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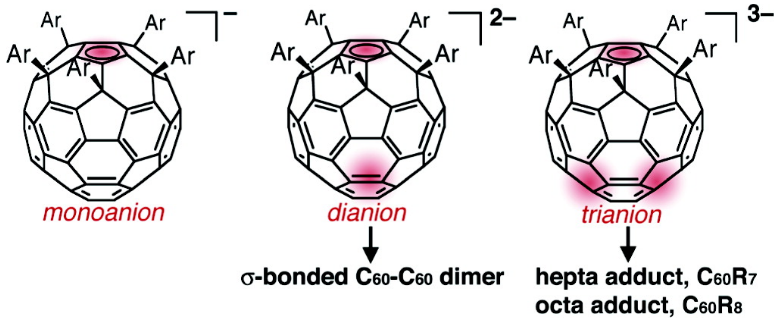

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Syntheses, Structure, and Derivatization of Potassium Complexes of Penta(organo)[60]fullerene-Monoanion, -Dianion, and -Trianion into Hepta- and Octa(organo)fullerenes

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Abstract: Two-electron reduction of penta(organo)[60]fullerenes $C_{60}Ar_5H$ (Ar = Ph and biphenyl) by potassium/mercury amalgam afforded potassium complexes of the corresponding open-shell radical dianions $[K^+(thf)_n]_2[C_{60}Ar_5^{2-\bullet}]$. These compounds were characterized by UV−visible-near-IR and electron spin resonance spectroscopy in solution. Anaerobic crystallization of $[K^+(thf)_n]_2[C_{60}(biphenyl)_5^{2-\bullet}]$ that exists largely as a monomer in solution gave black crystals of its dimer $[K^+(thf)_3]_4[(biphenyl)_5C_{60}-C_{60}(biphenyl)_5^{4-}]$, in which the two fullerene units are connected by a C−C single bond [1.577(11) Å] as determined by X-ray diffraction. Three-electron reduction of $C_{60}Ar_5H$ with metallic potassium gave a black−green trianion $[K^+(thf)_n]_3[C_{60}Ar_5^{3-}]$. The reaction of the trianion with an alkyl halide RBr (R = $PhCH_2$ and Ph_2CH) regioselectively afforded a hepta-organofullerene $C_{60}Ar_5R_2H$, from which a potassium complex $[K^+(thf)_n][C_{60}(biphenyl)_5(CH_2Ph)_2^-]$ and a palladium complex $Pd[C_{60}(biphenyl)_5(CH_2Ph)_2](\pi\text{-methallyl})$ as well as octa-organofullerene compounds $C_{60}(biphenyl)_5(CH_2Ph)_3H_2$ and $Ru[C_{60}(biphenyl)_5(CH_2Ph)_3H]Cp$ were synthesized. These compounds possess a dibenzo-fused corannulene π-electron conjugated system and are luminescent.

Introduction

Organic functionalization of [60]fullerene has created a number of organic derivatives, and has significantly expanded the scope of the science of carbon clusters. Water-soluble derivatives[1] and organometallic complexes[2,3] are representative of such organofullerene compounds. For the synthesis of structurally more complex, functional fullerene compounds, regio- and chemoselective derivatization of the fullerene core of the organofullerene compounds becomes necessary (cf. second-stage functionalization such as the one shown in Scheme 1): This poses synthetic problems even more challenging than those already imposed on the initial organo-derivatization of the parent fullerene.[4] Organic derivatization of organofullerene has been largely achieved in two ways: first, by addition of a nucleophile to neutral fullerene core[4] and, second, by electrophilic reaction of anionic fullerene core generated by deprotonation of hydrofullerene or by reduction of fullerene. Among the latter method, the hydrofullerene route has already proven useful for the two-stage functionalization. For instance, a cyclopentadienide anion **1** and a bucky ferrocene anion **2** have been alkylated in high yield to give a variety of functionalized fullerene derivatives[5] and metal complexes[3g] (Scheme 1). However, anion and polyanions of organofullerenes are less synthetically useful, in contrast to the case known for the parent fullerene-dianion C_{60}^{2-} that reacts with an alkyl halide giving $C_{60}(alkyl)_2$.[6−12] The organofullerene-polyanions have been

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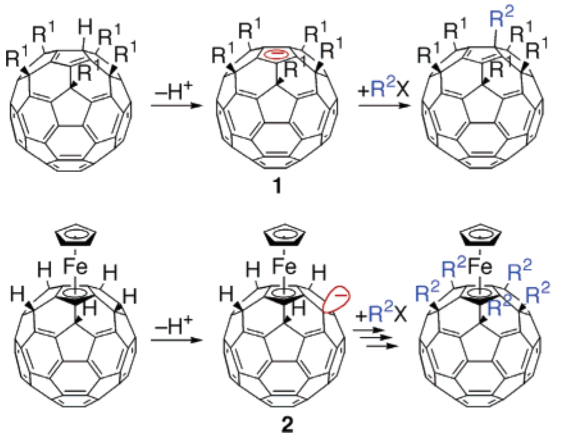
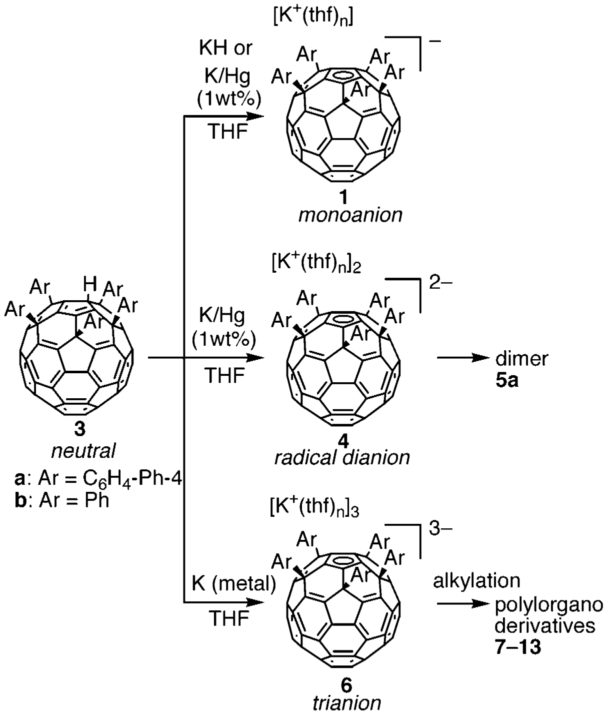
Scheme 1



generated and studied by cyclic voltammetry but seldom isolated,[13,14] structurally characterized, or examined for their synthetic utility. The reduction potentials required to reduce the functionalized fullerenes that are generally higher than those of the parent fullerene,[15] the symmetry of the functionalized fullerenes, inherently lower in level than that of [60]-fullerene, and the instability of reduced species sometimes observed[16,17] make the studies on the structures and reactivities rather difficult.

The anion **1**[2] (Scheme 1) is an electronically interesting compound as it contains a cyclopentadienide moiety homoconjugated with the bottom 50π-electron system.[2b] We considered that this structural feature may favorably affect the reduction chemistry so that the resulting polyanion can be used for further chemical functionalization. Described in this article are the results of controlled reduction of the penta(aryl)[60]-fullerene $C_{60}Ar_5H$ (Ar = biphenyl and Ph; **3**),[18] which led to generation and characterization of the potassium salts of the $C_{60}Ar_5$ mono-, di-, and trianions (Scheme 2) as well as their regioselective derivatization into new a type of fullerene molecules bearing seven and eight organic groups (**7**−**13**). The dianion was found to give upon crystallization a tetraanionic dimer $[K^+(thf)_3]_4[(biphenyl)_5C_{60}{-}C_{60}(biphenyl)_5{}^{4-}]$ (**5a**), where the two fullerene radical dianions are connected by a C−C σ-bond.

Scheme 2



Results and Discussion

Structure and Electrochemical Property of Pentakis(biphenyl)[60]fullerene Monoanion 1. To start the studies on the polyanions of penta(organo)[60]fullerene, we first examined the properties of the monoanion **1**, which will be further reduced to the di- and trianions. In our previous reports,[1−5] we often referred to the generation of the monoanion $C_{60}Ar_5{}^-$ (**1**) yet without any structural data. Treatment of $C_{60}Ar_5H$ (**3**) with K/Hg first reduces the bottom 50π-part, which is followed by loss of hydrogen from the top cyclopentadiene moiety to generate **1**.[2b] Alternatively, deprotonation of **3** with KH also generates **1**. Such operations generate $C_{60}Ar_5K$, which may be either a true anion $C_{60}Ar_5{}^-$ having a solvent separated K^+ (i.e., $[K^+(thf)_n][C_{60}Ar_5{}^-]$), or a complex having direct C−K contact. To probe this issue we have chosen pentakis(biphenyl)[60]fullerene $C_{60}(biphenyl)_5H$[19] (**3a**; pentakis(biphenyl) derivatives are denoted as "**a**") and penta(phenyl)[60]fullerene $C_{60}Ph_5H$ (**3b**; penta(phenyl) derivatives are denoted as "**b**").[2] The biphenyl compound was particularly intriguing for its ability to form a one-dimensional stacked array through inclusion of another molecule into the cavity created by the wall of the five biphenyl groups.[19,20,21]

$[K^+(thf)_6][C_{60}(biphenyl)_5{}^-]$ (**1a**) was prepared by deprotonation of $C_{60}(biphenyl)_5H$ with KH in THF (Scheme 2), and single crystals were obtained by slow diffusion of hexane into a THF solution of **1a** under Ar atmosphere. The crystal structure of **1a** (Figures 1 and 2) indicates that the potassium atom is trapped inside the biphenyl cavity, and hence, there is no one-dimensional stacking of the fullerene molecules.[19] The potassium ion in **1a** is solvated by six THF molecules leaving the fullerene−cyclopentadienide as a free anion. The positively

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[15] Fullerene derivatives bearing strong electron-withdrawing groups show lower reduction potential. Cf. Keshavarz-K, M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371−11372.

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[18] Though the chemistry of compounds with the Ar groups other than phenyl and biphenyl as well as $C_{60}Me_5$ is expected to be very similar to that of **3a,b**, these latter compounds gave much better defined products as described in the text.

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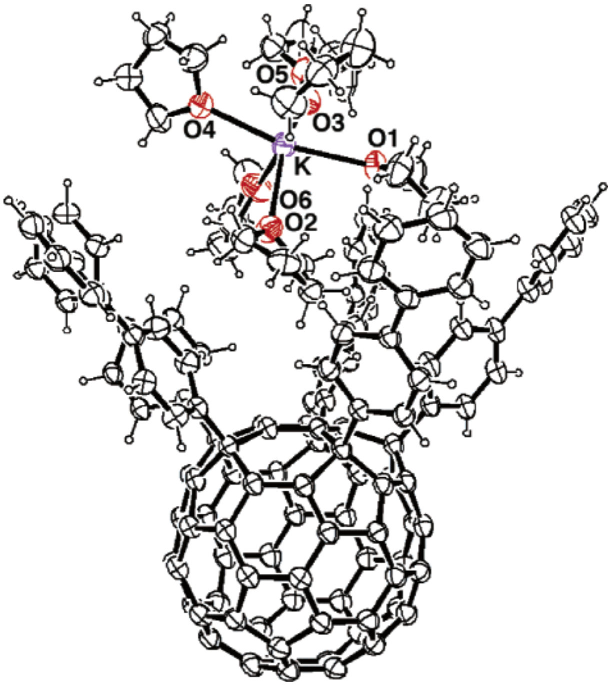


Figure 1. ORTEP drawing of **1a**·$(THF)_3$. THF molecules in the crystal packing are omitted for clarity. Thermal ellipsoids are drawn in 30% probability level. Bond lengths (Å): K−O1 = 2.674(4), K−O2 = 2.723(5), K−O3 = 2.759(6), K−O4 = 2.616(5), K−O5 = 2.707(6), K−O6 = 2.819(6).

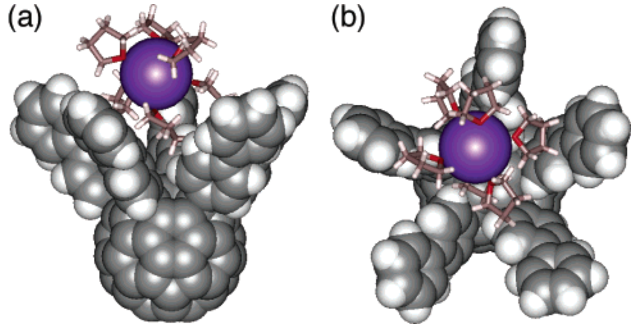


Figure 2. CPK model of **1a**. Six THF molecules coordinating to the potassium ion are drawn in stick representation. (a) Top view. (b) Side view.

charged $K^+(thf)_6$ is obviously a better guest to the cavity than the negatively charged $C_{60}Ar_5^-$. To create a one-dimensional stack of $C_{60}Ar_5^-$ as in the case of $C_{60}Ar_5H$, we need to consider further engineering. The bond lengths (Table S1 in Supporting Information) follow the conventional single/double bond notation shown for the structure **1** in Scheme 1. Thus, the average bond length (1.41 Å) in the cyclopentadienide [C(Cp)−C(Cp)]] is between the C−C bond (1.43−5 Å) and C═C bond (1.38−9 Å) found in **1**, and much shorter than the bond length on the (5,6) ring junction found in [60]fullerene (1.47 Å).[22] The bottom 50π-electron system of **1a** shows a smaller degree of bond alternation than that in [60]fullerene.

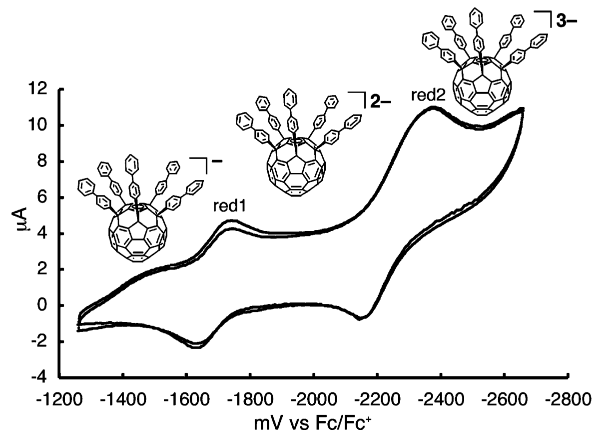
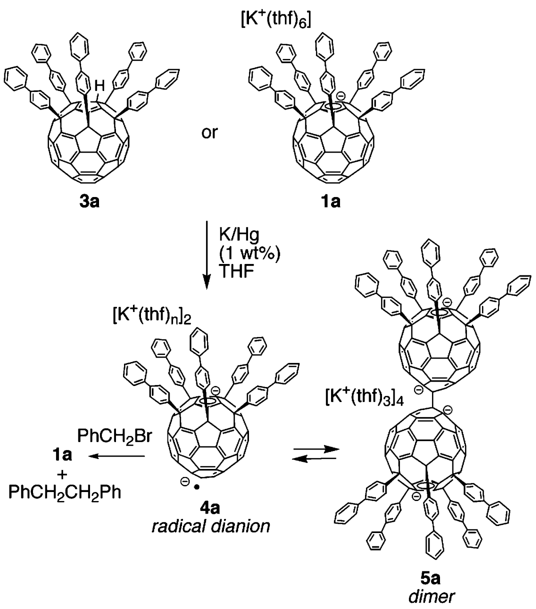


Figure 3. Cyclic voltammogram of **1a** at 25 °C in a 1.0 mM THF solution containing 100 mM $[^nBu_4N][ClO_4]$ as a supporting electrolyte. The red area indicates roughly where anionic charge may reside.

Scheme 3



Next we examined reduction potential of **1** to choose proper reducing reagents to obtain di- and trianion. The cyclic voltammogram of penta(phenyl)[60]fullerene anion (**1b**, $C_{60}Ph_5^-$) was previously reported[2b] and is compared here with that of the penta(biphenyl)[60]fullerene anion **1a**. The phenyl compound **1b** is reduced at $E_{1/2}^{red1} = -1.84$ and $E_{1/2}^{red2} = -2.52$ V (vs Fc/Fc$^+$) at −78 °C in THF under cyclic voltammetric condition, and the single-crystal-grade sample of **1a** showed reversible two-electron reduction at $E_{1/2}^{red1} = -1.69$ and $E_{1/2}^{red2} = -2.26$ V (vs Fc/Fc$^+$) at 25 °C in THF without decomposition (Figure 3).[23] We ascribe the difference between **1a** and **1b** to the effect of the electron-withdrawing *p*-phenyl groups. On the basis of the data, we decided to use potassium/mercury amalgam (reduction potential = ca. 2.0 V)[24] to reduce the monoanions **1a** and **1b** selectively into the penta(organo)[60]fullerene dianions and to use potassium metal (reduction potential = ca. 2.7 V) to synthesize the trianions.

Synthesis, Structure, and Spectral Properties of Pentakis(biphenyl)[60]fullerene Radical Dianion 4a. One-electron reduction of **1a** by 1 wt % K/Hg amalgam in THF at 25 °C gave the pentakis(biphenyl)[60]fullerene radical dianion, $[K^+(thf)_n]_2[C_{60}(biphenyl)_5^{2-\bullet}]$ (**4a**) (Scheme 3). The color of the THF solution changed gradually from dark red to black during

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(23) Fullerene is reduced at $E_{1/2}^{red1} = -0.86$ V and $E_{1/2}^{red2} = -1.44$ V (Fc/Fc$^+$) in THF. Cf. Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807−7813.

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the reaction for 12 h. After removal of excess K/Hg amalgam, solvent was removed under reduced pressure to obtain air- and moisture-sensitive black crystals in quantitative yield. The reduction of C_{60}(biphenyl)$_5$H (**3a**) was performed under the same conditions. A THF-d_8 solution of **4a** exhibited no ^{1}H and ^{13}C NMR signals, and a THF solution of **4a** was ESR active (vide infra). On the basis of a series of analyses discussed below, **4a** in solution exists predominantly as an open-shell radical dianion that can be formulated to have a negative charge on the cyclopentadienide and a radial anion on the bottom π-electron system (Scheme 3).

In contrast to the high nucleophilic reactivity of the trianion discussed later, the radial dianion **4a**,**b** acts only as a reducing agent, reacting with benzyl bromide at 25 °C to give bibenzyl and the starting material **3a**,**b** (after treatment with aqueous HCl). Apparently, a single-electron transfer from **4a**,**b** to benzyl bromide took place to generate benzyl radical, which then dimerized to give bibenzyl. The observed chemical behavior is typical of a monomeric radical dianion **4a**,**b** rather than a dimer $[K^+(thf)_3]_4[Ar_5C_{60}-C_{60}Ar_5{}^{4-}]$ (**5a**,**b**)—an issue that surfaced in the experimental finding described in the next paragraph.

Attempted isolation of this radical dianion by recrystallization (slow diffusion of hexane into a THF solution) unexpectedly gave a black-colored air-sensitive dimer **5a** (Scheme 3). The isolation of the dimer is a good indication of the radical dianionic nature of **4a**, in the light of the behavior of a radical anion $C_{60}{}^{-\bullet}$ that exists predominantly as a monomer in solution at room temperature but in equilibrium with its dimer $(C_{60}-C_{60})^{2-}$.[25,26] Similarly, the K/Hg reduction of $[K^+(thf)_n][C_{60}Ph_5{}^-]$ (or $C_{60}Ph_5$) afforded black crystals of $[K^+(thf)_n]_2[C_{60}Ph_5{}^{2-\bullet}]$ (**4b**), which are also ESR active and air-sensitive.

As found by X-ray crystallographic analysis at 153 K (Figure 4), the dimer exists in an *anti* conformation (i.e., for the interfullerene bond) as predicted by theory for $(C_{60}-C_{60})^{2-}$.[27,28] This provides the second example of a single-crystal structure of a dimer of [60]fullerene radical anion,[29] and the third of a fullerene dimer connected by a single σ-bond.[9] The bond length of the bridging intercage C−C bond of **5a** (1.577(11) Å) is halfway between those of the typical C(sp^3)−C(sp^3) bond (1.54 Å) and the fullerene interfullerene C−C bond in anionic dimer [$(C_{60}-C_{60})^{2-}$; 1.597(7) Å],[29a] and comparable to the intercage bond length in neutral dimer [$RC_{60}-C_{60}R$; 1.576(6) Å].[9] It is known that the interfullerene single bond in the negatively charged dimer $(C_{60}-C_{60})^{2-}$ starts to break at 200−220 K in crystals.[29a] The single bond in **5a** is thermally stable in the crystalline state as investigated by an X-ray analysis at 300 K.

The organometallic features of the potassio dimer **5a** is next discussed in some detail (Figure 5), as the crystal structure **5a** provides relevant information on the structure of organopotassium complexes that have not been studied very often.[30] In Figure 5a, we see that the potassium atom K1 is coordinated in an η^3-fashion both to the cyclopentadienide and to the phenyl group, forming a bent sandwich structure. In Figure 5b, we see that potassium ion K2 is attached in an η^2- and η^6-fashion to a C48*−C49* bond and a C44−C45−C53−C58−C57−C52 hexagon of two fullerene bottoms. Contact distances between K2 and each carbon atoms are 3.204(6) and 3.233(5) Å (K2−C49* and K2−C48*, respectively) for the η^2-coordination and 3.259(6)−3.663(7) Å for the η^6-coordination, the values of which are comparable to the typical distance found in the alkali metal cation−π interactions.[31,32] Such coordination implies that the negative charge in the bottom π-electron system is located around the C48* and C49* carbon atoms, and most likely at C49*.[33] Further discussion on the carbon skeleton is provided in Supporting Information (Table S2).

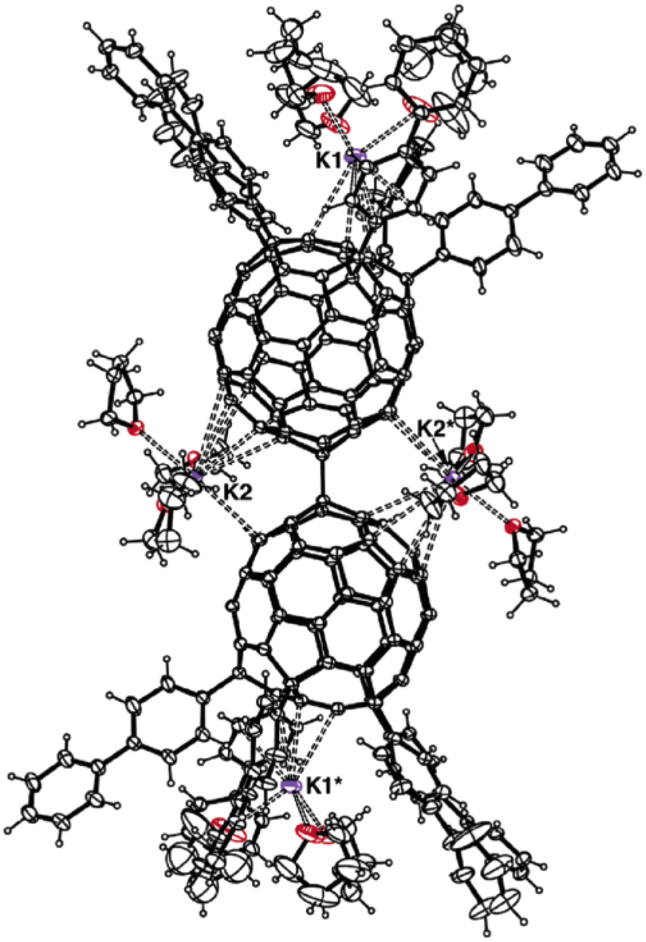

Figure 4. Crystal structure of **5a**·(THF)$_6$·(hexane). ORTEP drawing with 20% probability level ellipsoid. Solvent molecules in the crystal packing are omitted for clarity.

The single crystals of **5a** are ESR silent.[34] On the other hand, a black THF solution prepared by dissolving crystals of the dimer **5a** is ESR active at room temperature and shows no ^{1}H and ^{13}C NMR signals. These observations indicate that **5a** dissociates into a monomeric open-shell radical dianion **4a** (Scheme 3). The similar C−C bond dissociation in solution is

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(33) Location of a positive charge affects localization of a negative charge. Cf. Hoffman, D.; Bauer, W.; Hampel, F.; Hommes, N. J. R. v. E.; Schleyer, P. v. R.; Otto, P.; Pieper, U.; Stalke, D.; Wright, D. S.; Snaith, R. *J. Am. Chem. Soc.* **1994**, *116*, 528−536.
(34) Single-bonded dimer $(C_{60}-C_{60})^{2-}$ is known to be diamagnetic. Cf. ref 26.

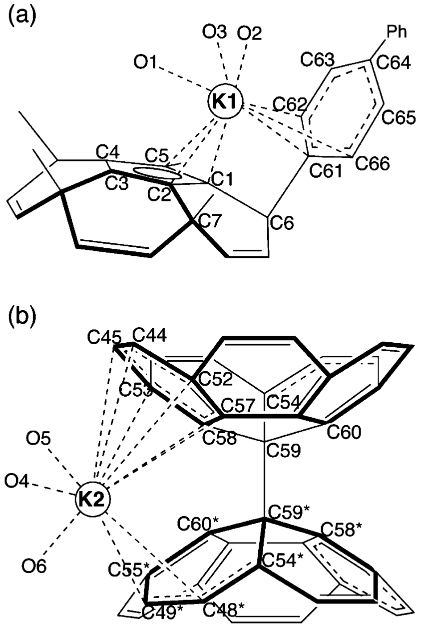


Figure 5. Schematic drawings of the structure of **5a** around potassium ions. Atoms denoted by asterisks represent crystallographically equivalent atoms as to the inversion center residing at the middle point between C59 and C59*. (a) A top part. (b) A bottom part. Solid double line < 1.40 Å < solid-dashed line < 1.43 Å < solid single line. Dashed lines represent coordination of the potassium ions. Bond lengths (Å): K1−O1 = 2.642(9), K1−O2 = 2.790(11), K1−O3 = 2.716(8), K1−C1 = 3.082(6), K1−C2 = 3.266(6), K1−C5 = 3.619(7), K1−C61 = 3.260(6), K1−C62 = 3.357(7), K1−C66 = 3.560(7), K2−O4 = 2.641(5), K2−O5 = 2.647(4), K2−O6 = 2.766(6), K2−C44 = 3.500(6), K2−C45 = 3.663(7), K2−C52 = 3.285(6), K2−C53 = 3.607 (7), K2−C57 = 3.259(6), K2−C58 = 3.392(6), K2−C48* = 3.233(5), K2−C49* = 3.204(6), C54−C59 = C54*-C59* = 1.534(7), C58−C59 = 1.527(8), C59−C60 = 1.534(8), C59−C59* = 1.577(11), C48*−C49* = 1.420(8), C48*−C54* = 1.402(8). Bond angles (deg): C58−C59−C60 = 100.3(4), C58−C59−C54 = 109.7(5), C60−C59−C54 = 108.9(5), C58−C59−C59* = 111.2(6), C60−C59−C59* = 112.6(6), C54−C59−C59* = 113.4(5). Sum of three angles around C59 (intracage) = 318.9°.

known for the dimer of neutral radical species $RC_{60}^{\bullet}$ (R = various alkyl groups).[9,28,35,36] The ESR spectrum of **4a** in THF at 290 K exhibited a broad signal that has a g value of 2.003, which is comparable to the value observed for most organic radicals and for a free electron ($g = 2.0023$), with a peak-to-peak line width (ΔH_{pp}) of 1.68 mT (Figure S1). The g value is much larger than the one observed for $C_{60}^{-\bullet}$ ($g = 1.9991$),[37] and close to the one observed for C_{60}^{3-} ($g = 2.0025$),[25,38] suggesting that the behavior of the radical dianion **4a** is closer to the fullerene trianion rather than to the fullerene radical anion because of the interaction between the top cyclopentadienyl anion and the bottom 50π-electron system.[2b]

The near-IR absorption is diagnostic of the charge state of the [60]fullerene anions[39] and, in conjunction with the above data, indicates that **4a** exists largely as a monomer in solution. Figure 6 shows the UV−vis−NIR absorption spectra of neutral $C_{60}(biphenyl)_5H$, monoanion **1a**, radical dianion **4a**, and trianion

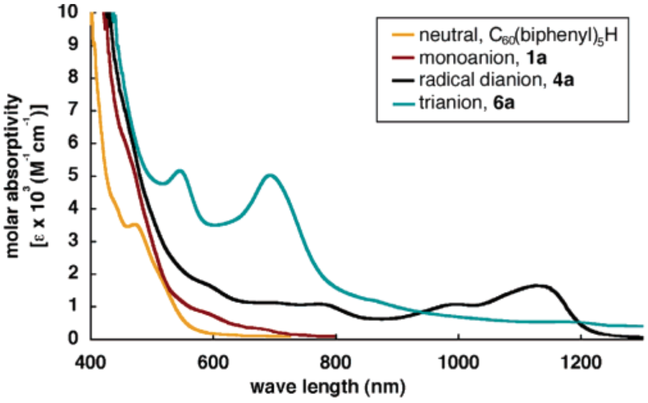
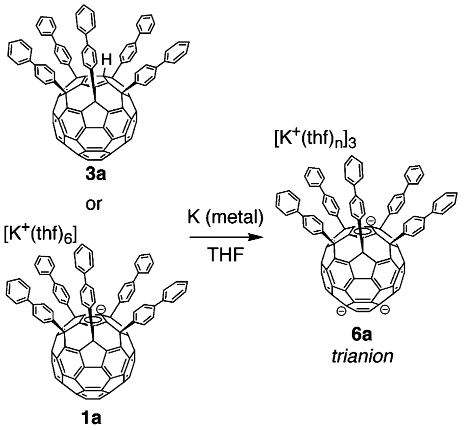


Figure 6. Absorption spectra of penta(biphenyl)[60]fullerene-polyanions. Orange line: neutral compound, $C_{60}(biphenyl)_5H$. Dark-red line: monoanion, **1a**. Black line: radical dianion, **4a**. Green line: trianion, **6a**. Conditions: THF solution (0.45 mM) under argon.

Scheme 4



6a in THF at 25 °C. Among these four, only **4a** exhibits near-IR bands at $\lambda_{max} = 771$ nm ($\epsilon = 1.09 \times 10^3$), 996 nm ($\epsilon = 1.08 \times 10^3$), and 1125 nm ($\epsilon = 1.65 \times 10^3$), characteristic of an open-shell species with a small band gap.[40] The other two are closed-shell species with a large HOMO−LUMO gap. The wavelength ($\lambda_{max} = 1125$ nm) is ca. 50 nm lower energy-shifted than that of $C_{60}^{-\bullet}$ ($\lambda_{max} = 1075-1080$ nm).[39] This difference is in accord with the intrinsically lower degree of symmetry of **4a** (i.e., less orbital degeneracy) than C_{60}^{2-}.

Synthesis and Properties of Pentakis(biphenyl)[60]fullerene Trianion 6. Treatment of the monoanion **1a** with 2.5 equiv of potassium metal in THF at 25 °C for 18 h afforded a dark-green solution of the pentakis(biphenyl)[60]fullerene-trianion $[K^+(thf)_n]_3[C_{60}(biphenyl)_5{}^{3-}]$ (**6a**) (Scheme 4). After removal of THF, an air- and moisture-sensitive black−green powder of **6a** was obtained. Similarly, $C_{60}Ph_5H$ gave the corresponding trianion $[K^+(thf)_n]_3[C_{60}Ph_5{}^{3-}]$ (**6b**). Reduction of $C_{60}Ar_5H$ (Ar = biphenyl and Ph) by excess potassium metal in THF also gave **6a** and **6b**. Effort to obtain single crystals of **6a** and **6b** suitable for X-ray diffraction analysis has so far been unsuccessful because of extreme air sensitivity.

As shown in Figure 6, the trianion **6a** absorbs at $\lambda_{max} = 545$ nm ($\epsilon = 5.17 \times 10^3$) and 692 nm ($\epsilon = 5.03 \times 10^3$). This spectrum is very different from the spectrum observed for C_{60}^{2-},[39] which shows characteristic near-IR absorptions with maximum peaks at λ_{max} = ca. 830 and ca. 952 nm. The reason

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(36) Bond dissociation temperature depends on the size of the R group.

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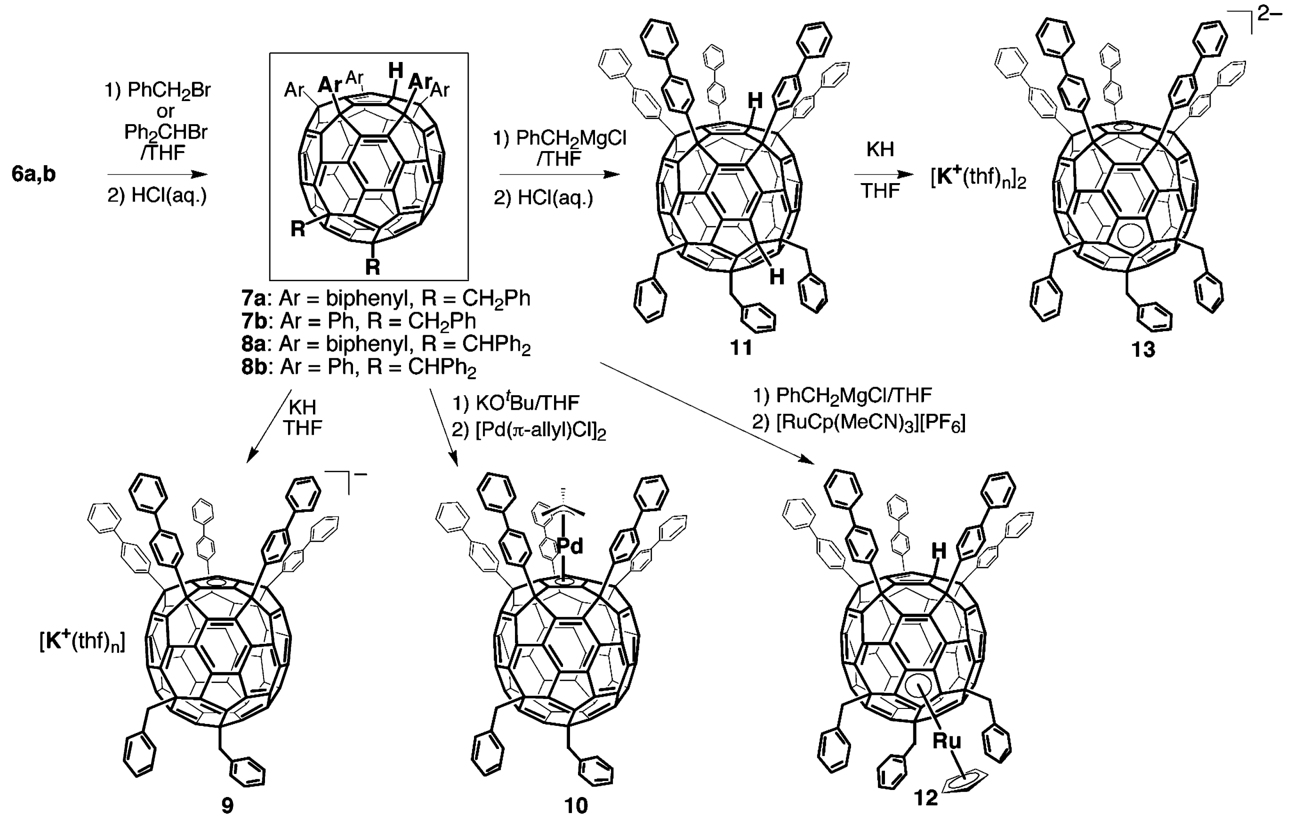
(40) $C_{60}^{-\bullet}$ exhibiting vibronic absorption at near-IR region. Cf. ref 39.

Scheme 5



for this difference can be ascribed to the contribution of the top cyclopentadienyl anion. We could not find any NMR signals of **6a** and observed a single broad ESR signal of **6a** at a temperature range from 290 to 4.4 K. A small amount of residual radical dianion **4a** as minor component in **6a** appears to hamper the NMR measurement. Interpretation of the NMR and ESR spectra of **6a** remains inconclusive.

The trianions **6a** and **6b** are useful nucleophiles (Scheme 5). Treatment of the black–green THF solution of **6a,b** with 3.5-equiv of a benzylic halide[41] (RX; R = CH_2Ph and $CHPh_2$) at 25 °C caused an immediate change of the color into dark red, and subsequent protonation with aqueous HCl afforded a doubly alkylated product $C_{60}Ar_5R_2H$ (**7a**: Ar = biphenyl and R = CH_2-Ph; **7b**: Ar = Ph and R = CH_2Ph; **8a**: Ar = biphenyl and R = $CHPh_2$; **8b**: Ar = Ph and R = $CHPh_2$) as a predominant product[42] in 65–75% yield. This chemical reactivity parallels that of the fullerene dianion C_{60}^{2-}.[6,7,8,11] The reaction may take place in three-stages as proposed for C_{60}^{2-} by Fukuzumi;[7,8] that is, electron transfer from **6a,b** to the alkyl halide (to generate a radical dianion **4a,b** and an alkyl radical) followed by radical–radical coupling to give a mono-alkylated product $C_{60}Ar_5R^{2-}$, and S_N2 reaction with the alkyl halide to generates $C_{60}Ar_5R_2^{-}$. We noted that **6a,b** is much more reactive than C_{60}^{2-} which requires a 20–100 fold excess of the benzyl halide to obtain a reasonable reaction rate.[7,8,11] The initial electron-transfer step being rate limiting for C_{60}^{2-},[43] we ascribe this efficiency to greater electron-transfer ability of **6a,b** (and likely greater nucleophilicity of $C_{60}Ar_5R^{2-}$).

The structure determination of **7a,b** and **8a,b** was not at all an easy issue because of numerous possibilities as to the position of the cyclopentadienyl proton and the two R groups. The first piece of information on symmetry was obtained by derivatization of **7a** into potassium and palladium complexes. Deprotonation of **7a** with 1.2 equiv of KH in THF afforded a single regioisomer $[K^+(thf)_n][C_{60}(biphenyl)_5(CH_2Ph)_2^-]$ (**9**) (Scheme 5), which is C_1 symmetric (^1H and ^{13}C NMR). Similarly, a deprotonation/palladation sequence[3i] afforded $Pd[C_{60}(biphenyl)_5(CH_2Ph)_2](\pi$-methallyl) (**10**) as a single regioisomer in 90% yield (Scheme 5), and its ^1H and ^{13}C NMR spectra also indicated the C_1 symmetry. These pieces of information limited the range of structural possibility, which was then reduced into one.

Addition of $PhCH_2MgCl$ to **7a** in THF at 25 °C afforded $C_{60}(biphenyl)_5(CH_2Ph)_3H_2$ (**11**) in 82% yield (Scheme 5). The ^1H NMR spectrum of **11** exhibited five sets of two C_{60}-*H* signals due to the top and bottom hydrogen atoms (i.e., five regioisomers). This as well as the UV–vis spectrum is essentially the same as that of a known compound $C_{60}Me_5Ph_3H_2$[4b] possessing the same regiochemistry as **11**. Reaction of **7a** with the benzyl Grignard reagent, followed by an addition of $[RuCp(MeCN)_3]$-$[PF_6]$ gave air-stable $Ru[C_{60}(biphenyl)_5(CH_2Ph)_3H]Cp$ (**12**) as a mixture of three regioisomers. It is a dark-green compound (λ_{max} = ca. 700 nm). Compound **11** emits orange-red light ($\lambda_{max} = 622$ nm, $\Phi = 1.0\%$) upon irradiation at $\lambda_{max} = 365$ nm, but ruthenium complex **12** is not luminescent. Then, **11**

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(41) Reactions with MeI, $(Me_3Si)_2CHCl$, and $BrCH_2CO_2Et$ gave a complex mixture of many regioisomers and the starting compound **3a,b**.

(42) Determination of regioselectivity of the reaction was impossible for numerous possibilities of nonessential regioisomers: For instance, even the compounds **7a,b** and **8a,b** consist of an inseparable mixture of regioisomers as to the location of the hydrogen atom. With this limitation in mind, we concluded that the regioselectivity of the alkylation reaction was very high.

(43) Electron transfer from C_{60}^{2-} to RX is the rate-limiting step in the formation of RC_{60}^{-}. See ref 7.

was doubly deprotonated by 4.5 equiv of KH into a dianion $[K^+(thf)_n]_2[C_{60}(biphenyl)_5(CH_2Ph)_3{}^{2-}]$ (**13**). The cyclopentadienyl proton surrounded by the five biphenyl groups was deprotonated upon addition of the first 1.5 equiv of KH, and the proton next to the benzyl groups was removed slowly with the remaining 3 equiv. The compound **13** was C_s symmetric (^{1}H and ^{13}C NMR). With the above pieces of information, we concluded that the dialkylation of the trianion **6a,b** took place regioselectively to introduce two benzyl groups on two fullerene carbon atoms located on the opposite side of the top cyclopentadienide moiety. The two benzyl groups in **7a,b** are in a 1,4-relation to each other in the hexagon. Interestingly, and perhaps not without reason, this 1,4-substitution is mechanistically related to the same 1,4-located carbon atoms in **5a**; that is, the C49* atom where anionic charge resides, and the C59* atom where the C−C bond forms (cf. Figure 5).

In conclusion, selective reduction of organofullerene compounds with carefully chosen reduction agents affords well-defined, synthetically useful organofullerene polyanions. The investigation has given basic information to the chemistry of reduced penta(aryl)fullerene molecules that have so far been generated as transient species and studied only through electrochemical measurements. The study not only elucidated the properties and reactivities of anion and polyanions of the organofullerenes about which rather little has so far been known, but also provided new synthetic entries to functionalized fullerenes. The reduction methodology has provided a variety of new structures such as dimer-, hepta- and octa-alkylated compounds such as **5** and **7**−**13**. Given the new conjugation networks[4,44] and the organometallic ligand systems[3] found in **7**−**13** (such as luminescent fused corannulene), we expect that the alkylation strategies based on the reduction chemistry is complementary to the organocopper routes,[2] and will provide useful possibilities for material science applications.[1,19,20,45] The selective reduction methodology will also find use in polyfunctionalization of carbon clusters other than [60]fullerene.

Experimental Section

General. All manipulations were carried out under argon using standard Schlenk techniques. THF, THF-d_8, and hexane were dried over Na/K alloy and purified by trap-to-trap distillation before use. Chloroform-*d* was used as received. The water content of the solvent was determined with a Karl Fischer Moisture Titrator (MK-210, Kyoto Electronics Company) to be less than 20 ppm for THF and THF-d_8. Penta(phenyl)[60]fullerene and penta(biphenyl)[60]fullerene were prepared according to the literature.[2a,d,19] Benzyl bromide was purchased from Tokyo Kasei Kogyo Co., Ltd. and was distilled under reduced pressure. Chemical yields of the potassium complexes were calculated on a postulate that three THF molecules coordinate to one potassium atom.

HPLC analyses for reactions affording air-stable neutral compounds were performed on Shimadzu LC-10A system equipped with SPD-M10A diode array detector. Preparative HPLC separations were performed by use of Buckyprep column (Nacalai Tesque Co., 20 mm × 250 mm) using toluene/2-propanol (5/5) or toluene/hexane (5/5) as eluent. All ^{1}H (400 MHz, 500 MHz) and ^{13}C (100 MHz, 125 MHz) NMR spectra were recorded on JEOL ECX400 and ECA500 spectrometers, respectively. When THF-d_8 and chloroform-*d* were used as solvent, spectra were referenced to residual solvent protons in the ^{1}H NMR spectra (3.58 and 7.26 ppm) and to solvent carbons in the ^{13}C NMR spectra (67.4 and 77.0 ppm). Mass spectra were measured on Shimadzu LCMS-QP8000 and Waters ZQ2000 LC-mass spectrometer. High-resolution mass spectra were measured on a JEOL JMS-T100LC APCI/ESI-TOF mass spectrometer.

Table 1. Crystal Data and Structure Analysis Results for **1a** and **5a**

	1a·(THF)$_3$	**5a**·(THF)$_6$·(hexane)
formula	$C_{156}H_{117}KO_9$	$C_{159}H_{124}K_2O_9$
crystal system	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
R, R_w ($I > 2\sigma(I)$)	0.1044, 0.3048	0.1174, 0.3077
R1, wR2 (all data)	0.1487, 0.3559	0.1820, 0.3651
GOF on F^2	1.286	1.226
a, Å	20.650(3)	15.777(3)
b, Å	27.279(2)	17.554(3)
c, Å	19.546(3)	21.761(4)
α, deg	90	81.860(9)
β, deg	91.404(5)	72.851(9)
γ, deg	90	77.342(9)
V, Å^3	11007(2)	5600(2)
Z	4	2
T, K	153(2)	153(2)
crystal size, mm	0.85, 0.65, 0.20	0.54, 0.26, 0.22
D_{calcd}, g/cm^3	1.312	1.338
$2\theta_{min}$, $2\theta_{max}$, deg	4.12, 51.72	4.34, 51.9
no. refl. measured (unique)	16563	16858
no. refl. measured ($I > 2\sigma(I)$)	9667	9159
no. parameters	1486	1524

Electrochemical Measurements. Cyclic voltammetry (CV) was performed using a BAS CV-50W voltammetric analyzer and three-electrode cell with a glassy carbon working electrode and a platinum wire counter electrode. All potentials were recorded against an Ag/Ag$^+$ reference electrode and corrected against Fc/Fc$^+$. CV was measured at a scan rate of 100 mV/s.

ESR Measurement. ESR spectra of **4a** and **6a** were recorded on a JEOL continuous wave X-band spectrometer, JES-RE2X, equipped with a helium flow-temperature controller. All measurements were performed by using sealed ESR tubes. THF solution samples were measured using 2-mm quartz ESR tubes.

UV−vis−NIR Measurement. UV−vis−NIR spectra of **4a** and **6a** were recorded on a HITACHI U3500 spectrometer. All solutions were prepared in spectrograde THF that was distilled from Na/K alloy by trap-to-trap distillation prior to the measurements.

X-ray Crystallographic Analysis. Single crystals of **1a** and **5a** suitable for X-ray diffraction studies were grown and subjected to data collection. The data sets were collected on a MacScience DIP2030 Imaging Plate diffractometer using Mo Kα (graphite monochromated, $\lambda = 0.71069$ Å) radiation. Crystal data and data statistics are summarized in Table 1. The structure of **1a** and **5a** was solved by the directed method (SIR97).[46] The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method, using SHELXL-97.[47] Hydrogen atoms were placed at calculated positions and refined "riding" on their corresponding carbon atoms. In the subsequent refinement, the function $\sum\omega(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $wR2 = [\sum\omega(F_o^2 - F_c^2)^2/\sum(\omega F_o^4)]^{1/2}$ CCDC No. 271756 (**1a**) and No. 271957 (**5a**).

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Preparation of [K(thf)$_n$][$C_{60}(C_6H_4$-Ph-4$)_5$] (1a). A Schlenk tube was charged with C_{60}(biphenyl)$_5$H (500 mg, 0.336 mmol) and potassium hydride (40 mg, 1.01 mmol) which was washed with dried hexane. Addition of THF (60 mL) to the Schlenk tube at 25 °C gave a dark-red solution with evolving H_2 gas. After stirring for 20 min at 25 °C, the reaction mixture was transferred to a centrifugation tube via cannula. The dark-red solution was separated from potassium hydride by centrifugation and transferred to a Schlenk tube. Solvent was removed under reduced pressure, and the dark-red microcrystalline solid was washed with dried hexane to obtain **1a** (568 mg, 0.326 mmol, 97% yield). ^{1}H NMR (THF-d_8, 500 MHz): δ 7.15 (t, Ph, 5H), 7.27 (t, Ph, 10H), 7.36 (d, C_6H_4, 10H), 7.51 (d, Ph, 10H), 8.04 (d, C_6H_4, 10H). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz): δ 62.18 (C_{60}(sp^3), 5C), 126.90 (biphenyl, 10C), 127.27 (biphenyl, 5C), 127.71 (biphenyl, 10C), 128.84 (biphenyl, 5C), 129.24 (biphenyl, 10C), 129.84 (biphenyl, 10C), 139.32 (biphenyl, 5C), 142.50 (biphenyl, 5C), 143.32 (C_{60}, 10C), 145.62 (C_{60}, 5C), 146.65 (C_{60}, 5C), 147.41 (C_{60}, 10C), 149.38 (C_{60}, 5C), 149.41 (C_{60}, 10C), 159.88 (C_{60}, 10C).

Preparation of [K(thf)$_n$]$_2$[$C_{60}(C_6H_4$-Ph-4$)_5$] (4a). Method A. To a potassium/mercury amalgam (1.0 wt %; K: 50 mg, 1.3 mmol; Hg: 5.0 g) was added a solution of **1a** (500 mg, 0.287 mmol) in THF (40 mL) at 25 °C. After stirring for 24 h at 25 °C, the reaction mixture was transferred to a centrifugation tube via cannula. The dark-brown solution was separated from the mercury amalgam by centrifugation. The supernatant solution was transferred to a Schlenk tube, and solvent was removed under reduced pressure. The resulting black microcrystalline solid was washed with dried hexane to obtain **4a** (550 mg, 0.275 mmol, 96% yield). Air-sensitive open-shell compound **4a** was characterized by the ESR, UV−vis−NIR spectroscopy and by the X-ray crystallography.

Method B. Alternatively, the title compound could be directly prepared by the treatment of C_{60}(biphenyl)$_5$H (500 mg, 0.336 mmol) and potassium/mercury amalgam (1.0 wt %; K: 50 mg, 1.3 mmol; Hg: 5.0 g). The same preparation procedure described above was performed to obtain **4a** (638 mg, 0.319 mmol, 95% yield).

Preparation of [K(thf)$_n$]$_2$[$C_{60}Ph_5$] (4b). Method A. Starting material [K(thf)$_n$][$C_{60}Ph_5$] **(1b)** was prepared according to a previous paper.[2] The same potassium/mercury amalgam reduction was performed to obtain **4b**. Complex **4b** (569 mg, 0.352 mmol, 96% yield) was derived from **1b** (500 mg, 0.367 mmol). The title compound **4b** is also an air-sensitive and ESR-active compound.

Method B. The procedure described for **4a** was performed to obtain **4b**. Reduction of $C_{60}Ph_5H$ (500 mg, 0.452 mmol) by using potassium/mercury amalgam (1.0 wt %; K: 50 mg, 1.3 mmol; Hg: 5.0 g) gave **4b** (711 mg, 0.440 mmol, 97% yield).

Preparation of [K(thf)$_n$]$_3$[$C_{60}(C_6H_4$-Ph-4$)_5$] (6a). Method A. Microcrystalline solids of **1a** (500 mg, 0.287 mmol) and potassium metal (28.0 mg, 0.717 mmol) were placed in a Schlenk tube, and THF (40 mL) was added at 25 °C to start the reduction. After stirring for 18 h at this temperature, a dark-green solution of **6a** was obtained. THF was removed under reduced pressure, and the resulting dark-green solid (*pyrophoric*) was washed with dry hexane to obtain **6a** (615 mg, 0.273 mmol, 95%). Characterization of the title compound was performed by UV−vis−NIR and ESR spectroscopy.

Method B. An alternative procedure for the preparation of **6a** is reduction of C_{60}(biphenyl)$_5$H. Treatment of microcrystalline solids of C_{60}(biphenyl)$_5$H (500 mg, 0.336 mmol) and potassium metal (112 mg, 2.86 mmol) in THF (40 mL) gave the same dark-green solution. The solution was transferred to a centrifugation tube via cannula under argon, and insoluble materials were removed by centrifugation. Drying under reduced pressure and washing with hexane afforded the air- and moisture-sensitive dark-green powder **6b** (725 mg, 0.322 mmol, 96%).

Preparation of [K(thf)$_n$]$_3$[$C_{60}Ph_5$] (6b). The procedures described for **6a** were performed to obtain **6b**. Reduction of **1b** (500 mg, 0.367 mmol) by using potassium metal (35.9 mg, 0.918 mmol) afforded **6b** (651 mg, 0.348 mmol, 95% yield). Alternatively, reduction of $C_{60}Ph_5H$ (500 mg, 0.452 mmol) by using potassium/mercury amalgam gave **6b** (809 mg, 0.432 mmol, 96% yield).

Preparation of C_{60}(biphenyl)$_5$(CH_2Ph)$_2$H (7a). Method A. To a black−green solution of **6a** (300 mg, 0.133 mmol) in THF (10 mL) was added benzyl bromide (79.7 mg, 0.466 mmol) at 25 °C. The color of the solution immediately changed to dark red. After stirring for 2 min, aqueous HCl (1 N, 0.2 mL) was dropped into the solution. Methanol (60 mL) was added to the reaction mixture to precipitate red microcrystals, which were collected by filtration. The crystalline crude solid was purified by silica gel column chromatography using eluent CS_2/toluene (from 10/0 to 8/2). The intense red band following the yellow band was collected, and the solution was concentrated under reduced pressure. Methanol was added to the concentrated solution to give a red crystalline precipitate, which was collected by filtration and washed with methanol to afford **7a** (167 mg, 0.100 mmol, 75% yield) as an inseparable mixture of five regioisomers as to the position of the hydrogen atom. The NMR and high-resolution APCI-TOF MS spectra were measured for the mixture. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.35−4.09 (m, 4H, CH_2Ph), 5.33, 5.36, 5.37, 5.42, and 5.46 (s × 5, 1H, C_{60}-*H*), 7.27−8.05 (m, 55H, aromatic protons). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 47.0−47.8 (*C*H_2Ph), 58.54−61.25 (C(sp^3)-H, C(sp^3)-Ph, and C(sp^3)-CH_2), 127.01−154.89 (aromatic carbons). HRMS (APCI-TOF, negative) *m*/*z* calcd for $C_{134}H_{59}$ [M − H]$^-$ 1668.4650, found: 1668.4645. Anal. Calcd for $C_{134}H_{60}$: C, 96.38; H, 3.62. Found: C, 96.21; H, 3.59.

Method B. C_{60}(biphenyl)$_5$H (1.00 g, 0.672 mmol) and potassium metal (263 mg, 6.72 mmol) were placed in a Schlenk tube to which was added THF (40 mL). Hydrogen gas evolved, and the color of the solution changed to dark red after stirring for 4 h at 25 °C. Further stirring for 18 h gave a dark-green solution which was transferred to an another Schlenk tube via cannula. To this solution was added benzyl bromide (402 mg, 2.35 mmol) at 25 °C. The color of the solution changed from dark green to dark red. After stirring for 2 min, aqueous HCl (1 N, 1.0 mL) and methanol (200 mL) were added to obtain crude microcrystal, which was subjected to purification as with method A described above. The title compound (751 mg, 0.450 mmol, 67% yield) was obtained as red crystals.

Preparation of $C_{60}Ph_5(CH_2Ph)_2H$ (7b). The procedure described for **7a** was performed to obtain **7b**. Compound **7b** (890 mg, 0.690 mmol, 69% yield) was synthesized from $C_{60}Ph_5H$ (1.11 g, 1.00 mmol), benzyl bromide (599 mg, 3.50 mmol), potassium metal (391 mg, 10.0 mmol), and THF (50 mL). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.3−3.6 (m, 2H, C*H*HPh), 3.8−4.1 (m, 2H, CH*H*Ph), 5.20, 5.22, 5.24, 5.29, and 5.33 (s × 5, 1H, C_{60}-*H*), 7.0−8.0 (m, 35H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 47.3−47.8 (*C*H_2Ph), 58.4−60.0 (C(sp^3)-Ph and C(sp^3)-CH_2), 61.82, 62.35, 62.82, 63.43, and 63.72 (C(sp^3)-H), 126.7−129.0 (Ph), 131.0−131.4 (Ph), 136.8−136.9 (*ipso*-Ph (CH_2Ph)), 137.5−137.6 (*ipso*-Ph (CH_2Ph)), 139.7−164.1 (C_{60}(sp^2) and *ipso*-Ph (C_{60}−Ph)). HRMS (APCI-TOF, negative) *m*/*z* calcd for $C_{104}H_{39}$ [M − H]$^-$ 1288.3085, found: 1288.3087. Anal. Calcd for $C_{104}H_{40}$: C, 96.87; H, 3.13. Found: C, 96.70; H, 3.03.

Preparation of C_{60}(biphenyl)$_5$($CHPh_2$)$_2$H (8a). The procedure described for **7a** was performed to obtain **8a**. Compound **8a** (174 mg, 0.0955 mmol, 71% yield) was synthesized from C_{60}(biphenyl)$_5$H (200 mg, 0.134 mmol), diphenylmethyl bromide (116 mg, 0.470 mmol), potassium metal (52.0 mg, 1.34 mmol), and THF (20 mL).^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.38−5.83 (m, 3H, C_{60}-*H* and C*H*Ph_2), 6.80−8.33 (m, 65H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 57.3−66.4 (sp^3 *C*(C_{60})-Ph, *C*(C_{60})-CH, *C*(C_{60})-H, and *C*HPh_2), 126.1−164.3 (sp^2 carbon of C_{60} and aromatic carbons). HRMS (APCI-TOF, negative) *m*/*z* calcd for $C_{146}H_{67}$ [M − H]$^-$ 1820.5276, found: 1820.5267. Anal. Calcd for $C_{146}H_{68}$: C, 96.24; H, 3.76. Found: C, 96.02; H, 3.64.

Preparation of $C_{60}Ph_5(CHPh_2)_2H$ (8b). The procedure described for **7a** was performed to obtain **8b**. Compound **8b** (187 mg, 0.130 mmol, 72% yield) was synthesized from $C_{60}Ph_5H$ (200 mg, 0.181 mmol), diphenylmethyl bromide (157 mg, 0.634 mmol), potassium metal (71.0 mg, 1.81 mmol), and THF (20 mL).^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.21−5.32 (s × 10, 2H, C*H*Ph_2), 5.67, 5.67, 5.69, 5.70, and 5.71 (s × 5, 1H, C_{60}-*H*), 6.82−8.45 (m, 45H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 57.5−66.1 (sp^3 *C*(C_{60})-Ph, *C*(C_{60})-CH, *C*(C_{60})-H, and *C*HPh_2), 126.5−158.0 (Ph). HRMS (APCI-TOF, negative) *m*/*z* calcd for $C_{116}H_{47}$ $[M - H]^-$ 1440.3711, found: 1440.3713. Anal. Calcd for $C_{116}H_{48}$: C, 96.64; H, 3.36. Found: C, 96.51; H, 3.32.

Preparation of [K(thf)$_n$][C_{60}(biphenyl)$_5$(CH_2Ph)$_2$] (9). Compound **7a** (100 mg, 0.060 mmol) and pre-washed KH (3.0 mg, 0.072 mmol) were placed in a Schlenk tube, and then THF (10 mL) was added at 25 °C. Hydrogen gas evolved, and the color of the solution changed from red brown to dark red. After stirring for 30 min at 25 °C, insoluble material was removed by centrifugation. Removal of a solvent and washing with dry hexane afforded air-sensitive dark-red powder **9** (110 mg, 0.057 mmol, 95% yield). ^{1}H NMR (THF-d_8, 400 MHz): δ 3.49 (d, $^{2}J_{H-H} = 12.8$ Hz, 1H, PhC*H*H), 3.56 (d, $^{2}J_{H-H} = 12.8$ Hz, 1H, PhC*H*H), 3.98 (d, $^{2}J_{H-H} = 12.8$ Hz, 1H, PhC*H*H), 4.03 (d, $^{2}J_{H-H} = 12.8$ Hz, 1H, PhC*H*H), 7.1−7.6 (m, 45H, Ph and C_6H_4), 7.82 (d, $^{3}J_{H-H} = 7.6$ Hz, 2H, *o*-C_6H_4), 7.90 (d, $^{3}J_{H-H} = 7.6$ Hz, 2H, *o*-C_6H_4), 7.97 (d, $^{3}J_{H-H} = 7.6$ Hz, 2H, *o*-C_6H_4), 8.20 (d, $^{3}J_{H-H} = 7.6$ Hz, 2H, *o*-C_6H_4), 8.25 (d, $^{3}J_{H-H} = 7.6$ Hz, 2H, *o*-C_6H_4). ^{13}C{^{1}H} NMR (THF-d_8, 100 MHz): δ 47.01 (Ph*C*H_2), 48.86 (Ph*C*H_2), 59.43 (C(sp^3)-CH_2), 60.72 (C(sp^3)-CH_2), 61.84 (C(sp^3)-C_6H_4), 61.85 (C(sp^3)-C_6H_4), 62.22 (C(sp^3)-C_6H_4), 62.23 (C(sp^3)-C_6H_4), 62.64 (C(sp^3)-C_6H_4), 126.01, 126.65, 126.70, 126.83, 127.15, 127.37, 127.64, 127.66, 127.71, 128.58, 128.72, 128.84, 129.18, 129.23, 129.65, 129.76, 129.82, 130.02, 130.17, 132.14, 132.37, 138.06, 138.88, 138.93, 139.03, 139.08, 139.48, 139.69, 140.00, 141.55, 142.39, 142.57,142.61, 142.76, 143.25, 143.49, 143.75, 143.87, 144.36, 144.98, 145.75, 145.98, 146.25, 146.35, 146.46, 147.21, 147.45, 147.81, 148.26, 148.52, 148.99, 149.48, 149.72, 150.39, 151.34, 151.67, 152.25, 152.41, 153.01, 153.31, 154.21, 155.70, 156.78, 158.33, 159.22, 160.31, 161.53, 162.27, 162.83, and 163.29 (sp^2 carbon of C_{60} and aromatic carbons).

Preparation of Pd[C_{60}(biphenyl)$_5$(CH_2Ph)$_2$](π-methallyl) (10). A THF solution of ^{t}BuOK (1.0 M, 0.033 mL, 0.033 mmol) was added to a solution of **7a** (50 mg, 0.030 mmol) in THF (5.0 mL). The color of the solution changed from red to dark red, indicating formation of **9**. After stirring for 10 min at 25 °C, [Pd(π-methallyl)Cl]$_2$ (3.6 mg, 0.018 mmol) was added to the solution. The resulting red solution was stirred for 5 min at 25 °C, and the solution was quenched with saturated NH_4Cl aqueous solution (0.10 mL). Insoluble products were separated through a pad of silica gel (eluent: toluene), and purification by HPLC (Nacalai Tesque, Buckyprep, 20 × 250 mm, eluent: toluene/hexane = 4/6) was performed. The fractions containing **10** were collected and evaporated to a small volume, and precipitation with methanol afforded **10** (49 mg, 0.027 mmol, 90% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.68 (s, Me, 3H), 2.04 (s, CH_2(anti), 2H), 3.08 (s, CH_2(syn), 2H), 3.37 (d, $^{2}J_{H-H} = 13.0$ Hz, 1H, PhC*H*H), 3.45 (d, $^{2}J_{H-H} = 13.0$ Hz, 1H, PhC*H*H), 3.91 (d, $^{2}J_{H-H} = 12.7$ Hz, 1H, PhC*H*H), 3.99 (d, $^{2}J_{H-H} = 12.7$ Hz, 1H, PhC*H*H), 7.1−8.1 (m, 55H, Ph and C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 21.60 (methallyl Me), 47.38 (*C*H_2Ph), 47.85 (*C*H_2Ph), 57.65 (methallyl CH_2), 58.51 (C(sp^3)-C_6H_4), 58.71 (C(sp^3)-C_6H_4), 58.81 (C(sp^3)-CH_2), 59.00 (C(sp^3)-C_6H_4), 59.13 (C(sp^3)-C_6H_4), 59.25 (C(sp^3)-C_6H_4), 59.92 (C(sp^3)-CH_2), 115.93 (methallyl *C*Me), 119.45 (fullerene cyclopentadienyl moiety), 120.05 (FCp), 120.38 (FCp), 120.52 (FCp), 120.77 (FCp), 126.35, 126.38, 126.42, 126.51, 126.53, 126.98, 127.01, 127.06, 127.40, 127.44, 128.10, 128.21, 128.38, 128.51, 128.65, 128.73, 128.76, 128.78, 128.82, 128.86, 129.01, 131.15, 131.44, 132.23, 135.72, 136.34, 136.86, 137.63, 137.84, 139.82, 139.92, 139.99, 140.01, 140.09, 140.32, 140.34, 140.37, 140.41, 141.64, 141.89, 142.86, 143.25, 143.59, 143.68, 143.70, 143.81, 143.87, 144.01, 144.16, 144.45, 144.58, 144.62, 144.72, 145.59, 145.67, 145.84, 146.22, 146.43, 146.96, 147.66, 147.69, 147.74, 147.86, 148.28, 148.82, 149.11, 149.32, 149.41, 149.63, 149.69,150.55, 150.93, 151.08, 151.68, 152.15, 152.21, 152.72, 152.81, 153.01, 153.75, 153.78, 154.71, 154.85, 155.05, 155.83, 158.85, 159.77, 160.68, and 164.37 (aromatic Ph and C_6H_4 carbons and fullerene sp^2 carbons). HRMS (APCI-TOF, positive) *m*/*z* calcd for $C_{138}H_{66}Pd$ $[M]^+$ 1828.4235, found: 1828.4238. Anal. Calcd for $C_{138}H_{66}Pd$: C, 90.55; H, 3.63. Found: C, 90.40; H, 3.49.

Preparation of C_{60}(biphenyl)$_5$(CH_2Ph)$_3$$H_2$ (11). To a solution of **7a** (200 mg, 0.120 mmol) in THF (20 mL) was added a THF solution of $PhCH_2MgCl$ (0.70 M, 0.34 mL, 0.24 mmol) at 25 °C. After stirring for 10 min at 25 °C, the solution was quenched with saturated NH_4Cl aqueous solution (0.05 mL). Solvent was removed under reduced pressure, and the resulting crude solid was purified by silica gel column chromatography using CS_2/toluene (from 10/0 to 7/3) eluent. The orange band was collected, and the solvent was evaporated to a small volume under reduced pressure. Methanol was added to the concentrated solution to give orange-yellow microcrystals **11** (173 mg, 0.098 mmol, 82% yield) as an inseparable mixture of five regioisomers as to the position of the hydrogen atom. The NMR and high-resolution APCI-TOF MS spectra were measured for the mixture. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.90−3.50 (m, 6H, C*H*$_2$Ph), 4.83, 4.84, 4.87, 4.88, and 4.91 (s × 5, 1H, C_{60}-*H* bottom indene moiety), 5.35, 5.35, 5.47, 5.51, and 5.57 (s × 5, 1H, C_{60}-*H* top cyclopentadiene moiety), 7.15−8.17 (m, 60H, aryl groups). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 44.45−49.90 (CH_2Ph), 56.05−62.84 (sp^3 carbon atoms of C_{60}), 127.01−157.39 (aryl groups). HRMS (APCI-TOF, negative) *m*/*z* calcd for $C_{141}H_{67}$ $[M - H]^-$ 1760.5276, found: 1760.5279. Anal. Calcd for $C_{141}H_{68}$: C, 96.11; H, 3.89. Found: C, 95.98; H, 3.83.

Preparation of Ru[C_{60}(biphenyl)$_5$(CH_2Ph)$_3$H]Cp (12). To a solution of **7a** (50 mg, 0.030 mmol) in THF (5.0 mL) was added a THF solution of $PhCH_2MgCl$ (0.70 M, 0.085 mL, 0.060 mmol) at 25 °C. After stirring for 10 min at 25 °C, [RuCp(MeCN)$_3$][PF_6] (30 mg, 0.070 mmol) was added to the solution. The resulting red solution was stirred for 5 min at 25 °C, and the solution was quenched with saturated NH_4Cl aqueous solution (0.10 mL). Insoluble products were separated through a pad of silica gel (eluent: toluene) and purified by silica gel column chromatography using CS_2/toluene (from 10/0 to 7/3) eluent. The brown-green band was collected, and the solvent was evaporated to a small volume under reduced pressure. Methanol was added to the concentrated solution to give orange-yellow microcrystals **12** (42.6 mg, 0.0221 mmol, 74% yield) as an inseparable mixture of three regioisomers as to the position of the hydrogen atom. The NMR and high-resolution APCI-TOF MS spectra were measured for the mixture. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.93−4.25 (m, 6H, CH_2Ph), 5.16, 5.18, and 5.20 (s × 3, 5H, Cp), 5.46, 5.55, and 5.63 (s × 3, 1H, C_{60}-*H* top cyclopentadiene moiety), 7.27−8.14 (m, 60H, aryl groups). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 52.98−56.02 (CH_2Ph), 58.75−61.69 (sp^3 carbon atoms of C_{60}), 71.75, 71.66, and 71.67 (Cp), 98.65−98.72 (fullerene indenyl moiety), 126.98−157.20 (aryl groups). HRMS (APCI-TOF, negative) *m*/*z* calcd for $C_{146}H_{71}Ru$ $[M - H]^-$ 1925.4640, found: 1925.4638. Anal. Calcd for $C_{146}H_{72}Ru$: C, 90.99; H, 3.77. Found: C, 90.88; H, 3.72.

Preparation of [K(thf)$_n$]$_2$[C_{60}(biphenyl)$_5$(CH_2Ph)$_3$] (13). Compound **11** (20 mg, 0.011 mmol) and pre-washed KH (1.4 mg, 0.035 mmol) were placed in a NMR tube and then was added THF-d_8 (0.5 mL) by trap-to-trap distillation. After evolution of hydrogen gas became complete, the NMR tube was sealed under reduced pressure. This sample was subjected to measurement of the ^{1}H NMR spectrum. ^{1}H NMR (THF-d_8, 500 MHz): δ 3.39 (d, $^{2}J_{H-H} = 12.6$ Hz, 2H, CH_2Ph), 3.60 (d, $^{2}J_{H-H} = 12.6$ Hz, 2H, CH_2Ph), 3.76 (s, 2H, CH_2Ph), 7.11−7.55 (m, 46H, Ar), 7.60 (d, 2H, Ar), 7.87 (d, 2H, Ar), 8.03 (d, 4H, Ar), 8.12 (d, 4H, Ar), 8.36 (d, 2H, Ar). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz): δ 52.42 (*C*H_2Ph), 52.65 (*C*H_2Ph), 58.85 (sp^3 *C*(C_{60})-CH_2), 60.25 (sp^3 *C*(C_{60})-CH_2), 60.88 (sp^3 *C*(C_{60})-Ar), 61.48 (sp^3 *C*(C_{60})-Ar), 61.67 (sp^3 *C*(C_{60})-Ar), 122.96, 123.62, 125.89, 126.16, 126.29, 126.57, 126.65, 126.82, 126.94, 127.14, 127.21, 127.44, 127.55, 127.62, 127.64, 127.86, 128.03, 128.42, 129.26, 129.30, 129.36, 130.01, 130.13, 130.36, 132.08, 132.15, 132.66, 137.76, 138.52, 138.59, 138.75, 139.85, 140.97, 141.52, 141.93, 142.75, 142.77, 144.21, 144.24, 144.54, 146.13, 146.18, 146.57, 147.09, 147.74, 148.29, 148.59, 148.75, 149.60, 150.47, 150.67, 150.85, 153.06, 156.49, 157.38, 159.37, 159.46, and 162.34 (sp^2 carbons of the C_{60} skeleton and aryl carbons).

When 1.2 equiv of KH was used for this reaction, a monodeprotonated product $[K^+(thf)_n][C_{60}(biphenyl)_5(CH_2Ph)_3H^-]$ was obtained. Deprotonation occurred at the top cyclopentadiene moiety, and thus the hydrogen atom on the bottom indene moiety remained. ^{1}H NMR (THF-d_8, 500 MHz): δ 2.89 (d, $^2J_{H-H} = 12.9$ Hz, 2H, $CH^1{}_2Ph$), 3.08 (d, $^2J_{H-H} = 12.9$ Hz, 2H, $CH^1{}_2Ph$), 3.25 (d, $^2J_{H-H} = 12.8$ Hz, 2H, $CH^2{}_2Ph$), 3.34 (d, $^2J_{H-H} = 12.6$ Hz, 2H, $CH^3{}_2Ph$), 3.44 (d, $^2J_{H-H} = 12.6$ Hz, 2H, $CH^3{}_2Ph$), 3.45 (d, $^2J_{H-H} = 12.8$ Hz, 2H, $CH^2{}_2Ph$), 4.85 (s, 1H, C_{60}-*H*), 7.10−7.56 (m, 46H, Ar), 7.61 (d, 2H, Ar), 7.71 (d, 2H, Ar), 7.74 (d, 2H, Ar), 7.74 (d, 2H, Ar), 8.09 (d, 2H, Ar), 8.11 (d, 2H, Ar), 8.37 (d, 2H, Ar).

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Supporting Information Available: Description for X-ray structure as well as CIF files of **1a** and **5a**, and ESR spectrum of **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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