

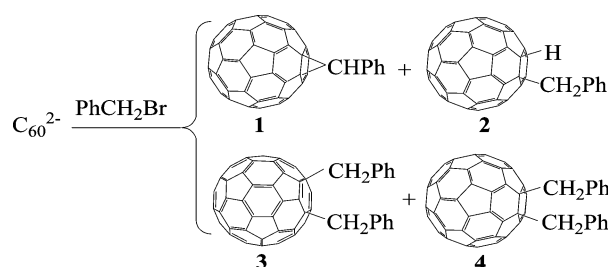
Electrosynthesis and Characterization of 1,2-Dibenzyl C₆₀: A Revisit

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A reinvestigation of the reaction between C₆₀²⁻ and benzyl bromide in benzonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) has shown that there are more reaction products than previously reported. Use of a silica rather than a “Buckyclutcher I” column for HPLC purification led to isolation of two previously unattained products in the reaction mixture, one of which was identified as 1,2-(PhCH₂)₂C₆₀ by UV–vis and NMR. The earlier incorrectly assigned 1,2-(PhCH₂)₂C₆₀ was identified as the methanofullerene C₆₁HPh by X-ray single-crystal diffraction. The electrochemistry of genuine 1,2-(PhCH₂)₂C₆₀ shows that its first reduction potential in PhCN containing 0.1 M TBAP is cathodically shifted by 100 mV with respect to *E*_{1/2} for reduction of 1,4-(PhCH₂)₂C₆₀, indicating that the addition pattern significantly affects the electrochemistry of derivatized C₆₀. Visible and near-IR spectra of the monoanion and dianion of 1,2-(PhCH₂)₂C₆₀ are also reported.

Introduction

Although there are theoretically 23 possible isomers for addition of segregated addends on C₆₀,¹ derivatization of this fullerene mainly results in two types of products: a 1,2-adduct where addition occurs between two hexagons and a 1,4-adduct where addition occurs across a six-membered ring.² It has been well established that the 1,4-adduct is generally less favorable than the 1,2-adduct since introduction of one double bond in a pentagon of C₆₀ will increase the energy of the 1,4-adduct by about 8 kcal/mol with respect to that of the other additional product.^{1,3} However, this unfavorable energy increase would

be compensated for by a decrease in steric hindrance when sterically demanding groups are added with a 1,4-addition.

The synthesis of C₆₀-based organic derivatives has attracted great attention due to possible promising applications in the area of materials, catalysis, and medical sciences.⁴ Studies involving additions to C₆₀ have also attracted much interest with respect to designing desired C₆₀ derivatives for potential applications

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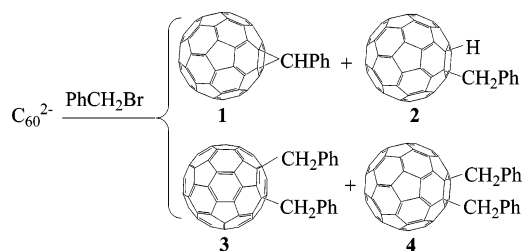
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SCHEME 1. Reaction of C₆₀ Dianion with Benzyl Bromide

of these derivatives. It has been shown that C₆₀ is electron deficient and can reversibly accept multiple electrons.⁵ The derivatives of C₆₀ can also accept multiple electrons, but these compounds are generally less electron deficient than C₆₀ due to cleavage of the π -electron conjugation of C₆₀ as evidenced by a cathodic shift of the reduction potentials.⁶ It has also been shown that the number and position of addends on C₆₀ can have a significant effect on the electrochemical properties of these organofullerenes.^{6g} Prato and co-workers have shown that the reduction potentials of methanofullerene bis-adducts can differ by as much as 140 mV among isomers.^{6g} However, no such difference has been observed between the 1,2- and 1,4-isomers of C₆₀.

Reactions involving the C₆₀ dianion and organic halides have been shown to be effective in preparing 1,2- and 1,4-adducts of this fullerene.⁷ For example, 1,4-dibenzyl C₆₀ was reported to be a major product in a reaction between C₆₀²⁻ and benzyl bromide. There was also a minor product identified in this reaction by HPLC using a “Buckyclutcher I” column.^{7e} The minor product was assigned as 1,2-dibenzyl C₆₀ and showed similar electrochemical behavior as 1,4-dibenzyl C₆₀.^{7e} However, we have now reinvestigated the reaction between C₆₀²⁻ and benzyl bromide using a silica column for HPLC purification of the reaction mixture, and under these conditions, we observed two new products in addition to the two products found with the “Buckyclutcher I” column. Use of the silica column in purification shows that the previously reported 1,2-(PhCH₂)₂C₆₀ is actually [6,6]-methanofullerene, C₆₁HPh, as determined in this study by X-ray single-crystal diffraction (see Supporting Information). A previously unobserved new minor fraction from HPLC was also isolated and is here identified as 1,2-

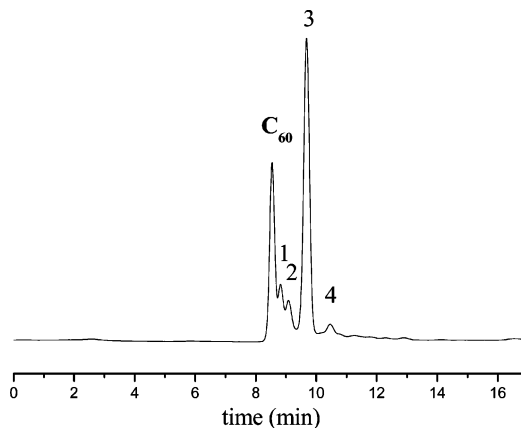


FIGURE 1. HPLC trace of the crude product eluted by a cyclohexane/toluene mixture (70:30 v/v) on a semipreparative silica column at a flow rate of 1.8 mL/min. Fractions 1, 2, 3, and 4 correspond to compounds **1**, **2**, **3**, and **4**.

(PhCH₂)₂C₆₀ based on various spectral characterizations. As a result, the four products purified using the silica column have been characterized by ¹H NMR, ¹³C NMR, MALDI TOF MS, UV–vis, and X-ray single-crystal diffraction and identified as methanofullerene C₆₁HPh (**1**), 1,2-dihydrofullerene HPhCH₂C₆₀ (**2**), 1,4-(PhCH₂)₂C₆₀ (**3**), and 1,2-(PhCH₂)₂C₆₀ (**4**) as shown in Scheme 1. Notably, the half-wave potentials for reduction of 1,2-(PhCH₂)₂C₆₀ are cathodically shifted by as much as 100 mV with respect to those of 1,4-(PhCH₂)₂C₆₀. Herein, we report results upon reinvestigation of the electrosynthetic method along with a full characterization of genuine 1,2-(PhCH₂)₂C₆₀.

Results and Discussion

HPLC of the Reaction Mixture. Figure 1 shows an HPLC trace of the crude product over a silica column. The trace over the silica column shows peaks for three minor fractions in addition to C₆₀ and 1,4-(PhCH₂)₂C₆₀ (peak 3). This result differs from our previous report of the reaction products using a “Buckyclutcher I” column where the main isolated fractions were identified as unreacted C₆₀, a minor product incorrectly assigned as 1,2-(PhCH₂)₂C₆₀, and a major 1,4-(PhCH₂)₂C₆₀ product.^{7e} The difference between the two results is probably related to the inherent property of the stationary phase used for the two kinds of columns. Fractions 1 and 2 have been identified as compounds **1** and **2**, while fraction 3 is identified as 1,4-(PhCH₂)₂C₆₀, and fraction 4 is confirmed to be 1,2-(PhCH₂)₂C₆₀. The 1,2-adduct has a longer retention time than the 1,4-adduct, suggesting that it is a more polar molecule, and this is consistent with a previous observation that the tetra-benzyl adduct bearing a 1,2-addition has a longer retention time than the tetra-adduct having only 1,4-additions.⁸ Since introduction of benzyl groups to C₆₀ increases the polarity of the derivatives, it is thus reasonable to suppose that the 1,2-adduct is a more polar molecule than the 1,4-adduct because the benzylys are positioned more closely to each other. Formation of methanofullerene C₆₁HPh (**1**) and 1,2-dihydrofullerene HPhCH₂C₆₀ (**2**) in the product was unexpected. The methanofullerene C₆₁HPh (**1**) probably derives from a reaction intermediate of C₆₀CH₂Ph⁻ which is formed during reaction of C₆₀²⁻ with PhCH₂Br.⁹ Previous studies have shown that reactions between C₆₀ dianion

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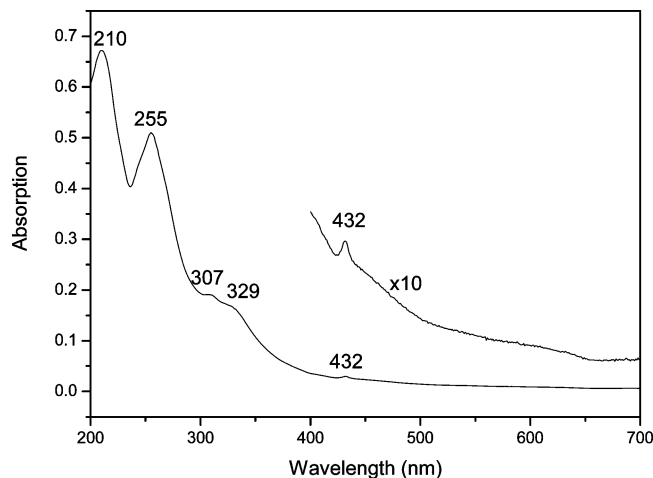


FIGURE 2. UV–visible spectrum of 1,2-(PhCH₂)₂C₆₀ in hexane.

and organic halides are proceeded by formation of RC₆₀[−] via an electron-transfer mechanism, followed by formation of R₂C₆₀ or R(R′)C₆₀ via an S_N2 mechanism.⁹ After formation of C₆₀CH₂Ph[−], a hydride transfer from C₆₀CH₂Ph[−] to PhCH₂Br might occur to afford C₆₁HPh (**1**) and PhCH₃ (and Br[−]). It is also possible that the methanofullerene C₆₁HPh (**1**) might come from a reaction involving C₆₀^{2−} and trace amount of α,α-dibromotoluene present in benzyl bromide as an impurity, as evidenced by GC-MS analysis of the commercially obtained benzyl bromide. Products with structures similar to **1** and **2** have also been observed from reactions involving the C₆₀ dianion and halogenated ketones or esters.¹⁰

UV–vis Spectrum of 1,2-(PhCH₂)₂C₆₀. Unlike C₆₁HPh (**1**), which has a pink color in a mixture of hexanes/toluene, 1,2-(PhCH₂)₂C₆₀ exhibits a yellow color under the same solution conditions. The UV–vis spectrum of 1,2-(PhCH₂)₂C₆₀ in hexane is shown in Figure 2 and characterized by two strong absorption bands at 210 and 255 nm. Similar absorptions are observed for C₆₀ and C₆₁HPh (**1**). A sharp absorption band at around 330 nm in C₆₀ is split into two broad bands at 307 and 329 nm in the spectrum of 1,2-(PhCH₂)₂C₆₀. This compound also displays a spike at 432 nm, which is characteristic for C₆₀ derivatives where addition has occurred at the [6,6]-double bond,¹¹ suggesting that the present compound is a 1,2-adduct.

NMR of 1,2-(PhCH₂)₂C₆₀. In the ¹H NMR spectrum of 1,2-(PhCH₂)₂C₆₀ (see Supporting Information) the methylene protons are characterized by a singlet resonance at 5.03 ppm and resonances corresponding to the phenyl protons are observed at 7.5–7.2 ppm, part of which overlap with the resonance of CHCl₃. In addition, the ratio of the peak area of the methylene protons to that of the phenyl protons is 2:5, consistent with the addends added to C₆₀ being benzyl groups. The ¹H NMR spectrum indicates a high symmetry for the molecule, and assignment of the isolated product as 1,2-(PhCH₂)₂C₆₀ is reasonable since it has C_{2v} symmetry. Although C₆₁HPh **1**, which was previously misassigned as 1,2-(PhCH₂)₂C₆₀, also

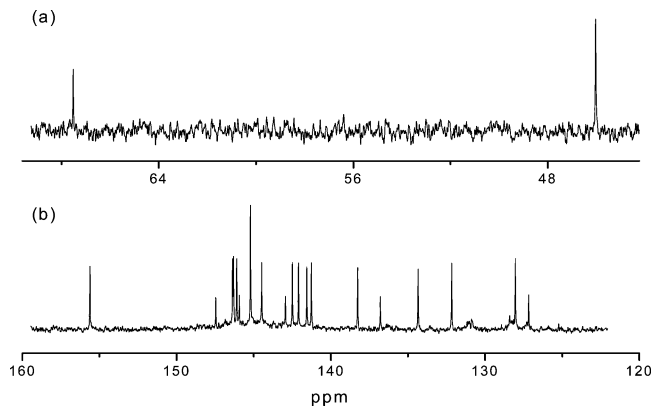


FIGURE 3. ¹³C NMR spectrum of 1,2-(PhCH₂)₂C₆₀ in CS₂/CDCl₃ for the region of (a) sp³ carbons and (b) sp² carbons.

shows a ¹H NMR spectrum which satisfies the symmetry of the molecule, the ratio of the peak area for the methylene protons to that of the phenyl protons is only 1:5 (see Supporting Information), indicating that the addend bonded to C₆₀ is CHC₆H₅, consistent with formation of the methanofullerene C₆₁HPh (**1**). Formation of **1** and its structure are further confirmed by an X-ray single-crystal diffraction study (see Supporting Information).

Figure 3 shows the ¹³C NMR of 1,2-(PhCH₂)₂C₆₀ in CS₂/CDCl₃. Two lines are seen in the region of the sp³ carbons. One resonance at 46.0 ppm is for the two methylene carbons,^{7b,e,9a,12} and the other at 67.5 ppm is for the two sp³ carbons of the C₆₀.^{7b,e,9a,13} As for resonances of the sp² carbons, a total of 19 lines are observed, four of which are assigned to the phenyl carbons and located at 127.2, 128.0, 132.2, and 136.8 ppm, similar to what was reported in a previous paper.^{7e} The remaining 15 lines from 134.4 to 155.6 ppm are assigned to sp² carbons for the C₆₀ of 1,2-(PhCH₂)₂C₆₀. This result is in agreement with the theoretically predicted 16 resonances for a 1,2-adduct of C₆₀ with C_{2v} symmetry, and the appearance of 15 lines is due to a coincidental overlapping of the C₆₀ carbons at 145.2 ppm.

Electrochemistry. Figure 4 shows a cyclic voltammogram of the isolated 1,2-(PhCH₂)₂C₆₀ in PhCN containing 0.1 M TBAP. The compound exhibits three well-defined reversible one-electron reductions within the cathodic potential limit of the solvent with E_{1/2} values of −0.62, −1.04, and −1.57 V vs SCE. It is expected that 1,2-(PhCH₂)₂C₆₀ should be less electron deficient and more difficult to reduce than C₆₀, but it is surprising to note that the reduction potentials of 1,2-(PhCH₂)₂C₆₀ are cathodically shifted by 100, 30, and 50 mV, respectively, with respect to the reduction potentials of genuine 1,4-(PhCH₂)₂C₆₀ (E_{1/2} = −0.52, −1.01, and −1.52 V vs SCE measured in this work). It was reported that the reduction potentials of C₆₀ derivatives are cathodically shifted by approximately 100 mV when two addends are bonded to C₆₀ in a

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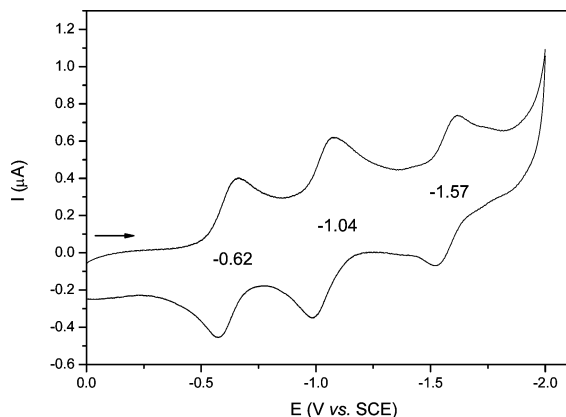


FIGURE 4. Cyclic voltammogram of 1,2-(PhCH₂)₂C₆₀ in PhCN containing 0.1 M TBAP.

1,4-addition pattern,^{7c} and it was earlier unexpected that changing the bonding sites from a 1,4- to a 1,2-position could also cause the same potential shift. Previous results on the electrochemistry of a mixture of 1,2- and 1,4-(CH₃)₂C₆₀ have shown that the two isomers are reduced at identical potentials of -0.58, -1.00, and -1.55 V vs SCE,^{7a} indicating that the type of addends may also play a role in causing the electrochemical difference for the 1,2- and 1,4-isomers. However, this is the first time that such a large difference in potentials has been observed between the 1,2- and 1,4-isomers of a C₆₀ diadduct. A smaller difference was reported for the tetra-benzyl adducts of 1,4,10,24-(PhCH₂)₄C₆₀ ($E_{1/2} = -0.69, -1.12, -1.88$ V vs SCE) and 1,2,4,15-(PhCH₂)₄C₆₀ ($E_{1/2} = -0.74, -1.15, -1.85$ V vs SCE), where the isomer bearing a 1,2-adduct is also generally more difficult to reduce than the isomer which bears only 1,4-addition products.⁸ The smaller difference in potentials between the first reductions of the two isomers (50 mV) is probably due to the fact that only one-half of the addition patterns are different in the two tetra-adduct isomers (two 1,4-additions for 1,4,10,24-(PhCH₂)₄C₆₀ and one 1,2-addition and one 1,4-addition for 1,2,4,15-(PhCH₂)₄C₆₀). This result suggests that the 1,2-adduct is less electron deficient than the 1,4-adduct when there is no substituent effect, and this is probably related to differences in the electronic structure of the two isomers, where a [5,6]-double bond is introduced into the 1,4-isomer.

Visible and Near-IR Spectra of Singly and Doubly Reduced 1,2-(PhCH₂)₂C₆₀. It was earlier shown that the mono- and dianions of the 1,2-adduct of C₆₀ possess characteristic absorption bands in the visible and near-IR region.^{7e,14} Figure 5 shows the visible and near-IR spectra of [1,2-(PhCH₂)₂C₆₀]^{•-} and [1,2-(PhCH₂)₂C₆₀]²⁻ generated electrochemically in DMF by application of a controlled potential of -0.70 and -1.20 V vs SCE, respectively. The singly reduced [1,2-(PhCH₂)₂C₆₀]^{•-} exhibits a strong absorption band at 1000 nm, while doubly reduced [1,2-(PhCH₂)₂C₆₀]²⁻ displays a strong absorption at 868 nm. The monoanions of 1,2-H(*t*-Bu)C₆₀,^{7e} 1,2-(CH₃)₃C₆₀,¹⁴ (*o*-xylyl)C₆₀,¹⁴ and C₆₁HPh 1^{7e} (which was incorrectly assigned as 1,2-(C₆H₅CH₂)₂C₆₀ previously) have visible and near-IR absorption bands at 995, 997, 1006, and 1030 nm, while the corresponding dianions have absorption bands at 880, 874, 868,

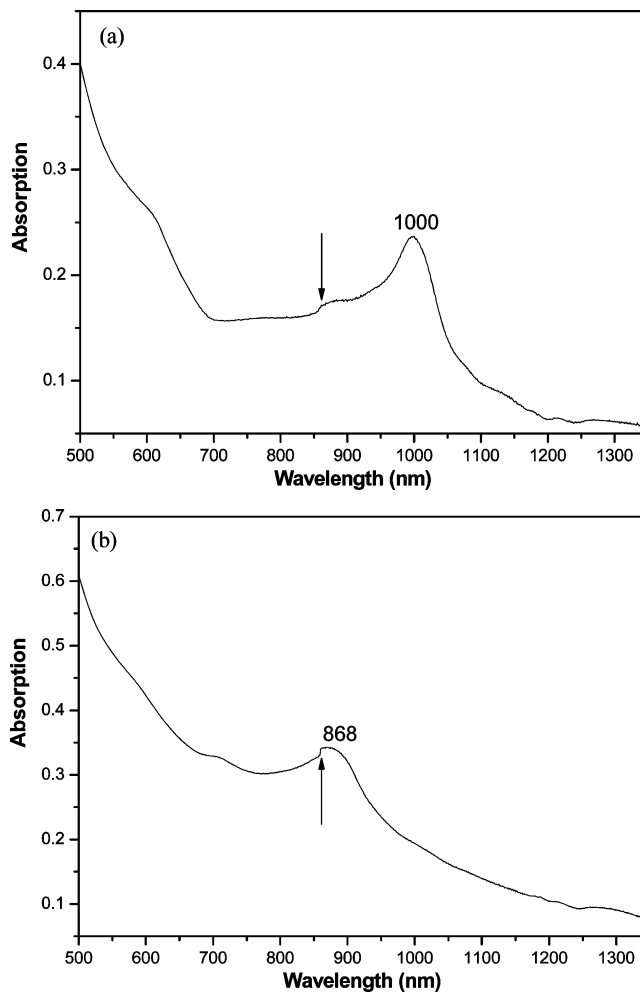


FIGURE 5. Visible and near-IR spectra of (a) [1,2-(PhCH₂)₂C₆₀]^{•-} and (b) [1,2-(PhCH₂)₂C₆₀]²⁻ generated electrochemically with a controlled potential of -0.70 and -1.20 V vs SCE, respectively, in DMF containing 0.1 M TBAP. The lamp was changed at 860 nm as indicated by an arrow.

and 905 nm. The results in the current study are therefore in agreement with the previous literature on the visible and near-IR absorptions for monoanions and dianions of the C₆₀ 1,2-adducts.^{7e,14}

Conclusions

The electrochemistry, isolation, and characterization of reaction products between C₆₀²⁻ and benzyl bromide in PhCN have been reinvestigated and indicate that purification of the product mixture with a silica column not only leads to better HPLC separation than with a "Buckyclutcher I" column but also affords two additional minor products not obtained under the same experimental conditions. The previously assigned 1,2-(PhCH₂)₂C₆₀ is now correctly characterized as the methanofullerene C₆₁HPh (1) by X-ray single-crystal diffraction while a new previously unobserved minor product is identified as genuine 1,2-(PhCH₂)₂C₆₀ based on its UV-vis and NMR spectra. The first reduction potential of 1,2-(PhCH₂)₂C₆₀ in PhCN containing 0.1 M TBAP is cathodically shifted by 100 mV with respect to $E_{1/2}$ for reduction of 1,4-(PhCH₂)₂C₆₀, thus indicating that 1,2-(PhCH₂)₂C₆₀ is less electron deficient than 1,4-(PhCH₂)₂C₆₀. These results indicate there is a significant effect of addition

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patterns on the electrochemistry of C_{60} derivatives. This is probably due to introduction of a [5,6]-double bond in the 1,4-addition, suggesting that a [5,6]-double bond is more electron deficient than a [6,6]-double bond. The monoanion and dianion of 1,2-(PhCH₂)₂C₆₀ are also characterized by visible and near-IR spectroscopy. The overall results of our current study are potentially useful for “tuning” the reduction potentials of C_{60} derivatives.

Experimental Section

Synthesis and Isolation of 1,2-(PhCH₂)₂C₆₀. A 50 mg (69.4 mmol) amount of C_{60} was electroreduced in 50 mL of freshly distilled PhCN solution containing 0.1 M TBAP at -1.10 V vs SCE under either a nitrogen or an argon atmosphere. The potentiostat was switched off after electrogeneration of C_{60}^{2-} was complete, a 10–50-fold excess of PhCH₂Br was then added to the solution all at once, and the reaction was allowed to proceed for 40 min with stirring. The solvent was removed with a rotary evaporator under vacuum, and the residue was washed with methanol to remove TBAP. The crude product was purified by HPLC with a semipreparative silica gel column using a mixture of cyclohexane/toluene (70:30 v/v) as the eluent. The UV–vis detector was set at $\lambda = 380$ nm. Along with ca. 15% recovered C_{60} , four products were identified in the reaction mixture. These were methanofullerene C₆₁HPh (**1**), 1,2-dihydrofullerene HPhCH₂C₆₀ (**2**), 1,4-(PhCH₂)₂C₆₀ (**3**), and 1,2-(PhCH₂)₂C₆₀ (**4**) (see Scheme 1) with an isolation yield of ca. 3%, 2%, 55%, and 3%, respectively. The remainder of the reaction product was insoluble in toluene and unidentified.

1,2-(PhCH₂)₂C₆₀ (4**).** Positive MALDI HRMS m/z : calcd for M⁺, 902.1096; found, 902.0722. FTIR (KBr) ν (cm⁻¹) 1428 (C₆₀), 1181 (C₆₀), 698 (Ph), 526 (C₆₀). UV–vis (hexane) λ_{\max} 210, 255, 307, 329, 432 nm. ¹H NMR (600 MHz, CS₂/CDCl₃) δ 7.50 (d, 4H), 7.30 (t, 4H), 7.23 (t, 2H), 5.03 (s, 4H). ¹³C NMR (150 MHz, CS₂/CDCl₃) 155.6 (4C), 147.5 (2C), 146.4 (4C), 146.3 (4C), 146.1 (4C), 145.9 (2C), 145.2 (8C), 144.5 (4C), 142.9 (2C), 142.5 (4C), 142.1 (4C), 141.6 (4C), 141.3 (4C), 138.3 (4C), 136.8 (2C), 134.3 (4C), 132.2 (4C), 128.0 (4C), 127.2 (2C), 67.5 (2C), 46.0 (2C).

Methanofullerene C₆₁HPh (1**).** Negative MALDI MS m/z : calcd for M⁻, 810; found, 810. UV–vis (hexane) λ_{\max} 210, 257, 327, 428 nm. ¹H NMR (600 MHz, CS₂/CDCl₃) δ 7.93 (d, 2H), 7.50 (t, 2H), 7.44 (t, 1H), 5.38 (s, 1H). ¹³C NMR (150 MHz, CS₂/CDCl₃) δ 149.3 (2C), 147.2 (2C), 145.3 (2C), 145.2 (1C), 145.2 (2C), 144.9 (2C), 144.8 (4C), 144.8 (2C), 144.5 (1C), 144.4 (4C), 144.1 (4C), 144.0 (2C), 143.5 (2C), 143.4 (2C), 142.8 (2C), 142.8 (2C), 142.7 (4C), 142.7 (2C), 142.4 (2C), 142.0 (2C), 141.9 (2C), 141.8 (2C), 140.9 (2C), 140.6 (2C), 138.2 (2C), 136.2 (1C), 132.7 (2C), 131.0 (2C), 128.6 (2C), 128.2 (1C), 75.0 (2C), 43.4 (1C).

The structure of compound **1** was determined by X-ray single-crystal diffraction of **1**·Co^{II}OEP (see Supporting Information). Black plate-like crystals of **1**·Co^{II}OEP·C₆H₆ were obtained by slowly diffusing a Co^{II}OEP chloroform solution into the benzene solution of **1**. Single-crystal X-ray diffraction data were collected on a Bruker SMART Apex equipped with a CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) in the scan range $1.47^\circ < \theta < 25.25^\circ$. The structure was solved with the direct method of SHELXS-97 and refined with full-matrix least-squares

techniques using the SHELXL-97 program within WINGX. Crystal data of **1**·Co^{II}OEP·C₆H₆: C₁₀₉H₅₆CoN₄, $M_w = 1480.51$, triclinic, space group $P-1$, $a = 14.0652(12)$ Å, $b = 14.3088(12)$ Å, $c = 17.4459(15)$ Å, $\alpha = 87.150(2)^\circ$, $\beta = 75.5360(10)^\circ$, $\gamma = 76.178(2)^\circ$, $V = 3301.2(5)$ Å³, $z = 2$, $D_{\text{calcd}} = 1.489$ g/cm³, $\mu = 0.326$ mm⁻¹, $T = 187(2)$ K, crystal size $0.36 \times 0.16 \times 0.12$ mm; reflections collected 18 140, independent reflections 11 733 ($R_{\text{int}} = 0.0343$); $R_1 = 0.0886$ [$I > 2\sigma(I)$], $wR_2 = 0.2228$ [$I > 2\sigma(I)$]; $R_1 = 0.1245$, $wR_2 = 0.2552$ for all data; GOF (on F^2) = 1.029.

1,2-Dihydrofullerene HPhCH₂C₆₀ (2**).** UV–vis (hexane) λ_{\max} 209, 255, 306, 325, 431 nm. ¹H NMR (600 MHz, CS₂/CDCl₃) δ 7.82 (d, 2H), 7.54 (t, 2H), 7.45 (t, 1H), 6.65 (s, 1H), 4.78 (s, 2H). ¹³C NMR (150 MHz, CS₂/CDCl₃) δ 155.1 (2C), 153.6 (2C), 147.3 (1C), 147.2 (1C), 146.8 (2C), 146.3 (2C), 146.2 (2C), 146.2 (2C), 146.1 (2C), 146.0 (2C), 145.6 (2C), 145.4 (2C), 145.3 (2C), 145.2 (4C), 144.6 (2C), 144.4 (2C), 143.1 (2C), 142.4 (4C), 142.1 (2C), 141.9 (2C), 141.8 (2C), 141.8 (2C), 141.5 (2C), 141.4 (2C), 140.1 (2C), 139.8 (2C), 136.2 (2C), 135.9 (1C), 135.6 (2C), 131.3 (2C), 128.7 (2C), 127.7 (1C), 65.7 (1C), 59.0 (1C), 53.0 (1C). Data are consistent with a previous report on the compound,^{7b} where the structure of the compound was established by FAB MS, ¹H and ¹³C NMR, UV–vis, and FTIR.

1,4-(PhCH₂)₂C₆₀ (3**).** UV–vis (hexane) λ_{\max} 209, 256, 329, 443 nm. ¹H NMR (600 MHz, CS₂/CDCl₃) δ 7.50 (d, 4H), 7.41 (t, 4H), 7.29 (t, 2H), 3.71 (quartet, 4H). ¹³C NMR (150 MHz, CS₂/CDCl₃) δ 157.6 (2C), 151.5 (2C), 148.4 (2C), 148.3 (2C), 146.9 (1C), 146.7 (2C), 146.6 (2C), 145.9 (2C), 145.3 (2C), 144.8 (2C), 144.6 (1C), 144.4 (2C), 144.4 (2C), 144.1 (2C), 144.0 (2C), 144.0 (2C), 143.8 (2C), 143.7 (2C), 143.5 (2C), 143.0 (2C), 142.9 (4C), 142.8 (2C), 142.4 (2C), 142.3 (1C), 142.2 (2C), 141.8 (2C), 141.8 (2C), 140.4 (1C), 138.5 (2C), 137.6 (2C), 135.9 (2C), 130.9 (4C), 128.3 (4C), 127.4 (2C), 60.2 (2C), 48.4 (2C). Data are consistent with previous reports on the compound,^{7e,9a} where the structure of the compound was resolved by X-ray single-crystal diffraction.^{9a}

Spectroscopic Measurements of [1,2-(PhCH₂)₂C₆₀]⁻ and [1,2-(PhCH₂)₂C₆₀]²⁻. The monoanion and dianion of 1,2-(PhCH₂)₂C₆₀ were generated electrochemically in DMF containing 0.1 M TBAP by applying a reducing potential at -0.70 and -1.20 V vs SCE, respectively. The generated anionic species were transferred into airtight quartz cuvettes under deaerated conditions. The near-IR spectra of the monoanion and dianion of 1,2-(PhCH₂)₂C₆₀ were measured under argon at room temperature.

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Supporting Information Available: General experimental methods, FTIR, ¹H NMR, MALDI TOF of 1,2-(PhCH₂)₂C₆₀, ¹H NMR and X-ray single-crystal structure of methanofullerene C₆₁HPh (**1**) and the CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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