of the apex BH unit (decapitation) in these species generates the respective open-faced complexes Cp*CoRR'$C_2B_3H_5$ (**6-8**) whose conversion to larger systems (e.g., multidecker sandwiches) is anticipated via deprotonation and reaction with transition-metal ions.[2-4]

This chemistry, in combination with the previously reported regiospecific B-functionalization of $LM(R_2C_2B_3H_5)$ complexes,[2c,d] allows the introduction of desired substituents at specific boron and/or carbon locations and thereby considerably augments the utility of such species in constructing large multimetal systems. Such derivatization at boron has already been exploited to create B-X-B linked oligomers and to electronically tailor the metal-complexing properties of the open C_2B_3 rim, e.g., in the recent synthesis[4] of tetradecker sandwiches via introduction of electron-withdrawing substituents at boron. In addition to the synthetic advantages, the electronic consequences of placing such groups at the cage carbon locations are clearly of interest and are among the numerous ramifications of these findings that we are currently exploring.

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First Easily Reproduced Solution-Phase Synthesis and Confirmation of Superconductivity in the Fullerene K_xC_{60} (T_c = 18.0 ± 0.1 K)

The number of novel molecular superconductors has risen markedly in recent years, especially in the case of the radical-*cation* ET-based organic materials[1] [ET is the abbreviation for BEDT-TTF, bis(ethylenedithio)tetrathiafulvalene]. The highest confirmed superconducting transition temperatures (T_c) for the organic materials occur for the salts κ-$(ET)_2Cu[N(CN)_2]X$, X = Br (T_c = 11.6 K)[2] and X = Cl (0.3 kbar, 12.8 K).[3] Very recent work has now established an even higher T_c for a molecular superconductor in the *anion*-based fullerene (buckminsterfullerene, C_{60}) system K_xC_{60}, with onset $T_c \approx 18$ K.[4] Because many higher fullerenes are known to exist,[5] this new system provides a fertile field for future research on novel superconducting materials. In this communication we report the first easily reproduced solution-phase synthesis of K_xC_{60} and the confirmation of T_c at 18.0 ± 0.1 K. It is especially noteworthy that we find that reduction of C_{60} in solution with *excess* K does not lead to a highly resistive material but rather to superconducting K_xC_{60}, in direct contrast to the K-vapor synthesis originally reported.[4]

Synthesis of C_{60}. Soot containing C_{60} was prepared in an apparatus described previously.[6] Our method is similar to the contact arc method reported by Haufler et al.[7] but uses a plasma instead of a contact arc to generate the soot. Current (80 A at 20 V) was passed through the graphite (National Carbon Co., spectroscopic grade) electrodes and ignited a plasma. The plasma was observed through a viewport, and the gap between the electrodes was continuously adjusted to attain maximum plasma brightness. Fine control of the gap distance resulted in a higher yield (up to 44%) of soluble material in the soot.[6] The soot was collected on a shim cooled by contact with a water-cooled shield. After each run, the shim was removed and the soot scraped from it and dissolved in toluene. Pure C_{60} was obtained from this mixture by chromatography on a neutral alumina column, as reported previously.[8] Laser desorption time-of-flight mass spectrometry[9] of the C_{60} starting material showed that only C_{60} was present. No C_{70} impurity was detected at a level above the detection limit of 0.2%.

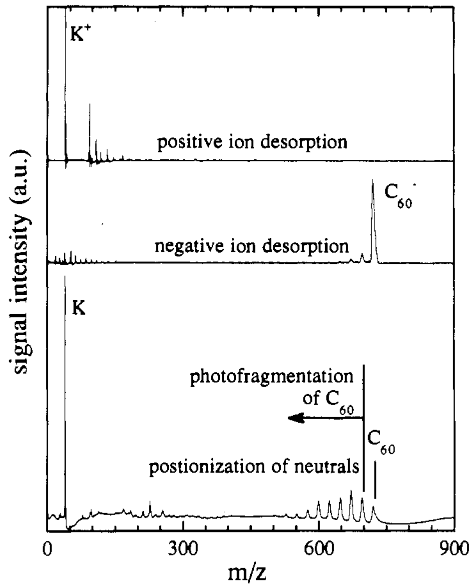

Figure 1. Laser-desorption TOF mass spectra of the K_xC_{60} sample from a stainless steel substrate with 50-ps 266-nm laser radiation. The top panel shows positive ion desorption, the center panel negative ion desorption, and the bottom panel postionization of desorbed neutrals with 308-nm 10-ns laser radiation.

Synthesis of K_xC_{60}. The preparation was carried out with a Schlenk apparatus under airless conditions. A 40-mL toluene solution containing ~15 mg of pure C_{60} (0.021 mmol) was freeze-thaw-degassed three times. Small potassium chips (~75 mg, 1.92 mmol, 90-fold excess) were added while the C_{60}/toluene solution was kept frozen. The reaction flask was immediately evacuated and back-filled with Ar three times. The mixture was warmed to room temperature and then refluxed for 2 h with vigorous magnetic bar stirring. The solution color turned from purple (pure C_{60}) to burgundy and finally to black with a large amount of black precipitate being formed. It was filtered to remove the almost colorless toluene solution and vacuum-dried at room temperature. The Schlenk flask containing the dried black powder was transferred to an Ar-filled drybox, and any large potassium beads were separated. The black powder (K_xC_{60}) containing tiny (nonsuperconducting) potassium beads was loaded into various sample containers and sealed under either Ar or vacuum for further physical characterization (vide infra). The same material could be formed also with a 180-fold excess of K.

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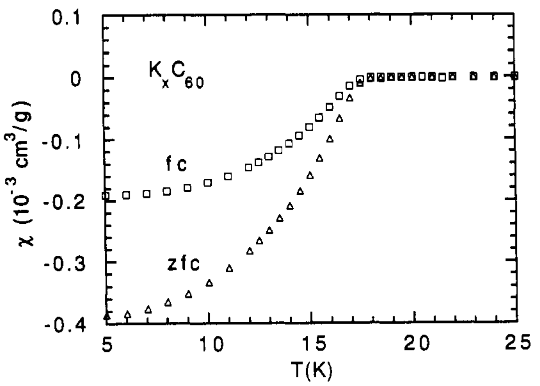

Figure 2. Temperature dependence of the mass susceptibility χ (cm^3/g) at an applied magnetic field of 10 Oe for a field-cooled (fc) and zero-field-cooled (zfc) sample of K_xC_{60}, showing T_c onset = 18.0 ± 0.1 K.

Mass Spectral Analysis of K_xC_{60}. The K_xC_{60} compound was placed on a stainless steel sample mount and inserted into a laser desorption time-of-flight mass spectrometer. The top two panels of Figure 1 display prompt ion desorption utilizing 266-nm, ≈50-ps laser pulses (positive ions on top, negative ions on center panel). The bottom panel displays postionization of the laser-desorbed neutrals using 308-nm, ≈10-ns laser pulses. In the positive ion spectrum the prominent peak is K^+ with some impurities from the sample mount. No C_{60}^+ was seen, which is in contrast to the positive ion spectrum from the original C_{60} sample. This implies that the precursor state for direct ion desorption of C_{60}^+ was different for the pure and the doped sample. This further suggests that K_xC_{60} has an ionlike bonding, with C_{60} forming the anion and K the cation. In the negative ion spectrum we observe only C_{60}^-, with little fragmentation showing up on the low-mass side as C_n^- clusters (n = 1–10). Finally, the postionized spectrum shows C_{60}^+ and K^+, but, unfortunately, no compound molecule of the kind K_xC_{60}. C_{60} exhibits the usual photofragmentation behavior that has been studied previously.[10] Since no K_xC_{60} molecule is observed directly in the mass spectra, it is not possible at present to quantify the stoichiometry of the solid, but some evidence for the existence of a K_xC_{60} molecule is given by the three mass spectra. Furthermore, the postionization mass spectrum hints that some of these molecules may laser-desorb intact, but postionization leads to detachment of (all) the potassium(s) even before the C_{60} molecule starts to fragment. This suggests that the potassium is less strongly bound to the C_{60} molecule, compared to the bonding of carbon atoms within the C_{60} molecule. Finally, we see no evidence for $C_{60}H_n$ species, at the 1% level, that might be expected from a modified Birch reduction.[7]

Superconductivity. Superconductivity of the bulk K_xC_{60} sample was confirmed by both rf penetration depth measurements[11,12] and low-field dc magnetization measurements. Both methods gave comparable results of $T_c \approx 18$ K, but the latter method provides more quantitative information. The magnetization measurements were carried out with the use of a superconducting quantum interference device (SQUID) magnetometer. For these measurements, the black polycrystalline K_xC_{60} powder was sealed under vacuum in a quartz ampule, and the magnetization was determined for both zero field (zfc) and field cooling (fc) in a magnetic field of 10 Oe. The magnetization curves, expressed as the mass susceptibility $\chi = M/HW$, where M is the magnetization, H the magnetic field, and W the mass of the sample, are illustrated in Figure 2. This figure shows a diamagnetic onset of 18.0 ± 0.1 K. The curves are very comparable to those reported by Hebard et al.[4] The shielding (i.e., zero-field cooled) susceptibility at 5 K corresponds approximately to 1% of the value for a perfect superconductor ($-1/4\pi$), on the assumption of a density of ~ 2 g/cm^3. This indicates that only about 1% by volume of the specimen is superconducting, inasmuch as the shielding volume susceptibility (zfc) of a pure superconducting phase is expected to be close to 100%. This finding is also in close agreement with that of Hebard et al.[4] The curves also indicate a remarkably high Meissner fraction of about 50%, indicating that flux trapping is not very severe. Our observations in high magnetic fields are that the upper critical magnetic field slope, $-dH_{c2}/dT$, is quite steep and that the temperature of irreversibility is ~14 K in a magnetic field of 1 T.

Conclusions. This work demonstrates that superconducting K_xC_{60} can be synthesized by a much simpler solution chemistry route that avoids the use of vapor-phase K transfer and reaction. It is curious, however, that the bulk product seems to be similar in the extent of volume superconductivity (~1%) to that reported by Hebard et al.[4] This suggests that the actual compound composition will become known only when highly crystalline single-phase material is synthesized and characterized. As such material is obtained, the T_c's will also likely increase significantly, especially as C_{60} spheroid static[13a] disorder below 77 K is suppressed.

Note Added in Proof. Contrary to the suggestion[4] that the C_{60} spheroids should be in contact for an enhanced T_c, our experience[1] with superconducting organic charge-transfer salts leads us to expect that T_c may actually increase with increase in the size of the alkali metal as it pries apart the C_{60} spheroids and *softens* their interactions.[13b] Thus, we have recently found that Rb_xC_{60} prepared by the same solution-phase synthesis has T_c = 28.6 K.[13c]

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