of the apex BH unit (decapitation) in these species generates the respective open-faced complexes \( \text{C}_{60}^\circ \text{CO} \text{RR}_2 \text{C}_{6} \text{B}_{10} \text{H}_{14} \) (6-8) whose conversion to larger systems (e.g., multidecker sandwiches) is anticipated via deprotonation and reaction with transition-metal ions.\(^{1,2}\)

This chemistry, in combination with the previously reported regiospecific B-functionalization of \( \text{LM}(\text{R}_2 \text{C}_{6} \text{B}_{10} \text{H}_{14}) \) complexes,\(^{2,4}\) 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 multitemetals. 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 \( \text{C}_{6} \text{B}_{10} \) rim, e.g., in the recent synthesis\(^{6}\) 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 \( \text{K}_{x} \text{C}_{60} \)

\( (T_c = 18.0 \pm 0.1 \text{ K}) \)

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 \( \kappa-(\text{ET})_2 \text{Cu}[\text{N(CN)}_2]X \), \( X = \text{Br} \) \( (T_c = 11.6 \text{ K}) \) and \( X = \text{Cl} \) \( (1.0 \text{ K}) \).\(^{2,3}\) Very recent work has now established an even higher \( T_c \) for a molecular superconductor in the \( \text{anion}-\text{based fullerene (buckminsterfullerene, } \text{C}_{60} \text{) system } \text{K}_{x} \text{C}_{60} \) with onset \( T_c \approx 18 \text{ K} \).\(^{4}\) 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 \( \text{K}_{x} \text{C}_{60} \) and the confirmation of \( T_c \) at \( 18.0 \pm 0.1 \text{ K} \). It is especially noteworthy that we find that reduction of \( \text{C}_{60} \) in solution with excess \( K \) does not lead to a highly resistive material but rather to superconducting \( \text{K}_{x} \text{C}_{60} \) in direct contrast to the \( K \)-vapor synthesis originally reported.\(^{6}\)

Synthesis of \( \text{K}_{x} \text{C}_{60} \) Soot containing \( \text{C}_{60} \) was prepared in an apparatus described previously.\(^{6}\) Our method is similar to the contact arc method reported by Hauffler et al.\(^{1}\) but uses a plasma


Mass Spectral Analysis of K$_2$Ca. The K$_2$Ca 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, field-cooled (zfc) sample of K$_2$Ca, showing $T_c$ onset $= 18.0 \pm 0.1$ K.

Figure 2. Temperature dependence of the mass susceptibility $\chi$ (cm$^3$/g) at an applied magnetic field of 10 Oe for a field-cooled (fc) and zero-field-cooled (zfc) sample of K$_2$Ca, showing $T_c$ onset $= 18.0 \pm 0.1$ K.

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of 18.0 $\pm$ 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 ($\chi_s/4\pi$), on the assumption of a density of $\sim 2$ 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 $\sim 14$ K in a magnetic field of 1 T.

Conclusions. This work demonstrates that superconducting K$_2$Ca 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 ($\sim 1\%$) 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 Ca$_2$ spheroid static$^{13}$ disorder below 77 K is suppressed.

Note Added in Proof. Contrary to the suggestion$^4$ that the Ca$_2$ spheroids should be in contact for an enhanced $T_c$, our experience$^3$ 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 Ca$_2$ spheroids and softens their interactions.$^{16}$ Thus, we have recently found that Rb$_2$Ca$_2$ prepared by the same solution-phase synthesis has $T_c = 28.6$ K.$^{16}$

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