2H, **17a**), 3.74, (d, J = 13.4 Hz, PhCH*H*, 1H, **17b** or **17c**), 3.75 (d, J = 13.4 Hz, PhCH*H*, 1H, **17b** or **17c**), 3.83 (d, J = 13.2 Hz, PhCH*H*, 1H, **17b** or **17c**), 5.05 (s, 1H, **17a**), 5.18 (s, 1H, **17b** or **17c**), 5.27 (s, 1H, **17b** or **17c**), 6.85–8.05 (m, 25H + 25H + 25H, Ph, **17a** + **17b** + **17c**); APCI-MS *m*/*z* 1120 (M^-).

Nomenclature

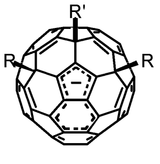
All fullerene compounds in this paper are named on the basis of the latest IUPAC recommendation.[26] Recently numbering system of the fullerene skeletons has changed into a more systematic method than the previous one. A comparison between the new and the old methods is shown below.



A



B



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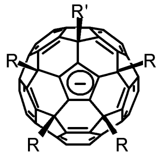

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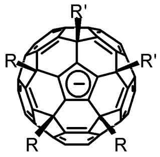

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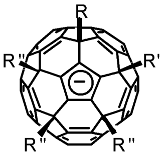

F

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18 Upon treatment of $(PhCH_2)_2PhC_{60}H$ (**2**) with a phenylcopper reagent, $(PhCH_2)_2Ph_3C_{60}H$ (**16**) was produced in a moderate yield. This experiment also supports the structural assignment.

19 *cf.* 1-$(PhCH_2)$-9-PhC_{60} has C_s symmetry.

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23 Note that the indenyl plane of $K(H_3C_{70})$ is rather flat due to the decreased degree of curvature in the equatorial belt region of C_{70} cage.

24 Benzyl radical would also add to the anionic species such as $(PhCH_2)_3C_{60}^-$.

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