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Reaction of C_{60}^{2-} with Organic Halides Revisited in DMF: Proton Transfer from Water to RC_{60}^{-} and Unexpected Formation of 1,2-Dihydro[60]fullerenes

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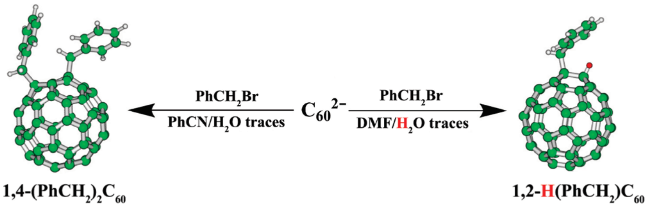
Received March 8, 2010



The reactions of dianionic C_{60} with organic halides, which have been studied extensively in benzonitrile (PhCN), are revisited in a different solvent medium, *N*,*N*-dimethylformamide (DMF), by using $ArCH_2Br$ (Ar = Ph, $C_6H_4CH_3$, C_6H_4Br). Interestingly, instead of the 1,4-R_2C_{60} adducts, which are the typical products when the reactions are carried out in PhCN, the 1,2-dihydro[60]fullerenes (1,2-HRC_{60}) have been obtained as the major products in DMF, except for the case of *o*-$CH_3C_6H_4CH_2Br$ probably due to the steric effect. The obtained 1,2-dihydro[60]fullerenes have been characterized with single-crystal diffraction, ^1H and ^{13}C NMR, high-resolution mass spectrometry (HRMS), and UV−vis. Further examination with deuterated reagents including $PhCD_2Br$, DMF-d_7, and D_2O has revealed that the fullerenyl hydrogen of 1,2-dihydrofullerenes originates from traces of water residue in DMF. When the reaction is re-examined in PhCN with the addition of an excessive amount of water, the yield of 1,2-dihydrofullerene increases significantly, but is still lower compared with that obtained in DMF, demonstrating a considerable solvent effect on the reactivity of C_{60}^{2-}. A possible mechanism accounting for such a difference is proposed. The work has presented an alternative protocol for effective preparation of 1,2-dihydro[60]fullerenes, and may also provide clues toward a better understanding of the proton transfer process for anionic C_{60}-mediated reducing reactions involving H_2O.

Introduction

Carbanions are important intermediates in organometallic and organic chemistry, and have played key roles in the functionalization of organic compounds.[1] Due to the weak electronegativity of the carbon atom, carbanions are usually strong bases, good electron donors, and strong nucleophiles. As a result, they are moisture and oxygen sensitive.[1,2] Anionic C_{60}, which is readily available by either chemical or electrochemical reduction of electron-deficient neutral C_{60},[3] has shown promising potentials in the functionalization of C_{60}.[4−6] Similar to typical carbanions, C_{60} anions are good electron donors[5,7] and strong bases.[8] However, they are not good nucleophiles due to the delocalization of the negative charges over the C_{60} sphere.[5b] It is noteworthy that C_{60} anions have displayed an unusual stability toward water, as shown by the fact that C_{60}^{-}, C_{60}^{2-}, $[(\gamma\text{-CD})_2\text{-}C_{60}]^{-}$ (CD: cyclodextrin),

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DOI: 10.1021/jo100430a

and $[(\gamma\text{-CD})_2\text{-}C_{60}]^{2-}$ can be generated in the presence of large amounts of water without protonation, although they are still very sensitive toward oxygen.[9–11]

Among various anionic C_{60}, the chemistry of $C_{60}{}^{2-}$ has drawn extensive attention[4,5] since the early studies by Kadish and co-workers.[4a] $C_{60}{}^{2-}$ has been recognized as an important building block for fullerene functionalization by reactions with organic halides (RX, X = I, Br, Cl), where $C_{60}{}^{2-}$ plays a key role in initiating the reactions via a single-electron transfer to organic halides.[5] In addition, $C_{60}{}^{2-}$ encapsulated in bis-γ-cyclodextrins has also shown interesting catalytic reducing activities, including C═O, C═C, and N—N$^+$ bond reduction[11] and dinitrogen fixation[12] in the presence of water, where protons are likely to be transferred from water substrate to the reduced species mediated by $C_{60}{}^{2-}$. However, little is known regarding such a proton transfer process since no organofullerene intermediate has been reported from the reactions.

Orfanopoulos and co-workers have recently proposed the reaction of $RC_{60}{}^{-}$ with water moisture to account for the partial formation of 1,2-dihydro[60]fullerenes for the radical reactions of C_{60} with aldehydes mediated by decatungstate and photoirradiation.[13] However, no such proton transfer reaction has been recorded in the literature, even though there are $RC_{60}{}^{-}$ intermediates[5] and traces of water residue[14] available in the reaction system of $C_{60}{}^{2-}$ with RX. Instead, strong proton donors such as trifluoroacetic acid have been used to protonate the $RC_{60}{}^{-}$ intermediates, which are formed either from anionic C_{60}[4h,j,5b,8a] or nucleophilic addition of organolithiums or Grignard reagents to C_{60}.[4l,15] The water residue in the solvent has shown little effect on the bulk generation of $C_{60}{}^{2-}$,[14] which further reacts with organic halides to form 1,2- and/or 1,4-di(organo)fullerenes as the major products depending on the size of addends,[4,5,16] along with minor products of methanofullerenes and 1,2-dihydrofullerenes.[4i,k] The formation of 1,2-dihydrofullerenes is quite unusual, and the fullerenyl hydrogen has been proposed to originate from the methylene protons of the organic halides (XCH_2A, A = ester, ketone; X = Br, I) via the formation of $C_{60}H^-$ intermediate.[4i] It is therefore of importance to investigate if H_2O is involved in the reaction of reduced C_{60} species, not only because it may provide further information on the reaction mechanism proposed for radical acylation of C_{60},[13] but also because it may provide clues on the proton transfer mechanism from water molecule to the reduced species during anionic C_{60}-mediated reducing reactions, since the resulting fullerenyl proton can also be easily removed from the C_{60} sphere.[4h,j,l,8b]

Benzonitrile is the most typical solvent medium used for the bulk generation and reactions of anionic C_{60}.[4a,d,e,h,k,l,5,6] It has a fair solubility for neutral C_{60},[17] and a good solubility for anionic C_{60}.[18] Other solvents, including CH_3CN,[4f,g,i,j] a mixture of toluene and CH_3CN,[4c] and tetrahydrofuran (THF),[4b,19] have also been used, even though it has been indicated that the solubility of mono- and dianionic C_{60} is rather low in CH_3CN.[18,20] Surprisingly, no report on using DMF as the solvent medium for reactions of $C_{60}{}^{2-}$ with organic halides has appeared, although it has been shown that DMF has a good solubility for both the mono- and dianionic C_{60}.[18,21] Notably, recent work by Nakamura and co-workers has shown that the formation of 1,2-dihydrofullerenes via monoaddition of Grignard reagents can be facilitated by addition of DMF.[4l] In addition, the reactivity of carbanions may also be affected by the traces of water residue,[22] which is expected to be present

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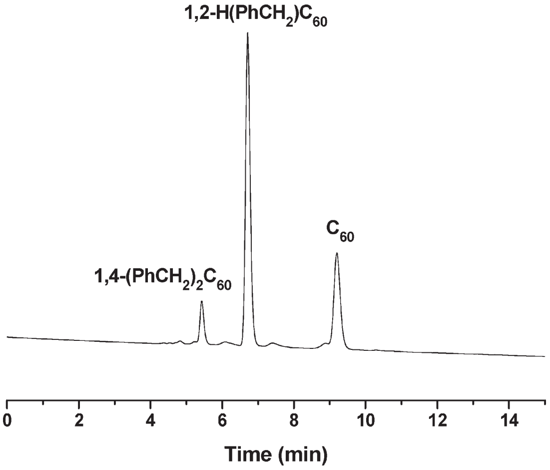

FIGURE 1. HPLC trace of the crude reaction mixture of C_{60}^{2-} with benzyl bromide (molar ratio of C_{60}^{2-}/benzyl bromide = 1:10). The mixture was eluted with toluene over a semipreparative Buckyprep column (20 × 250 mm) at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm.

with a greater amount in DMF than that in PhCN due to the miscibility of DMF with H_2O.[23] It is therefore of interest to study the reaction of C_{60}^{2-} with organic halides in a DMF solvent system other than PhCN. Herein, we report the reaction of C_{60}^{2-} with $ArCH_2Br$ (Ar = Ph, $C_6H_4CH_3$, C_6H_4Br) in DMF. It shows explicitly that the water residue is involved in the reaction of C_{60}^{2-} with organic halides, which is very different from the case when PhCN is used.

Results and Discussion

Formation and Characterization of 1,2-Dihydrofullerenes from the Reactions of Dianionic C_{60} with $ArCH_2Br$ (Ar = Ph, $C_6H_4CH_3$, C_6H_4Br) in DMF. Procedures for generating C_{60}^{2-} in DMF and reactions of C_{60}^{2-} with organic halides were carried out in a manner similar to those reported in PhCN,[4k] and details of the synthesis and purification are described in the Experimental Section. Figure 1 shows the HPLC chromatogram of the crude reaction mixture of C_{60}^{2-} with benzyl bromide. Three fractions appear at 5.4, 6.7, and 9.2 min, corresponding to the 1,4-$(PhCH_2)_2C_{60}$, 1,2-H$(PhCH_2)C_{60}$, and C_{60}, respectively, consistent with previous HPLC assignment.[6a] Notably, different from the results obtained when PhCN is used,[4a,d,k,5] where 1,4-$(PhCH_2)_2C_{60}$ is the exclusive major product, 1,2-H$(PhCH_2)C_{60}$ is formed as the predominant product when the same reaction is carried out in DMF, while the amount of 1,4-$(PhCH_2)_2C_{60}$ is greatly reduced, demonstrating a distinctive solvent effect on the reactivity of C_{60}^{2-}. Under typical conditions, the isolated yield is ca. 50%, 10%, and 25% for 1,2-H$(PhCH_2)C_{60}$, 1,4-$(PhCH_2)_2C_{60}$, and C_{60}, respectively.

The structure of 1,2-H$(PhCH_2)C_{60}$ is established by X-ray single-crystal diffraction, ^{1}H and ^{13}C NMR, high-resolution MS, and UV−vis spectroscopy. The single crystal of the compound was obtained by slow evaporation of an *n*-hexane solution, and the structure is shown in Figure 2. The benzyl group is orientated toward the C_{60} core in the crystal structure, while in fact the benzyl can be positioned with a direction either toward or away from the C_{60} core as shown in the single-crystal structures of C_{60} derivatives bearing two benzyls.[5a,6a] Previous reports on the single-crystal structure of 1,2-dihydrofullerene compounds are very limited, but interestingly, the same orientation of the organic addend is observed as compared with the single-crystal structure of 1,2-H$(SiMe_2O^iPr)C_{60}$,[41] suggesting that the orientation of the organic addends for 1,2-dihydrofullerene compounds is likely controlled by similar unidentified driving forces.

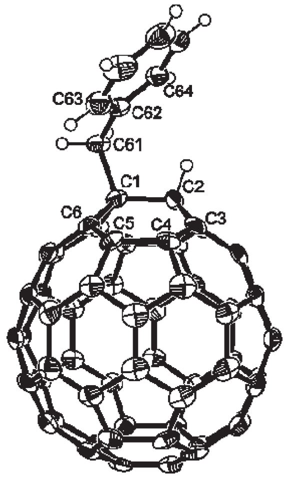

FIGURE 2. ORTEP drawing of 1,2-H$(PhCH_2)C_{60}$ with 50% thermal ellipsoids. Selected bond distances (Å) and bond angles (deg): C1−C2, 1.577(6); C2−C3, 1.527(6); C3−C4, 1.354(6); C4−C5, 1.474(6); C5−C6, 1.371(6); C6−C1, 1.547(6); C1−C61, 1.580(6); C61−C62, 1.498(6); C6−C1−C2, 113.4(4); C1−C2−C3, 115.8(4); C1−C61−C62, 114.7(4).

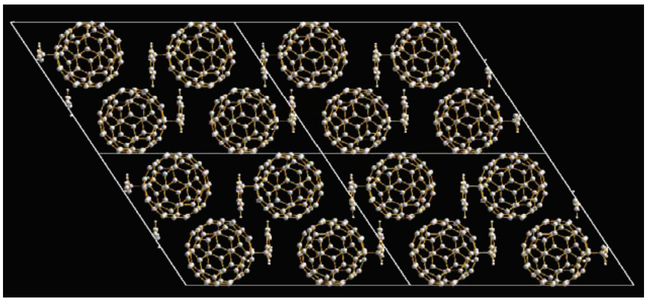

FIGURE 3. Crystal packing diagram of 1,2-H$(PhCH_2)C_{60}$ viewed along the *b*-axis. Space group = $P2_1/c$, a = 16.9920(18) Å, b = 10.2389(11) Å, c = 24.0163(18) Å, α = 90°, β = 123.714(5)°, γ = 90°, and V = 3475.62 Å^3.

Figure 3 shows the crystal packing diagram of 1,2-H$(PhCH_2)C_{60}$ molecules viewed along the *b*-axis. It reveals that the molecules are packed with the distance between the centroids of C_{60} cages being 10.2, 12.5, and 13.7 Å respectively within the same layer, consistent with reported data for organofullerenes.[24] The molecules are organized into well-aligned 1-D stacks probably due to the C···C and $\pi \cdots \pi$ van der Waals interactions between the closely positioned benzyl addend and C_{60} core, and the neighboring columns of the stacks are antiparallel with each other. The well-ordered 1-D stacking structure of fullerene molecules suggests a potential application of the compound in the area

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of organic electronic materials as photovoltaic devices.[25] In addition, it is noteworthy that there is no solvent molecule in the crystal packings, which is quite unusual for the crystals of C$_{60}$ derivatives, but has been previously observed.[41]

The ^{1}H NMR of 1,2-H(PhCH$_2$)C$_{60}$ (see the Supporting Information) shows two singlets at 4.77 and 6.65 ppm, which correspond to the methylene protons of the benzyl group and *H*−C$_{60}$, respectively. The resonance of the methylene protons is upper field shifted compared with that of 1,2-(PhCH$_2$)$_2$-C$_{60}$ (5.03 ppm),[4k] but is lower field shifted with respect to that of 1,4-(PhCH$_2$)$_2$C$_{60}$ (3.71 ppm),[4k] demonstrating a subtle influence of the addend and addition pattern on the electronic structure of the derivatives. Previous work has shown that the electronic structure of C$_{60}$ derivatives is closely related to the half-wave potentials of the first reductions ($E_{1/2}^{\mathrm{red1}}$).[26] It is therefore of interest to correlate the $E_{1/2}^{\mathrm{red1}}$ values of the compounds with the chemical shifts of the methylene protons. The $E_{1/2}^{\mathrm{red1}}$ for 1,2-(PhCH$_2$)$_2$C$_{60}$, 1,2-H(PhCH$_2$)C$_{60}$, and 1,4-(PhCH$_2$)$_2$C$_{60}$ in PhCN containing 0.1 M TBAP is −0.62,[4k] −0.54 (see the Supporting Information), and −0.52 V[4k] vs SCE, respectively. This indicates that first, a 1,2-adduct is much less electron-deficient than a 1,4-adduct by demonstrating a more cathodically shifted reduction potential (1,2-(PhCH$_2$)$_2$C$_{60}$ vs 1,4-(PhCH$_2$)$_2$C$_{60}$), suggesting that more electrons are pulled over toward the electron-deficient C$_{60}$ sphere from the benzyls when the addends are positioned with 1,2-pattern than the case when the addends are positioned with 1,4-pattern; and second, it indicates that a stronger electron-donating group (benzyl) can push more electrons to the C$_{60}$ sphere via the inducing effect than a weaker electron-donating group (H) (1,2-(PhCH$_2$)$_2$C$_{60}$ vs 1,2-H(PhCH$_2$)C$_{60}$). Consequently, the methylene protons of benzyls for the 1,2-adducts are more deshielded than those for 1,4-adducts, and the methylene protons of benzyls for 1,2-(PhCH$_2$)$_2$C$_{60}$ are also more deshielded than those for 1,2-H(PhCH$_2$)C$_{60}$, resulting in the appearance of methylene protons of 1,2-(PhCH$_2$)$_2$C$_{60}$, 1,2-H(PhCH$_2$)C$_{60}$, and 1,4-(PhCH$_2$)$_2$C$_{60}$ in the order from upper field to lower field as observed in the ^{1}H NMR.

Resonances due to the phenyl protons are observed between 7.46 and 7.84 ppm. The ^{13}C NMR spectrum exhibits 27 signals from 155.4 to 131.6 ppm for the sp^2 C$_{60}$ carbons, and two resonances at 66.0 and 59.1 ppm corresponding to the sp^3 C$_{60}$ carbon atoms bonded to benzyl and hydrogen atom respectively as shown by the heteronuclear multiple quantum coherence (HMQC) NMR (see the Supporting Information), in agreement with previous peak assignment.[4d,27] In addition, resonances due to the sp^2 benzyl carbon atoms are also shown in the spectrum from 135.9 to 127.7 ppm. The compound ($C_{67}H_8$) was also subjected to the negative ESI FI-ICR (electrospray ionization Fourier transform ion cyclotron) MS measurement, and the monoisotopic $[M - H]^-$ ion is observed at 811.0543, which is deviated from the calculated value (811.0553) by only −1.2 ppm. The UV−vis spectrum of the compound shows typical absorptions of C$_{60}$ derivatives at 254, 304, and 324 nm, along with the characteristic absorption for 1,2-C$_{60}$ adducts at 431 nm.[28] The spectroscopic data are therefore consistent with the X-ray single-crystal diffraction result for the structural assignment of the 1,2-H(PhCH$_2$)C$_{60}$.

To further examine the generality of the formation of 1,2-dihydrofullerenes from C_{60}^{2-} in DMF, organic halides including *o*-, *m*-, *p*-CH$_3$PhCH$_2$Br and *m*-, *p*-BrPhCH$_2$Br were used with a 10:1 molar ratio to C_{60}^{2-}. The obtained crude products were subjected to HPLC separation eluting with toluene over a semipreparative Buckyprep column as shown in Figure 4, with the isolation yield of ca. 10%, 35%, 45%, 40%, and 50% for the 1,2-dihydro[60]fullerene compound from the reaction of C_{60}^{2-} with *o*-, *m*-, *p*-CH$_3$PhCH$_2$Br and *m*-, *p*-BrPhCH$_2$Br, respectively. The structures of the isolated 1,2-dihydrofullerenes have been characterized by UV−vis, ^{1}H and ^{13}C NMR, and HRMS (see the Supporting Information), while the formation of 1,4-di(organo)fullerenes is confirmed by ^{1}H NMR. Two conclusions can be drawn from the results. First, the yield of 1,2-dihydrofullerene is improved significantly as compared with the case where PhCN[4a,d,k,5] or CH$_3$CN[4f,i,j] is used as the reaction medium, confirming that the solvent does have a significant effect on the reactivity of C$_{60}$ dianion; and second, there is a substituent effect on the product distribution. For *o*-CH$_3$PhCH$_2$Br, the 1,4-di(organo)fullerene is still the predominant product, while for *m*-CH$_3$PhCH$_2$Br and *m*-BrPhCH$_2$Br, both 1,2-dihydrofullerene and 1,4-di(organo)fullerene are formed as the major products, and as for the *p*-CH$_3$PhCH$_2$Br and *p*-BrPhCH$_2$Br, the 1,2-dihydrofullerenes are the exclusive products, and only trace amounts of 1,4-di(organo)fullerenes are formed.

The observed product distribution difference for the ortho-, meta-, and para-substituted organic halides is likely due to the steric effect. For addend with substituent at the ortho-position, it may exhibit a greater steric hindrance than the one with the substituent at meta- or para-position, since the ortho-substituent is closer to the C$_{60}$ core. The ortho-substituent is likely to restrain the access of the C2 of RC_{60}^- formed by the radical coupling of $C_{60}^{-\bullet}$ and $R^\bullet$, which are generated via the electron transfer between C_{60}^{2-} and RX,[5] therefore decreasing the yield of 1,2-HRC$_{60}$, and leading to the formation of more 1,4-adducts via the subsequent S$_N$2 reaction of RC_{60}^- with RX,[5] even though the ortho-substituted benzyl bromide is actually the most unfavorable substrate for the S$_N$2 reaction among the ArCH$_2$Br used. As for the addend with para-substituent, the steric hindrance between the addend and C$_{60}$ is very small since the substituent is far away from the C$_{60}$ core, and the C2 is easily accessible by water molecules, leading to 1,2-dihydrofullerene as the predominant product. The steric hindrance for addend with meta-substituent is in between those for addends with ortho- and para-substituent, consequently, both 1,2-dihydrofullerene and 1,4-di(organo)fullerene are found as major products in the reactions.

Origin of the Hydrogen Atom in 1,2-Dihydrofullerenes. It is surprising that the yields of 1,2-dihydrofullerenes improve significantly for the reactions of C_{60}^{2-} with organic halides when DMF is used as the solvent medium. As for the same reaction carried out in PhCN, the formation of 1,2-dihydrofullerenes is very unfavorable, and only a trace amount of 1,2-dihydrofullerenes can be detected even if the organic addend is less hindered.[4k] One possible source for the fullerenyl hydrogen has been proposed to be the methylene

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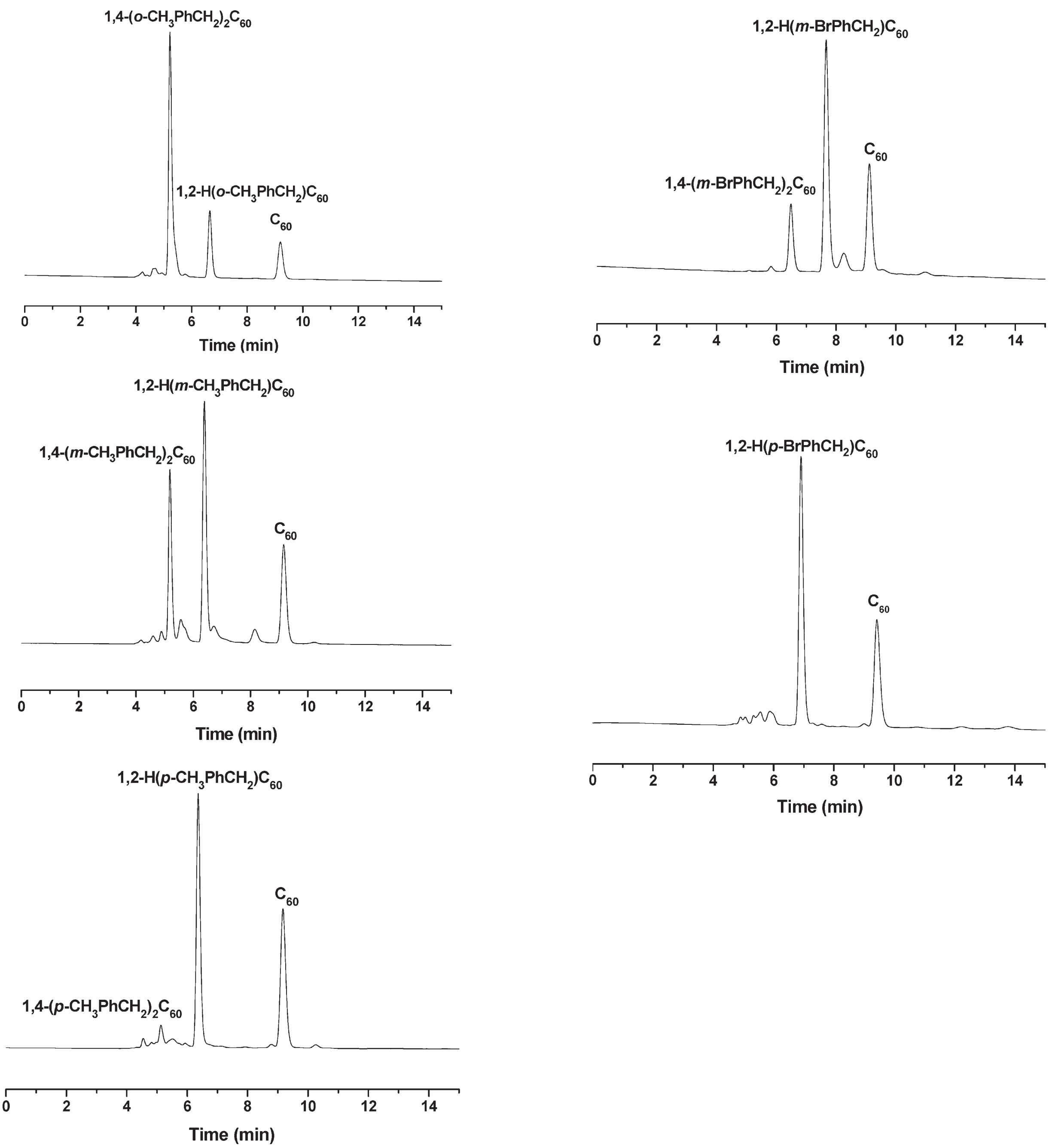

FIGURE 4. HPLC traces of the crude reaction products containing 1,2-H(*o*-CH_3PhCH_2)C_{60}, 1,2-H(*m*-CH_3PhCH_2)C_{60}, 1,2-H(*p*-CH_3PhCH_2)C_{60}, 1,2-H(*m*-$BrPhCH_2$)C_{60}, and 1,2-H(*p*-$BrPhCH_2$)C_{60} eluted by toluene over a semipreparative Buckyprep column at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm.

protons of $ArCH_2Br$ used for the reaction.[4i] Therefore, $PhCD_2Br$ was used to examine if 1,2-dihydrofullerene with deuterated fullerenyl proton would be formed. ^1H NMR (see the Supporting Information) of the obtained 1,2-dihydrofullerene shows that the singlet corresponding to the methylene protons (δ 4.77 ppm) is missing, consistent with the use of $PhCD_2Br$ for reaction. However, the integration ratio of fullerenyl proton (δ 6.65 ppm) to phenyl protons (δ 7.84, 7.56, and 7.47 ppm) is found to be exactly 1:5, indicating that the fullerenyl proton is not from the methylene protons of $ArCH_2Br$.

One of the other possible sources for the fullerenyl hydrogen is DMF, the solvent medium of this reaction, since recent work has shown that the fullerenyl proton can come from the carbonyl hydrogen of aldehydes.[13] Consequently, DMF-d_7 was used as the reaction medium to examine if it is the source of fullerenyl proton. The ^1H NMR of the isolated 1,2-dihydrofullerene (see the Supporting Information) from the reaction shows typical resonances for the compound, with singlets at 4.77 and 6.65 ppm corresponding to the methylene and fullerenyl protons, respectively, and resonances at 7.84, 7.56, and 7.47 ppm due to the phenyl protons. More importantly, the integration ratio of the fullerenyl proton to the methylene protons is 1:2, indicating no deuterium is attached directly to the C_{60} sphere, implying that the

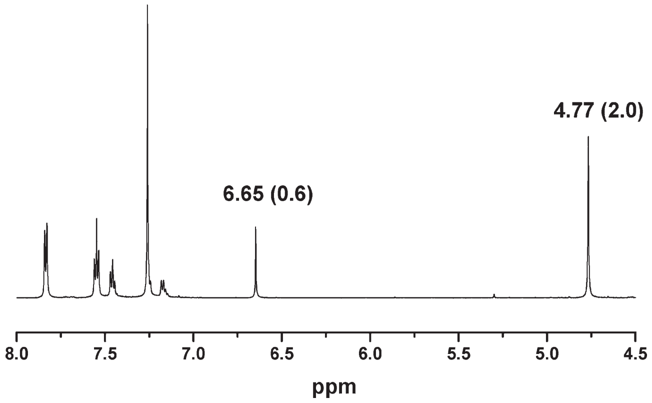

FIGURE 5. ^1H NMR spectrum of 1,2-dihydro[60]fullerene compound obtained from the reaction of C_{60}^{2-} with $PhCH_2Br$ in a DMF solution into which 30 μL of D_2O was added. The spectrum was recorded on a 600 MHz instrument in $CDCl_3$. The number in the parentheses refers to the integration area.

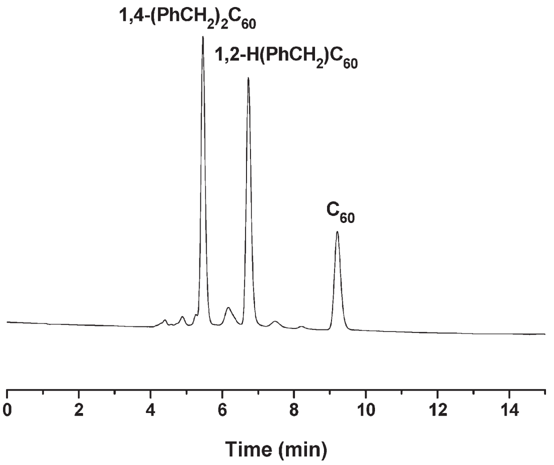

FIGURE 6. HPLC trace of the crude product obtained from the reaction of C_{60}^{2-} with $PhCH_2Br$ in PhCN into which 100 μL of water was added. The mixture was eluted by toluene over a semipreparative Buckyprep column at a flow rate of 4.0 mL/min with the detector wavelength set at 380 nm.

carbonyl hydrogen of DMF is not the source of the fullerenyl proton, and DMF is not involved in the reaction.

Another possible source of the fullerenyl proton is the water residue in DMF. It has been shown that the water residue is extremely difficult to be completely removed from the organic solvent even after strict drying treatment.[14] Under our experimental conditions, the amount of water residue is about 180 ppm in the freshly distilled DMF, as determined using the Karl Fischer titration method; it is therefore of interest to examine the reaction with the addition of a small amount of D_2O.

Figure 5 shows the ^1H NMR spectrum of the isolated 1,2-dihydrofullerene obtained from a DMF solution into which 30 μL of D_2O was added. The most notable feature is the intensity decrease of the $H{-}C_{60}$ resonance at 6.65 ppm, the integration ratio of this proton to the methylene protons at 4.77 ppm is only 0.6:2.0, significantly less than the expected 1:2 value, indicating that some of the fullerenyl hydrogen atoms have been replaced by deuterium atoms, demonstrating unambiguously that the fullerenyl hydrogen atoms are from the water residue in DMF. The result also suggests that H/D exchange between the benzyl group and D_2O is unlikely to occur during the reaction, since the integration ratio of the methylene protons to the phenyl hydrogen atoms remains exactly 2:5.

Reaction in Benzonitrile Containing a Large Amount of Water. Similar to DMF, there is also water residue in freshly distilled PhCN under our experimental conditions. The amount of water residue is measured to be about 90 ppm, corresponding to about 4.5 μL of H_2O in 50 mL of PhCN used as the reaction solvent medium, which is about three times more than the theoretical amount of water (1.25 μL) needed for reaction with 50 mg of C_{60}. However, no significant formation of 1,2-H($PhCH_2$)C_{60} has been observed when the reaction is carried out in PhCN solution as shown previously.[4k] To gain a better understanding on the reactivity of water residue in PhCN, 100 μL of water was added into 50 mL of PhCN before electrolysis, which makes the water content about 2100 ppm including the 90 ppm water residue. Small water droplets can be seen in this PhCN solution due to the very low solubility of water. After addition of benzyl bromide (molar ratio: $PhCH_2Br/C_{60}$ = 10:1) to this C_{60}^{2-} solution, a significant increase in the formation of 1,2-H($PhCH_2$)C_{60} is observed in the HPLC (Figure 6), confirming that water molecules are involved in the reaction of C_{60}^{2-} with organic halides. However, different from the case where DMF is used, the 1,4-($PhCH_2$)$_2C_{60}$ is still formed as the major product, even though the amount of water in PhCN is much more than that in DMF, suggesting that the water residue in PhCN is less reactive than that in DMF.

Solvent Effect of DMF and PhCN on the Reactivity of H_2O toward RC_{60}^-. To further explore the reaction of C_{60}^{2-} with organic halides involving H_2O, the reaction was carried out in freshly distilled PhCN by first adding 10-fold benzyl bromide into the C_{60}^{2-} solution, followed by addition of 250 μL of H_2O after about 2−4 min reaction time between C_{60}^{2-} and benzyl bromide. The solution turned from the deep red of C_{60}^{2-} to dark-green, which is the typical color of RC_{60}^- intermediate.[4h,j,5a,19] The reaction was allowed to proceed under stirring for about 3 h. Visible and near-IR spectroscopy was used to follow the reaction, and the results are shown in Figure 7. The dianionic C_{60} displays a strong absorption band at 954 nm, consistent with results recorded in literature.[14] The intensity of the band decreases rapidly after adding benzyl bromide to the C_{60}^{2-} solution, and this is accompanied by the increase of a new absorption band at 660 nm, which has been assigned to the absorption of RC_{60}^-,[5b] indicating that $PhCH_2C_{60}^-$ has formed after the addition of benzyl bromide into the C_{60}^{2-} solution. In the mean time, the absorption band due to $C_{60}^{-\bullet}$ at 1078 nm also increases, indicating that $C_{60}^{-\bullet}$ has also formed during the reaction. The observations are consistent with the previous proposed reaction mechanism, which shows that reaction is initiated by the electron transfer between C_{60}^{2-} and RX to form $C_{60}^{-\bullet}$ and $R^\bullet$, followed by the formation of RC_{60}^- via radical coupling.[5] Deaerated water was then added into the system, and no apparent change is observed in the visible−near-IR spectrum, suggesting that protonation of RC_{60}^- is a rather slow process. After about 2.5 h, the absorptions corresponding to anionic C_{60} species disappear completely, along with the appearance of new absorption bands in the range from 420 to 480 nm due to the formed organofullerenes, suggesting that

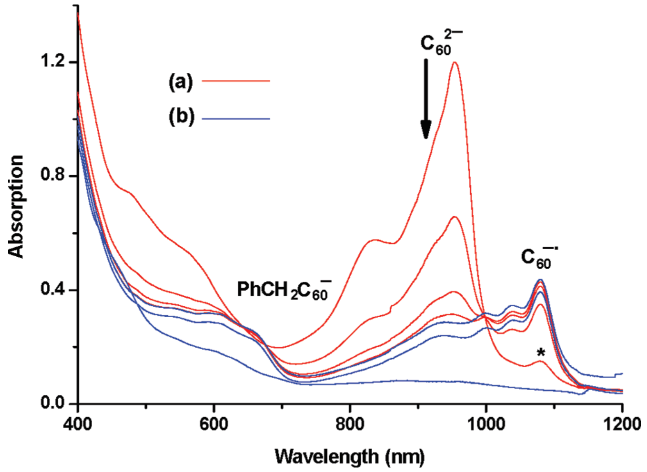

FIGURE 7. In situ electronic absorption spectra observed for the reaction of C_{60}^{2-} (1.0×10^{-4} M) with the addition of (a) $PhCH_2Br$ (1.0×10^{-3} M) (about 90 s interval) and (b) H_2O (2.0×10^{-2} M) (top to bottom, t = 1, 30, 150 min) in PhCN. The small peak at 1080 nm labeled with an asterisk in the initial C_{60}^{2-} spectrum is likely due to a slight amount of $C_{60}^{-\bullet}$ produced during the handling of C_{60}^{2-}.

reaction of C_{60}^{2-} with $PhCH_2Br$ and H_2O is finished. The results demonstrate explicitly that the proton transfer from H_2O to C_{60} core takes place after the formation of RC_{60}^-.

The HPLC of the crude product (see the Supporting Information) shows the formation of both 1,4-$(PhCH_2)_2C_{60}$ and 1,2-$H(PhCH_2)C_{60}$ as major products, similar to the result when the reaction was carried out in PhCN containing an excessive amount of water before electrolysis. The results are consistent with the mechanism hypothesis proposed by Orfanopoulos and co-workers regarding the involvement of RC_{60}^- during the acyl radical reactions; however, different from their work, where the carbonyl proton of aldehydes is shown to be the major source of fullerenyl hydrogen,[13] the current work demonstrates that the fullerenyl hydrogen is exclusively from water.

On the basis of the results of reactions of $ArCH_2Br$ (Ar = Ph, $C_6H_4CH_3$, C_6H_4Br) with C_{60}^{2-} in DMF and benzonitrile, a better understanding of the solvent effect can be inferred. First, the rate difference in DMF and PhCN for the S_N2 reaction of RC_{60}^- with RX, which leads to the formation of 1,4-R_2C_{60}, has to be considered. Both DMF and PhCN are aprotic solvents, with DMF being more polar than PhCN. It is therefore expected that the S_N2 reaction rate involving carbanions is faster in DMF than that in benzonitrile since the cations are better solvated by DMF and the nucleophiles are freed,[29] consistent with the reported DMF-enhanced nucleophilic addition of Grignard reagents to C_{60}.[41] Consequently, more 1,4-R_2C_{60} is expected to form when the reaction is carried out in DMF. In contrast, 1,2-HRC_{60} is obtained as the major product when the reaction is carried out in DMF as long as R is less hindered, and 1,4-R_2C_{60} is obtained as the major product in DMF only when the most unfavorable S_N2 substrate of a bulky ortho-substituted benzyl bromide is used, indicating that the S_N2 reaction rate difference is unlikely to be the real cause for the reactivity difference of water residue toward RC_{60}^- in DMF and PhCN. Since it has been shown that traces of water residue may form hydrogen bonding with carbanions to affect their reactivities in different solvents,[22] the observed steric effect indicates that the availability of the C2 of RC_{60}^- to water molecules is crucial in forming 1,2-HRC_{60}, suggesting that the solvent effect of DMF and PhCN is likely related to the availability of water residue to the RC_{60}^- intermediates.

Both DMF and PhCN have large solubility for anionic C_{60} species, including the reaction intermediates of RC_{60}^-, suggesting that the formed RC_{60}^- can be well solvated by the solvent molecules.[30] The RC_{60}^- intermediates can undergo either protonation by water to form 1,2-HRC_{60}, or an S_N2 reaction with benzyl bromide to form di(organo)[60]fullerenes. In the case of DMF, since water residue is miscible with the solvent,[23] it can be present in the DMF solvation shell in a significant amount, and form hydrogen bonding with $PhCH_2C_{60}^-$ in a manner similar to that of other carbanions.[22] The formation of such a hydrogen bonding may facilitate the subsequent proton transfer from water molecule to C_{60} sphere, and decrease the nucleophilicity of $PhCH_2C_{60}^-$ for further S_N2 reaction with $PhCH_2Br$, resulting in 1,2-$H(PhCH_2)C_{60}$ as the major product. In contrast, the water molecules are very ineffective in entering into the PhCN solvation shell since they are immiscible with PhCN,[31] making it difficult for H_2O to approach $PhCH_2C_{60}^-$, resulting in the formation of 1,4-$(PhCH_2)_2C_{60}$ as the major product via the S_N2 pathway instead. The increase of the amount of water in PhCN can help more water molecules to enter into the PhCN solvation shell, leading to the formation of more 1,2-HRC_{60}. However, the water molecules are still not effective in approaching RC_{60}^- due to the immiscibility of water with PhCN. The reaction mechanism showing the different reactivity of C_{60}^{2-} in DMF and PhCN is therefore proposed based on the above discussions and previous study,[5] and is illustrated in Scheme 1.

Notably, previous work has shown that no water residue is involved in the reaction of C_{60}^{2-} with organic halides when the reaction is carried out in CH_3CN, where the major products are only the di(organo)[60]fullerenes[4f,i,j] although CH_3CN is miscible with H_2O.[32] Such a discrepancy between the results obtained in DMF and CH_3CN is likely due to the involvement of anionic C_{60} species with lower oxidation states such as C_{60}^{3-}, when the reaction was carried out in CH_3CN. Previous work has indicated that the solubility of C_{60}^{2-} in CH_3CN is very low.[18,20] The low solubility of C_{60}^{2-} in CH_3CN is also confirmed by controlled-potential bulk electrolysis.[33] In addition, the reported utilization of C_{60}^{2-} in CH_3CN for fullerene functionalization was carried out by chemical reducing methods,[4f,i,j] which is less selective in

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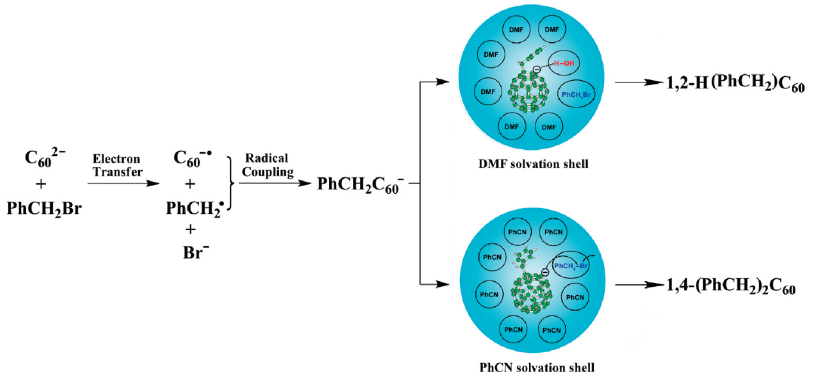
(33) Controlled-potential bulk electrolysis was performed to examine the solubility of C_{60}^{2-} in CH_3CN. In 50 mL of CH_3CN containing 0.1 M TBAP, 40 mg of C_{60} was added. The reducing potential was set at −1.00 V vs SCE, which is about 170 mV more negative than the $E_{1/2}$ of the C_{60}^-/C_{60}^{2-} redox couple in CH_3CN. After the theoretical number of coulombs required for a complete conversion of C_{60} to C_{60}^{2-} had been reached, there were still large amounts of insoluble species in the solvent, and no clear solution could be obtained, indicating that the dianionic C_{60} is either insoluble or only very slightly soluble in CH_3CN.

SCHEME 1. **Proposed Reaction Mechanism of $C_{60}{}^{2-}$ with $PhCH_2Br$ Involving Water Residue in DMF and PhCN**



generating anionic C_{60} with specific oxidation state than the potential-controlled bulk electrolysis. It is therefore likely that anionic C_{60} species with lower oxidation state such as $C_{60}{}^{3-}$ is involved in the reported reaction carried out in CH_3CN, thus resulting in stronger nucleophilicity of the subsequently formed anionic intermediate ($RC_{60}{}^{2-}$), which may favor the S_N2 reaction with organic halides rather than protonation by H_2O.

Conclusion

The well-studied reactions of $C_{60}{}^{2-}$ with organic halides have been revisited in DMF. It shows that traces of water residue in DMF are involved in the reaction of $C_{60}{}^{2-}$, leading to the formation of 1,2-dihydro[60]fullerenes via the proton transfer from H_2O to the intermediate of $RC_{60}{}^-$. The reactivity difference of the water content in DMF and PhCN is ascribed to the miscibility of the solvent with water. This is the first time that water has been shown to be able to participate in the reaction of $C_{60}{}^{2-}$. The result not only provides a new method in the preparation of 1,2-dihydro[60]fullerenes, which have been shown to be important precursors for further generation of a various of organofullerenes,[41] but may also provide clues toward a better understanding of the proton transfer mechanism from water to the reduced species for the reducing reactions mediated by $C_{60}{}^{2-}$, since the fullerenyl proton can be easily removed from C_{60} core as shown in the literature.[4h,j,l,8b]

Experimental Section

General Methods. C_{60} (99.5%) was purchased and used without further purification. Electrochemical grade tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from absolute ethanol and dried in a vacuum at 298 K prior to use. PhCN was distilled over P_2O_5 under vacuum at 305 K prior to use. DMF was distilled over P_2O_5 under vacuum at 300 K prior to use. $C_6H_5CH_2Br$ (98%), *o*-$CH_3C_6H_4CH_2Br$ (98%), *m*-$CH_3C_6H_4CH_2Br$ (96%), *p*-$CH_3C_6H_4CH_2Br$ (97%), *m*-$BrC_6H_4CH_2Br$ (99%), *p*-$CH_3C_6H_4CH_2Br$ (98%), benzyl bromide-α,α-d_2 (98 atom % D), and other chemicals were commercially obtained and used as received. Controlled-potential bulk electrolyses were carried out with a potentiostat/galvanostat. Typically, 50 mg (69.4 μmol) of C_{60} was electrolyzed at −1.10 V versus SCE in 50 mL of freshly distilled DMF or PhCN solution containing 0.1 M TBAP under an argon atmosphere. The potentiostat was switched off after the electrogeneration of $C_{60}{}^{2-}$ was complete, and a 10-fold excess of $ArCH_2Br$ (Ar = Ph, $C_6H_4CH_3$, C_6H_4Br) was added to the solution under inert atmosphere. The reaction was allowed to proceed for about 3 h with stirring. The mixture was dried with a rotary evaporator under reduced pressure, and the residue was washed with methanol to remove TBAP and excessive $ArCH_2Br$. The obtained crude mixture was put into toluene and sonicated for 10 min, and the soluble part was further purified by HPLC over a semipreparative Buckyprep column with toluene as the eluent. NMR spectra were measured with a 600 MHz instrument, using $CDCl_3$ as solvent. Mass spectrometry experiments were performed on a FT-ICR MS equipped with a 7.0 T actively shielded superconducting magnet. The quantity of water residue in the solvent is determined by using the Karl Fischer titration method.

Spectral Characterization of 1,2-H$(PhCH_2)C_{60}$. Negative ESI FT-ICR MS: $C_{67}H_8$, *m*/*z* $[M - H]^-$ calcd 811.0553, found 811.0543; ^1H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 4.77 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.4 (2C), 153.9 (2C), 147.5 (1C), 147.3 (1C), 147.0 (2C), 146.5 (2C), 146.4 (2C), 146.4 (2C), 146.3 (2C), 146.2 (2C), 145.9 (2C), 145.5 (2C), 145.4 (6C), 144.8 (2C), 144.6 (2C), 143.3 (2C), 142.6 (2C), 142.3 (4C), 142.1 (2C), 142.0 (2C), 142.0 (2C), 141.7 (2C), 141.6 (2C), 140.2 (2C), 140.0 (2C), 136.4 (2C), 136.1 (2C), 135.9 (1C, Ph), 131.3 (2C, Ph), 128.7 (2C, Ph), 127.7 (1C, Ph), 66.0 (1C, sp^3, C−CH_2), 59.1 (1C, sp^3, C−H), 53.1(1C, sp^3, CH_2); UV−vis (hexane) λ_{max}/nm 254, 304, 324, and 431.

Spectral Characterization of 1,2-H(*o*-$CH_3PhCH_2)C_{60}$. Negative ESI FT-ICR MS: $C_{68}H_{10}$, *m*/*z* $[M - H]^-$ calcd 825.0710, found 825.0730; ^1H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.1 Hz, 1H), 7.30 (m, 3H), 6.63 (s, 1H), 4.85 (s, 2H), 2.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.3 (2C), 153.9 (2C), 147.5 (1C), 147.3 (1C), 147.0 (2C), 146.6 (2C), 146.5 (2C), 146.4 (2C), 146.3 (2C), 146.2 (2C), 145.9 (2C), 145.5 (2C), 145.5 (2C), 145.4 (4C), 144.7 (2C), 144.6 (2C), 143.3 (2C), 142.6 (2C), 142.6 (2C), 142.2 (2C), 142.1 (2C), 142.0 (2C), 141.9 (2C), 141.7 (2C), 141.6 (2C), 140.3 (2C), 139.7 (2C), 137.6 (2C), 136.4 (2C), 135.7 (1C, Ph), 134.2 (1C, Ph), 132.3 (1C, Ph), 131.2 (1C, Ph), 127.8 (1C, Ph), 126.1 (1C, Ph), 66.4 (1C, sp^3, C−CH_2), 60.4 (1C, sp^3, C−H), 49.8(1C, sp^3, CH_2), 21.0 (1C, sp^3, CH_3); UV−vis (hexane) λ_{max}/nm 254, 306, 324, and 431.

Spectral Characterization of 1,2-H(*m*-$CH_3PhCH_2)C_{60}$. Negative ESI FT-ICR MS: $C_{68}H_{10}$, *m*/*z* $[M - H]^-$ calcd 825.0710, found 825.0718; ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.43 (partially overlapped with the solvent, 1H), 6.65 (s, 1H), 4.72 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.6 (2C), 154.0 (2C), 147.5 (1C), 147.4 (1C), 147.1 (2C), 146.5 (2C), 146.4 (2C), 146.4 (2C), 146.3 (2C), 146.2 (2C), 145.9 (2C), 145.5 (2C), 145.4 (6C), 144.7 (2C), 144.6 (2C), 143.3 (2C), 142.6 (4C), 142.3 (2C), 142.1 (2C), 142.0 (2C), 142.0 (2C), 141.7 (2C), 141.6 (2C), 140.2 (2C), 140.0 (2C), 138.4 (1C, Ph), 136.4 (2C), 136.0 (2C), 135.8 (1C, Ph), 132.3 (1C, Ph),128.7 (1C, Ph), 128.6 (1C, Ph), 128.5 (1C, Ph), 65.9 (1C, sp^3, C−CH_2), 59.0 (1C, sp^3, C−H), 52.9 (1C, sp^3, CH$_2$), 21.7 (1C, sp^3, CH$_3$); UV−vis (hexane) λ_{max}/nm 254, 305, 324, and 431.

Spectral Characterization of 1,2-H(*p*-CH$_3$PhCH$_2$)C$_{60}$. Negative ESI FT-ICR MS: $C_{68}H_{10}$, *m*/*z* [M − H]$^-$ calcd 825.0710, found 825.0710; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.73 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 6.64 (s, 1H), 4.72 (s, 2H), 2.45 (s, 1H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 155.6 (2C), 154.0 (2C), 147.5 (1C), 147.4 (1C), 147.1 (2C), 146.4 (3C), 146.4 (2C), 146.3 (2C), 146.2 (2C), 145.9 (2C), 145.5 (2C), 145.4 (6C), 144.7 (2C), 144.6 (2C), 143.3 (2C), 142.6 (3C), 142.3 (2C), 142.1 (2C), 142.0 (2C), 142.0 (2C), 141.7 (2C), 141.6 (2C), 140.2 (2C), 140.0 (2C), 137.4 (1C, Ph), 136.4 (2C), 136.1 (2C), 132.8 (1C, Ph), 131.3 (2C, Ph), 129.5 (2C, Ph), 66.1 (1C, sp^3, C−CH$_2$), 59.0 (1C, sp^3, C−H), 52.6 (1C, sp^3, CH$_2$), 21.3 (1C, sp^3, CH$_3$); UV−vis (hexane) λ_{max}/nm 253, 305, 323, and 431.

Spectral Characterization of 1,2-H(*m*-BrPhCH$_2$)C$_{60}$. Negative ESI FT-ICR MS: $C_{67}H_7Br$, *m*/*z* [M − H]$^-$ calcd 888.9658, found 888.9646; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.98 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 6.58 (s, 1H), 4.72 (s, 2H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 154.8 (2C), 153.6 (2C), 147.6 (1C), 147.4 (1C), 146.9 (2C), 146.5 (2C), 146.5 (2C), 146.3 (2C), 146.25 (2C), 146.18 (2C), 145.8 (2C), 145.6 (2C), 145.5 (6C), 144.8 (2C), 144.6 (2C), 143.3 (2C), 142.6 (4C), 142.2 (2C), 142.1 (2C), 142.0 (2C), 141.9 (2C), 141.7 (2C), 141.6 (2C), 140.3 (2C), 140.0 (2C), 138.2 (1C, Ph), 136.3 (2C), 136.1 (2C), 134.3 (1C, Ph), 131.0 (1C, Ph), 130.3 (1C, Ph), 130.0 (1C, Ph), 122.8 (1C, Ph), 65.6 (1C, sp^3, C−CH$_2$), 59.1 (1C, sp^3, C−H), 52.4 (1C, sp^3, CH$_2$); UV−vis (hexane) λ_{max}/nm 253, 306, 324, and 431.

Spectral Characterization of 1,2-H(*p*-BrPhCH$_2$)C$_{60}$. Negative ESI FT-ICR MS: $C_{67}H_7Br$, *m*/*z* [M − H]$^-$ calcd 888.9658, found 888.9661; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.69 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 6.56 (s, 1H), 4.72 (s, 2H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 154.8 (2C), 153.6 (2C), 147.5 (1C), 147.4 (1C), 147.0 (2C), 146.5 (2C), 146.5 (2C), 146.3 (2C), 146.2 (4C), 145.8 (2C), 145.6 (2C), 145.5 (6C), 144.8 (2C), 144.6 (2C), 143.3 (2C), 142.6 (4C), 142.2 (2C), 142.1 (2C), 142.0 (2C), 141.9 (2C), 141.7 (2C), 141.6 (2C), 140.3 (2C), 140.0 (2C), 136.3 (2C), 136.1 (2C), 134.9 (1C, Ph), 133.1 (2C, Ph), 131.9 (2C, Ph), 122.0 (1C, Ph), 65.7 (1C, sp^3, C−CH$_2$), 59.2 (1C, sp^3, C−H), 52.4 (1C, sp^3, CH$_2$); UV−vis (hexane) λ_{max}/nm 253, 307, 321, and 431.

X-ray Crystallographic Data Collection and Structure Refinement. Black lamellar crystals of 1,2-H(PhCH$_2$)C$_{60}$ suitable for an X-ray analysis were obtained by slow evaporation of a hexane solution, which was achieved by first dissolving the compound in neat CS$_2$, and then eluted over a silica gel column with *n*-hexane as the eluent. Single-crystal X-ray diffraction data were collected on an instrument equipped with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) in the scan range 1.44° < θ < 25.14°. The structure was solved with direct methods using SHELXS-97 and refined with full-matrix least-squares techniques using the SHELXL-97 program within WINGX. Non-hydrogen atoms were refined anisotropically. Crystal data of 1,2-H(PhCH$_2$)C$_{60}$: $C_{67}H_8$, M_w = 812.73, dark brown, monoclinic, space group = $P2_1/c$, a = 16.9920(18) Å, b = 10.2389(11) Å, c = 24.0163(18) Å, β = 123.714(5)°, and V = 3475.62 Å^3, z = 4, D_{calcd} = 1.553 Mg m^{-3}, μ = 0.089 mm^{-1}, T = 296(2) K, crystal size 0.216 × 0.121 × 0.102 mm^3; reflections collected 20452, independent reflections 6199; 3419 with $I > 2\sigma(I)$; R_1 = 0.0750 [$I > 2\sigma(I)$], wR_2 = 0.1966 [$I > 2\sigma(I)$]; R_1 = 0.1294 (all data), wR_2 = 0.2199 (all data), GOF (on F^2) = 1.043.

Acknowledgment. We are grateful to Mr. Yi-jie Wu of National Research and Analytical Center of Electrochemistry and Spectroscopy, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, for NMR measurement. The work was supported by the National Natural Science Foundation of China (Grant No. 20972150), Solar Energy Initiative of the Chinese Academy of Sciences, and the State Key Laboratory of Electroanalytical Chemistry of China.

Supporting Information Available: X-ray crystallographic files of 1,2-H(PhCH$_2$)C$_{60}$ (CIF), ^{1}H and ^{13}C NMR spectra, MS spectra of all compounds, HMQC NMR spectrum, and cyclic voltammogram of 1,2-H(PhCH$_2$)C$_{60}$. This material is available free of charge via the Internet at http://pubs.acs.org.