^{3}He NMR of He@C$_{60}$$^{6-}$ and He@C$_{70}$$^{6-}$. New Records for the Most Shielded and the Most Deshielded ^{3}He Inside a Fullerene[1]

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Abstract: The reduction of ^{3}He@C$_{60}$ and ^{3}He@C$_{70}$ by lithium metal to give solutions of the corresponding hexaanions in THF-*d*$_8$ has been achieved under gentle conditions, at subambient temperatures, without sonication, by capitalizing on the ability of corannulene (**1**) to serve as an efficient electron carrier between the lithium metal and the solid fullerenes, which are virtually insoluble in the reaction medium. The ^{3}He inside the C$_{60}$ hexaanion is found to be more strongly shielded (by nearly 20 ppm!) than any previously reported ^{3}He in a fullerene [δ(^{3}He@C$_{60}$$^{6-}$) = −48.7 ppm, relative to dissolved ^{3}He gas in the solution], whereas the ^{3}He inside the C$_{70}$ hexaanion is actually *deshielded* [δ(^{3}He@C$_{70}$$^{6-}$) = +8.3 ppm], resonating at nearly 15 ppm lower field than any previously reported ^{3}He in a fullerene. These results stand in complete accord with earlier predictions that the magnetic properties of C$_{60}$ and C$_{70}$ would be altered dramatically, and in opposite directions, by reduction of the fullerenes to their hexaanions. The phenomenal ability of C$_{60}$$^{6-}$ to shield an endohedral ^{3}He from a powerful external magnetic field provides the most compelling evidence to date for the ability of electrons to move freely about the surface of a spheroidal π-system.

Electron Delocalization and the Aromaticity of Fullerenes

Delocalized π-electrons represent a defining feature of aromatic organic molecules. Their presence is often associated with unusual thermodynamic and kinetic stability and can result in distinctive reactivity, such as a bias toward substitution rather than addition reactions. Characteristic magnetic properties are also commonly associated with the response of the delocalized π-electrons to an applied magnetic field.[2] A unified theory of aromatic character encompassing all of these properties has been developed for the monocyclic annulenes, wherein "aromaticity" correlates with the circulation of ($4N + 2$) π-electrons, and "antiaromaticity" correlates with the circulation of ($4N$) π-electrons.[3] For polycyclic π-systems, however, no such correlation exists between aromatic character and the total number of π-electrons. The latter circumstance is exemplified by the fullerenes, which are not only polycyclic but three-dimensional as well. Considerable ambiguity has arisen concerning the aromatic character of fullerenes because their chemical and physical properties transcend many of the traditional concepts of aromatic character.[4] There is evidence for delocalized π-electrons, but the fullerenes are incapable of undergoing substitution reactions, since they have no hydrogens to replace. In sharp contrast to traditional polycyclic aromatic hydrocarbons, fullerenes exhibit a rich chemistry resulting from their susceptibility to a variety of addition reactions. It is now clear, however, that the resonance energy of fullerenes is little reduced from that of graphite and that the aberrant chemistry of the fullerenes stems from the tremendous strain inherent in the spheroidal structure.[4] The subtle interplay of these features—a three-dimensional geometry of conjugated π-orbitals without boundaries, significant strain, and "nonaromatic" reactivity—defies the usual classifications of aromatic character.

The important question to be answered concerns the degree to which the π-electrons are free to move about the surface of the sphere. For most compounds the question of π-electron delocalization is addressed through magnetic measurements. This problem is considerably complicated in the fullerenes, however, by the theoretical finding that the ring currents are usually paramagnetic in the five-membered rings (5-MRs) and diamagnetic in the 6-MRs,[5,6] the cancellation of which obscures the observation of ring current effects in measurements of the magnetic susceptibility or the chemical shift of an endohedral atom, such as a ^{3}He inside the fullerene. Some information can be obtained from observations on surface nuclei in derivatives,[7] but the subtle interplay of the 5- and 6-MRs in the complex topology of the fullerenes leads to a nonmonotonic dependence of fullerene magnetism on cluster size.[8] So far,

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C_{70} has produced the strongest evidence for ring currents in the fullerenes; measurements of the magnetic susceptibility[9,10] and the ^{3}He chemical shift in He@C_{70}[11] show magnetic effects that cannot be accounted for by localized contributions alone.[12]

Predicted Magnetic Properties for C_{60}^{6-} and C_{70}^{6-}

In keeping with the behavior of two-dimensional polycyclic π-systems,[13] the anions of the fullerenes are expected to have magnetic properties that are entirely distinct from those of their neutral counterparts.[14] At least for C_{60} and C_{70}, the hexaanions are calculated to show diamagnetic circulations in all of the rings, both the 6-MRs and the 5-MRs. In this reduced state, however, C_{60} is expected to show the largest magnetic effects.

The first calculation of the ring current chemical shift for an atom at the center of C_{60}^{6-} was made with the finite-field London theory, and a value $\delta_{RC}(@C_{60}^{6-}) = -35$ ppm was reported (parametrization A).[15] In this method the secondary magnetic field at the center of the C_{60} molecule is calculated, so the result is insensitive to the presence of a central atom. Taken together with the contribution of the localized electrons ($\delta_{local} = -5.5$ ppm),[12,16] the London calculation gives $\delta(@C_{60}^{6-}) \approx -40.5$ ppm, although some correction should be made for the charge in this calculation.

In the case of C_{60}, the ring current contribution to the endohedral chemical shift and the magnetic susceptibility are simply related, and the δ_{RC} value given above corresponds to a π-electron magnetic susceptibility that is 12.9 times that of benzene (field perpendicular to the molecular plane).[15] This value is in very good agreement with a recent measurement of the bulk magnetic susceptibility of Rb_6C_{60}.[17]

More recently ab initio calculations have been used to examine the magnetic properties of the fullerenes. While current methodologies overestimate the magnetic susceptibility of large delocalized molecules, they are able to satisfactorily reproduce the chemical shifts of neutral endohedral fullerenes, ^{3}He@C_n.[16,18] These calculations likewise indicate a large shielding for the hexaanion of C_{60}; Bühl et al.[16] predict $\delta(^3\text{He}@C_{60}^{6-}) = -58.3$ ppm, whereas Cioslowski[19] predicts $\delta(^3\text{He}@C_{60}^{6-}) = -56.1$ ppm.

Thus, the calculations all predict that C_{60}^{6-} will provide convincing evidence of delocalized π-electrons in the fullerenes. In fact, as may be seen from above, the six electrons added to the t_{1u} molecular orbital of C_{60} are calculated to confer a much larger diamagnetism than do the six π-electrons in benzene.

Are the ^{3}He chemical shifts in *any* He@C_n fullerenes or fullerides expected to exceed that of C_{60}^{6-}? From all the calculations on all the fullerenes and fullerides examined to date, the answer seems to be no.[8,18] Although the diamagnetism in icosahedral fullerenes increases with cluster size, and fullerenes up to C_{540} have been examined by a variety of theoretical methods, no closed shell species has been found that has a predicted endohedral shielding that is larger than that in C_{60}^{6-}, because the field at the center of the cage decreases rapidly with cluster size. Thus, an experimental determination of the ^{3}He chemical shift in He@C_{60}^{6-} is expected to provide the most convincing evidence for delocalized π-electrons, and hence aromatic character, in the fullerenes.

While the He atom in He@C_{60} is predicted to be strongly shielded on reduction to the hexaanion, theory predicts the opposite result in He@C_{70}. London calculations give a value of $\delta_{RC}(@C_{70}^{6-}) = -6.6$ ppm.[8] Taken together with the contribution of the localized electrons ($\delta_{local} = -5.5$ ppm), the London calculation gives $\delta(@C_{70}^{6-}) \approx -12$ ppm, although some correction should be made for the charge in this calculation. Ab initio calculations by Bühl give $\delta(^3\text{He}@C_{70}^{6-}) = -10.6$ ppm.[20] Both of these values are considerably *deshielded* relative to that of the neutral system: $\delta(^3\text{He}@C_{70}) = -28.8$ ppm.

Thus with C_{60} and C_{70} we have a situation where reduction to the hexaanions is predicted to lead to dramatic, but opposite, consequences for the magnetic environment of a central atom. Previous experimental work has shown the power of ^{3}He NMR to assess these effects,[11,21] so we set out to prepare the hexaanions and to measure their ^{3}He NMR spectra.

Results and Discussion

Clear evidence for electrochemical production of the C_{60} and C_{70} hexaanions can be seen in the cyclic voltammetry data of Echegoyen,[22] which show reversible six-electron reduction for each fullerene: $E_{1/2}(C_{60}) = -0.98, -1.37, -1.87, -2.35, -2.85$, and -3.26 V and $E_{1/2}(C_{70}) = -0.97, -1.34, -1.78, -2.21, -2.70$, and -3.07 V. The triply degenerate LUMO of C_{60} has a capacity for six extra electrons, and the doubly degenerate LUMO+1 of C_{70} lies close enough in energy to the nondegenerate LUMO that a hexaanion is accessible here as well.[23] Both C_{60} and C_{70} have also been reduced to hexaanions in the solid state by exposing them to vapors of various alkali metals,[24] and NMR spectra (^{13}C and ^{6}Li) have been reported by Olah et al. for the anions of C_{60} and C_{70} prepared in solution under strongly reducing conditions (excess lithium metal with sonication).[25] Previous attempts to prepare the hexaanion of He@C_{60} by this latter reduction method, unfortunately, failed to give any ^{3}He NMR signal.[26]

To solve this problem another way, we have taken advantage of a serendipitous discovery made in connection with completely unrelated experiments in our own lab.[27] Our finding that the bowl-shaped "fullerene fragment" corannulene (**1**) can be

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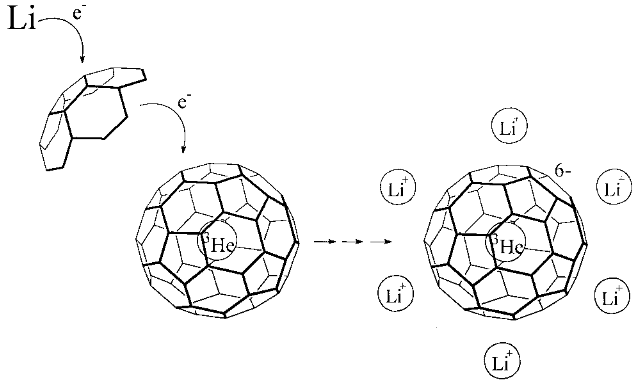
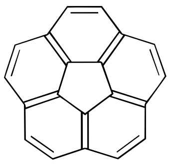


Figure 1. Corannulene-mediated reduction of ^{3}He@C_{60}.

reduced under mild conditions with excess lithium metal to give a tetraanion that exists as a robust lithium bound dimer (**2**)[28] prompted us to try generating lithium bound mixed aggregates between the corannulene tetraanion and the C_{60} hexaanion.



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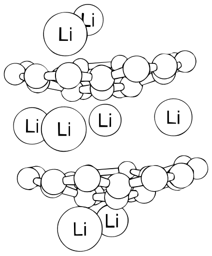

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Though unsuccessful (so far) in achieving that original objective, we did observe that the reduction of C_{60} to its hexaanion is dramatically accelerated by the presence of corannulene in the reaction medium and can thereby be achieved quite gently, at subambient temperatures, without sonication. Presumably, corannulene is capable of serving as an efficient electron carrier that shuttles back and forth between the lithium metal and the solid C_{60} (Figure 1), which is virtually insoluble in the reaction medium (THF-d_8). Thus, reduction of ^{3}He@C_{60} (ca. 0.1% occupancy) with excess lithium metal in THF-d_8 containing an equimolar quantity of corannulene gave beautiful NMR spectra of ^{3}He@C_{60}^{6-}. Repetition of the corannulene-mediated reduction starting with a mixture of ^{3}He@C_{60} and ^{3}He@C_{70} gave NMR spectra of both endohedral fullerene hexaanions together in the same solution (Figure 2).[29] As predicted, the ^{3}He inside the C_{60} hexaanion is more strongly *shielded* (by nearly 20 ppm!) than any previously reported ^{3}He in a fullerene [$\delta(^3\text{He@C}_{60}^{6-}) = -48.7$ ppm], and the ^{3}He inside the C_{70} hexaanion is more strongly *deshielded* (by nearly 15 ppm) than any previously reported ^{3}He in a fullerene [$\delta(^3\text{He@C}_{70}^{6-}) = +8.3$ ppm].

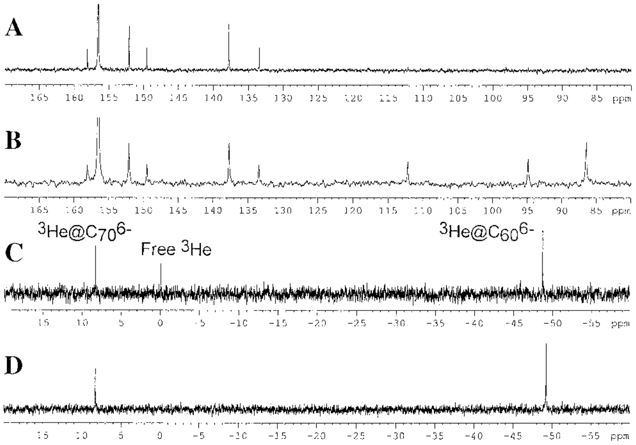

Figure 2. (a) ^{13}C NMR (100 MHz, THF-d_8) of a 1:1 mixture of ^{3}He@C_{60}^{6-} ($\delta = 156.7$ ppm) and ^{3}He@C_{70}^{6-} (the five other signals) in solution with the corannulene dianion ($\mathbf{1}^{2-}$); see text for details. (b) ^{13}C NMR (100 MHz, THF-d_8) of a 1:1 mixture of ^{3}He@C_{60}^{6-} and ^{3}He@C_{70}^{6-} in solution with the corannulene tetraanion dimer (**2**). (c) ^{3}He NMR (305 MHz, THF-d_8, 290 K) of a 1:1 mixture of ^{3}He@C_{60}^{6-} ($\delta = -48.7$ ppm) and ^{3}He@C_{70}^{6-} ($\delta = +8.3$ ppm) in solution with the corannulene tetraanion dimer (**2**). (d) Same as in part c but at 190 K.

The reductions were carried out in constricted NMR tubes, sealed with a piece of lithium wire in the upper chamber and predried THF-d_8 containing the fullerene(s), corannulene, and dissolved ^{3}He as an internal chemical shift reference in the lower part. The solution was then brought into contact with the lithium metal by repeatedly inverting the tube at low temperature (200 K), and the progress of the reduction was followed by ^{1}H and ^{13}C NMR spectroscopy. Since the solubility of the neutral fullerenes in THF is less than 10^{-6} mol/L, the initial ^{1}H and ^{13}C NMR spectra always show just the known peaks of corannulene (**1**).

In the first experiment, a sample comprising 5.0 mg each of ^{3}He@C_{60} and corannulene (molar ratio = ca. 1:3) was reduced with excess lithium metal at 200 K. After 48 h, the ^{1}H NMR spectrum showed only the familiar singlet at $\delta = 6.9$ ppm for the corannulene tetraanion dimer (**2**);[28] the ^{13}C NMR spectrum showed only the three known peaks for **2** plus the peak at $\delta = 156.7$ ppm previously reported for C_{60}^{6-};[25] and the ^{3}He NMR spectrum showed a single new peak at $\delta = -48.7$ ppm for ^{3}He@C_{60}^{6-}, relative to dissolved free ^{3}He (external standard).

In the second experiment, a 1:1 mixture of ^{3}He@C_{60} and ^{3}He@C_{70} (10.7 mg) was reduced in the presence of corannulene (3.6 mg, ca. 1.0 molar equiv) under the conditions described above. After the first color change (to green), the reduction process was temporarily interrupted by inversion of the NMR tube. A ^{1}H NMR spectrum recorded at this stage showed that the signal for corannulene (**1**) had disappeared and that no new signals had grown in. These observations are consistent with formation of the known, green corannulene radical anion, which has previously been identified by ESR spectroscopy and a similar disappearance of all ^{1}H NMR signals.[30] In the ^{13}C NMR spectrum recorded at this stage, on the other hand, peaks for the C_{60} and C_{70} hexaanions, although broad and weak, could already be seen growing in.

Resuming contact with the lithium metal led to a second color change (to purple-brown) and the appearance of clear ^{1}H NMR signals for the corannulene dianion ($\mathbf{1}^{2-}$). The ^{13}C NMR spectrum of the same solution was now highly resolved and showed all the peaks for C_{60}^{6-} and C_{70}^{6-} (Figure 2a); rapid equilibration of the corannulene dianion with residual corannulene radical anion (paramagnetic) presumably accounts for the absence of ^{13}C NMR signals for $\mathbf{1}^{2-}$.

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(29) Subsequent experiments demonstrated that naphthalene and anthracene can also serve as electron carriers to accelerate the reduction of C_{60} and C_{70} to their anions without sonication, although they both appear to function less efficiently than corannulene, i.e., the reductions mediated by these planar polycyclic aromatic hydrocarbons gave lower yields of the fullerene anions (weaker spectra) even after several days.

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Prolonged contact with the metal yielded first the dianion and ultimately the fully reduced corannulene tetraanion dimer (**2**), the known ^{13}C NMR signals for which could be seen to grow in, with no change detected in the ^{13}C NMR signals for the fullerene hexaanions (Figure 2b).

After reaching the stage that gave this strong, highly resolved ^{13}C NMR spectrum, a ^{3}He NMR spectrum was recorded. The peak at $\delta = -48.7$ ppm for $^{3}He@C_{60}^{6-}$ was again seen, accompanied this time by a new peak at $\delta = +8.3$ ppm for $^{3}He@C_{70}^{6-}$ (Figure 2c). Cooling the solution from room temperature to 190 K led to disappearance of the signal for free ^{3}He, as a result of its decreased solubility, but no change was observed in the NMR signal for either endohedral ^{3}He (Figure 2d).[31]

A ^{7}Li NMR spectrum recorded at this final stage of reduction showed two signals at 250 K: $\delta = -11.6$ ppm (sharp) and $+0.5$ ppm (broad). The former corresponds to the signal seen before for the strongly bound lithium cations sandwiched between the two corannulene tetraanion decks of **2** (contact ion pairs), whereas the latter represents the weighted average signal of all loosely bound lithium ions (solvent separated ion pairs), which appear at $\delta = -4.5$ ppm in **2** and at $\delta = +1.6$ ppm in the mixture of C_{60}^{6-} and C_{70}^{6-}. Warming the solution above room temperature leads to a broadening of both signals and finally to one broad signal at $\delta = -3.3$ ppm as a result of fast exchange among all lithium cations.

Attempts to evaluate possible variations in the NMR spectra of the fullerene hexaanions as a function of the counterions were thwarted by solubility problems. Reduction of C_{60} and C_{70} with sodium, potassium, rubidium, and cesium gives colored solutions that probably contain the anion radicals in the beginning, but further reduction leads to products that are too insoluble to be detected by NMR spectroscopy. Our extensive experience with the tetraanions of corannulene and its derivatives has shown the NMR chemical shifts of the corannulene nuclei to be relatively insensitive to variations in the alkali metal (Li, K, Rb, and Cs), and we would be surprised to see different behavior with the fullerene anions.

Conclusions

Figure 3 graphically summarizes the ^{3}He NMR chemical shift data for $^{3}He@C_{60}$, $^{3}He@C_{70}$, and the hexaanions derived therefrom. Prior to this work, all of the known endohedral ^{3}He in fullerenes were seen to be shielded by the fullerene; $^{3}He@C_{70}$ was the most strongly shielded, $^{3}He@C_{60}$ was the least strongly shielded, and all the higher $^{3}He@C_{n}$ fell in between.[21] Now, however, we have found that upon reduction to the corresponding hexaanion, C_{60} is transformed into the most strongly shielding fullerene known for an endohedral ^{3}He, and C_{70} is transformed into the most strongly *deshielding* fullerene known for an endohedral ^{3}He. The explicit prediction, prior to any knowledge of the experimental facts, that the magnetic properties of C_{60} and C_{70} would be altered so dramatically, and in opposite directions, by reduction to their hexaanions stands as a magnificent triumph for modern molecular orbital theory and should engender confidence in the future use of such theoretical methods. Most importantly, however, the phenomenal ability of C_{60}^{6-} to shield an endohedral ^{3}He from a powerful external magnetic field provides the most compelling evidence to date for the ability of electrons to move freely about the surface of a spheroidal π-system.

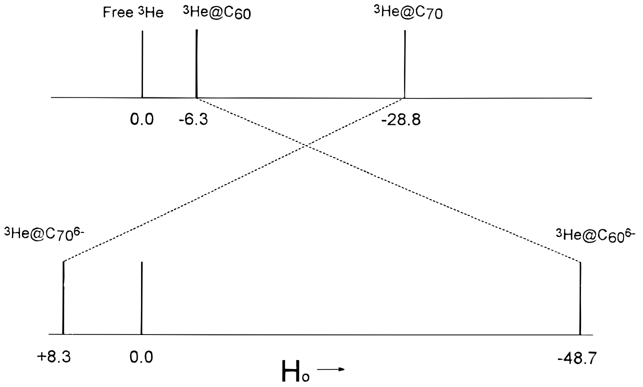

Figure 3. ^{3}He NMR chemical shifts of $^{3}He@C_{60}$ and $^{3}He@C_{70}$ (respectively the most deshielded and the most shielded previously known ^{3}He inside a fullerene) and the ^{3}He NMR chemical shifts of their respective hexaanions.

Experimental Section

Solvent Purification. [$^{2}H_{8}$]Tetrahydrofuran (THF-d_8) was placed in a flask equipped for a vacuum line and degassed several times before being transferred into a flask containing distilled Na−K 5:1 alloy. The solvent was then allowed to stand in contact with the alloy for several days. After a permanent blue color developed, the solvent was vacuum transferred into another flask containing distilled Na−K alloy.

Preparation of the Anions. Extended NMR tubes were prepared with a constriction to separate two chambers (upper and lower). Under an argon atmosphere, the fullerene(s) and corannulene were introduced into the lower chamber of the tube. A piece of lithium metal having dimensions too large to pass through the constriction in the tube was then introduced into the upper chamber, and the tube was attached to a vacuum line. Predistilled THF-d_8 was vacuum transferred into the tube and frozen in order to survive high vacuum. ^{3}He gas in a sealed tube (for a chemical shift reference) was released into the vacuum line and dissolved in the solution, and the tube was sealed. The solution was brought into contact with the lithium metal by repeatedly inverting the tube at low temperature (−78 °C), and the formation of the anions was detected by ^{1}H and ^{13}C NMR spectroscopy.

NMR Spectrometer Configuration for ^{3}He NMR Measurements. ^{1}H, ^{3}He, ^{7}Li, and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer. For ^{3}He NMR measurements, a broad band inverse probe from a 300 MHz spectrometer was used. ^{3}He resonates at 304.815 MHz relative to ^{1}H at 400.13 MHz. The ^{3}He channel (labeled X on the preamplifier) was attached to the "^{1}H" of the 300 MHz probe and the deuterium lock to the broad band of the probe, and the broad band was tuned to the spectrometer's deuterium frequency. It should be noted that the probe is not specified to tune to the ^{3}He frequency, and not all commercially supplied 300 MHz probes can be tuned. The usual 1D acquisition pulse sequence was modified to send the signal through the X channel and receive with the "fluorine" preamplifier. In our spectrometer, the "fluorine" preamplifier covers the range 200−400 MHz. The commands used were QNP_X and SWITO_F, which were inserted at the start of the pulse sequence.

^{3}He NMR Measurements. Longitudinal relaxation times (T_1) for endohedral ^{3}He in fullerenes vary little with temperature and chemical environment. We found T_1 to fall in the range between 300 and 500 s in all cases, using the DESPOT[32] method. Since no relaxation agent could be added into the sample, these exceptionally long longitudinal relaxation times exacerbated the sensitivity problem inherent in the ^{3}He

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[31] Although we are unable to ascertain directly the reduction states of the species that we observe, the assignment of the C_{60} species to the hexaanion seems secure, based on the orbital degeneracies of C_{60} and the fact that we are dealing with a diamagnetic species (^{13}C NMR spectrum). Furthermore, this assignment is strongly supported by the theoretical calculations. In the case of the reduction product of C_{70}, on the other hand, both calculations predict a paramagnetic shift, but of much smaller magnitude than is actually observed. Preliminary investigations show that the orbital separations in the vicinity of 6, 8, and 10 added electrons are quite small in the case of C_{70}, so we cannot dismiss the possibility that the carrier of the signal at $\delta = +8.3$ ppm corresponds to a C_{70} species that is even more highly reduced than the hexaanion.

NMR measurements. A repetition time of approximately T_1 and a pulse angle of 68° yielded the best signal-to-noise ratio.

NMR Chemical Shift Standards. Since alkali metals react with TMS, ^{1}H and ^{13}C chemical shifts were measured relative to the most downfield solvent peak, which had in turn been calibrated against TMS. In the temperature range 155−390 K, the chemical shift of H1 of THF-d_7 in THF-d_8 is $3.5749 + [(4.71 \times 10^{-5})T'] - [(5.1 \times 10^{-8})T'^2] + [(8.2 \times 10^{-10})T'^3)] - [(3.3 \times 10^{-12})T'^4]$ ppm. The chemical shift of C1 in THF-d_8 in the temperature range 155 to 340 K is $67.3937 + [(8.242 \times 10^{-4})T'] + [(6.6281 \times 10^{-6})T'^2] + [(1.65 \times 10^{-9})T'^3]$ ppm, where T' = temperature − 295 K.[33] ^{3}He chemical shifts were measured relative to dissolved ^{3}He gas. ^{7}Li chemical shifts were measured relative to 1 M LiCl in D_2O at 298 K. The temperature was determined by using a standard methanol NMR thermometer.[34]

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