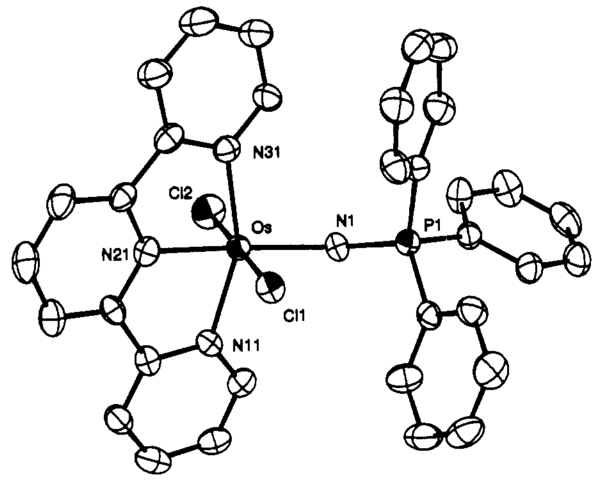


Figure 1. ORTEP[15] view of the cation *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]^+$. Relevant bond distances (Å) and angles (deg): Os–N(1), 2.093 (5); Os–Cl(1), 2.3717 (18); Os–Cl(2), 2.3626 (19); Os–N(11), 2.081 (5); Os–N(21), 1.988 (5); Os–N(31), 2.075 (5); N(1)–P(1), 1.618 (5); Os–N(1)–P(1), 132.5 (3); Cl(1)–Os–Cl(2), 178.65 (6); Cl(1)–Os–N(1), 92.46 (15); Cl(2)–Os–N(1), 87.41; N(11)–Os–N(1), 100.8 (2); N-(12)–Os–N(1), 176.4 (2); N(31)–Os–N(1), 102.1 (2); N(11)–Os–N(21), 78.6 (2); N(11)–Os–N(31), 156.6 (2); N(21)–Os–N(31), 78.9 (3).

(**2**).[8] In a typical reaction, **1** (200 mg, 0.37 mmol) and PPh_3 (140 mg, 0.53 mmol) were dissolved in CH_2Cl_2 (200 mL) and the mixture was stirred at room temperature for 2 h. Following filtration and column chromatography on alumina, elution with CH_2Cl_2/CH_3CN and finally with methanol gave a brown fraction. Reduction of the volume to 30 mL and addition of KPF_6 (200 mg) gave a brown precipitate, which was filtered off, washed with methanol, hexanes, and diethyl ether, and dried in vacuo to give 180 mg (53%) of **2**. By using the same or closely related procedures, it was possible to isolate the series of salts $[Os(tpy)(Cl)_2(NPPh_{3-n}R_n)]PF_6$ (n = 1–3; R = Me, Et).[9] Crystals of **2** were grown by redissolving the salt (20 mg) in CH_3CN (ca. 2 mL) and layering the solution with diethyl ether. The structure of the salt was determined by X-ray crystallography;[10] the cation is illustrated in Figure 1. This is one of nine structurally characterized examples of transition-metal complexes that contain a phosphoraniminato ligand.[5] The structure is distinctive in having the longest M–N bond distance (2.093 (5) Å) and smallest MNP bond angle (132.5 (3)°) of the examples that have been characterized structurally. The N–P bond distance was 1.618 (5) Å.

We formulate the cation as a paramagnetic, d^4 phosphoraniminato complex of Os(IV). This formulation is consistent with its room-temperature magnetic moment of 1.8 μ_B[13] and its temperature-dependent, strongly paramagnetically shifted ^1H NMR spectrum.[14]

It appears that *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]^+$ can act as a chemical oxidant with transfer of the phosphoraniminato group. When **2** was heated at reflux in CH_3CN, with excess PPh_3, for an extended period, $Ph_3PNPPh_3^+$ appeared in the solution, as shown by the appearance of its characteristic ^{31}P resonance at 21.67 ppm vs 85% H_3PO_4.

The phosphoraniminato complex also has an extensive one-electron-transfer chemistry. In a cyclic voltammogram of *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]PF_6$ in 0.1 M $[N(n\text{-}Bu)_4]PF_6$-CH_3CN at 200 mV/s vs SSCE, a chemically reversible, one-electron reduction appeared at $E_{1/2} = -0.27$ V, a further, pseudoreversible reduction at −1.70 V, and a one-electron oxidation at $E_{1/2} = 0.92$ V. These potentials are dependent upon the phosphine in the phosphoraniminato complex. For example, for *trans*-$[Os(tpy)(Cl)_2(NPMe_3)]PF_6$, the corresponding waves for the $Os^{V/IV}$ and $Os^{IV/III}$ couples appear at $E_{1/2} = 0.83$ and −0.37 V, respectively. Coulometric reduction of **2** past the first reduction wave at $E_{app} = -0.5$ V occurred reversibly with $n = 1$ to give $[Os^{III}(tpy)(Cl)_2(NPPh_3)]^0$, with $\lambda_{max} = 518$ nm.

Although stable on the cyclic voltammetric time scale at a scan rate of 200 mV/s, the one-electron-oxidation product, $[Os^V(tpy)(Cl)_2(NPPh_3)]^{2+}$, is unstable on longer time scales. Coulometric oxidation past the $E_{1/2}$ value occurred with $n = 1$ to give as products the starting nitrido complex, *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ ($E_{p,c} = -0.3$ V),[7] and an additional product that remains to be identified but has electrochemical waves at $E_{1/2} = 1.42$, 0.14 V and $E_{p,c} = -1.58$ V. The chemistry that can be induced following one-electron oxidation is currently under investigation.

Acknowledgments are made to the National Institutes of Health under Grant 2-RO1-GM322906-06 for support of this research, to Xiaohong Chen for assistance with the ^{31}P NMR experiments, and to Martin L. Kirk for his assistance with magnetic susceptibility measurements.

Registry No. **1**, 127571-46-4; **2**, 133930-95-7; **2**·CH_3CN, 133930-96-8; $Ph_3PNPPh_3^+$, 48236-06-2; PPh_3, 603-35-0; N^{3-}, 18851-77-9; *trans*-$[Os(tpy)(Cl)_2(NPPh_3)]^{2+}$, 133930-97-9; *trans*-$Os(tpy)(Cl)_2(NPPh_3)$, 133930-98-0; *trans*-$[Os(tpy)(Cl)_2(NPPh_2Me)](PF_6)$, 133931-00-7; *trans*-$[Os(tpy)(Cl)_2(NPPhMe_2)](PF_6)$, 133931-02-9; *trans*-$[Os(tpy)(Cl)_2(NPMe_3)](PF_6)$, 133931-04-1; *trans*-$[Os(tpy)(Cl)_2(NPPh_2Et)](PF_6)$, 133931-06-3; *trans*-$[Os(tpy)(Cl)_2(NPPhEt_2)](PF_6)$, 133931-08-5; *trans*-$[Os(tpy)(Cl)_2(NPEt_3)](PF_6)$, 133931-10-9; Ph_2PMe, 1486-28-8; $PhPMe_2$, 672-66-2; PMe_3, 594-09-2; Ph_2PEt, 607-01-2; $PhPEt_2$, 1605-53-4; PEt_3, 554-70-1; *trans*-$[Os(tpy)(Cl)_2(NPMe_3)]^{2+}$, 134054-72-1; *trans*-$[Os(tpy)(Cl)_2(NPMe_3)]$, 134054-73-2.

Supplementary Material Available: A fully labeled diagram of the cation and tables of crystal data, atomic positional and thermal parameters, bond distances, and bond angles for **2** (10 pages); a listing of observed and calculated structure factors for **2** (30 pages). Ordering information is given on any current masthead page.

Department of Chemistry
The University of North Carolina
Chapel Hill, North Carolina 27599-3290

Mohammed Bakir
Peter S. White
Angelos Dovletoglou
Thomas J. Meyer*

Received November 9, 1990

---

[8] Anal. Calcd for $C_{33}H_{26}Cl_2N_4P_2OsF_6$: C, 43.29; H, 2.86; Cl, 7.74; N, 6.12. Found: C, 44.52; H, 3.47; Cl, 7.76; N, 5.91.

[9] Bakir, M.; Klesczewski, B. Unpublished results.

[10] Crystals of $[Os(tpy)(Cl)_2(NPPh_3)]PF_6 \cdot CH_3CN$ were monoclinic, of space group $P2_1/n$, with $a = 13.384$ (5) Å, $b = 15.222$ (7) Å, $c = 17.717$ (6) Å, $\beta = 103.10$ (3)°, $V = 3516$ (2) Å^3, $Z = 4$, $d_{calc} = 1.807$ Mg/m^{-3}, and $\mu = 3.94$ mm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by using an ω–2θ scan with $2\theta_{max} = 50°$, resulting in 6155 unique reflections of which 4454 were observed ($I > 2.5\sigma(I)$). The structure was solved by Patterson methods, and an empirical absorption correction was applied by using DIFABS.[11] Refinement by full-matrix least-squares techniques, with all non-hydrogen atoms assigned anisotropic thermal parameters, gave residuals of $R = 0.034$, $R_w = 0.035$ (0.060 and 0.039 including all reflections). H atoms were included in calculated positions with thermal parameters derived from the atom to which they were bonded. All computations were performed by using the NRCVAX suite of programs.[12]

[11] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[12] Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

[13] (a) Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, 417. (b) Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1965**, *6*, 37.

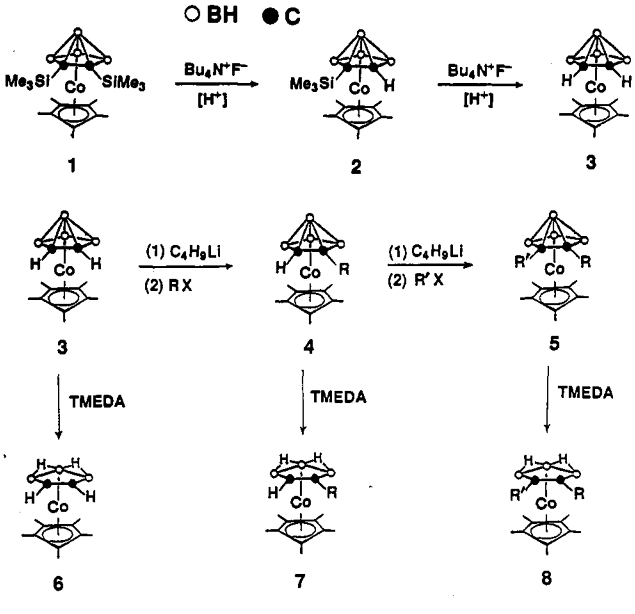
[14] In the ^1H NMR spectrum of **2** recorded in CD_3CN at room temperature, resonances appear for the tpy ligand at 29.3, 28.0, 24.0, 19.5, 18 (d), 4.0, 0.5, −7.0, −13.8, and −16 ppm vs CHD_2CN.

[15] Johnson, C. K. ORTEP-II: A FORTRAN Thermal Ellipsoid Program for Crystal Structure Illustrations. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Organotransition-Metal Metallacarboranes. 20.[1] Fluoride-Catalyzed C–Si Bond Cleavage in $Cp^*Co(Me_3Si)_2C_2B_4H_4$. Synthesis of Parent $Cp^*CoC_2B_4H_6$ and Conversion to C-Substituted $Cp^*CoRR'C_2B_4H_4$ Derivatives

Previous papers in this series[1,2] have described pathways by which small metallacarborane complexes of the types *closo*-LM-

Scheme I



R, R' = alkyl, arylalkyl

$(RR'C_2B_4H_4)$ or *nido*-$LM(RR'C_2B_3H_5)$ (where L is Cp, Cp*, or an arene and M is a transition metal) are employed in the designed synthesis of multiunit complexes having specified molecular architectures. In our laboratory, several approaches have been utilized to this end: (1) vertical stacking of $MC_2B_3^{n-}$ units to generate triple-decker[3] or tetradecker[4] sandwiches; (2) linkage of two or more MC_2B_n clusters via coordination of the metal centers to polyaromatic hydrocarbon ligands;[2,3] (3) linkage of two or more such clusters via groups attached at cage boron atoms.[2] However, functionalization of the cage *carbon* atoms has not been achieved, in the absence of a viable synthetic route to the parent complexes $(LMC_2B_4H_6)$ containing framework C–H bonds.[5] Intrigued by the discovery of Hosmane et al.[7] that the reaction of *nido*-2,3-$(Me_3Si)_2C_2B_4H_6$ with HCl gas removes the trimethylsilyl groups to generate the parent $C_2B_4H_8$, we prepared[8] $Cp^*Co(Me_3Si)_2C_2B_4H_4$ (**1**) via the combination of $(Me_3Si)_2C_2B_4H_5^-$ ion with $CoCl_2$ and $C_5Me_5^-$ ion in THF.[9] However, in contrast to *nido*-$(Me_3Si)_2C_2B_4H_6$, complex **1** proved unreactive toward dry HCl gas, and we explored alternative methods for desilylation. Addition of 1.0 M $Bu_4N^+F^-$ (TBAF) (commercially purchased THF solution containing ca. 5% water) to **1** in THF at 0 °C resulted in replacement of one or both $SiMe_3$ units with H to give, respectively, $Cp^*Co(Me_3Si)C_2B_4H_5$ (**2**) and/or the parent species $Cp^*CoC_2B_4H_6$ (**3**), depending on conditions (Scheme I). To our surprise, the reaction was found to be catalytic.[12] Thus, in the presence of 0.1 molar equiv of TBAF solution **1** was converted to the parent complex **3** in essentially quantitative yield in 5 min at room temperature, while 0.01 equiv of TBAF gave 40% completion in the same time period.[10] The same products were obtained in the presence of catalytic amounts of other tetraalkylammonium fluorides ($R_4N^+F^-$ (R = Me, Et), but at substantially slower rates than in the case of $Bu_4N^+F^-$; however, CsF gave no observable reaction.

The catalysis mechanism has not been established, but several observations will be noted. The reaction is solvent dependent; it does not occur, for example, in chloroform. Experiments with TBAF conducted in THF-d_8 produced some deuteration at cage carbon positions, indicating that limited exchange with THF solvent does occur; however, it appears that the principal stoichiometric source of protons for the reaction is water.

On treatment with *n*-butyllithium in THF, the parent cobaltacarborane **3** readily undergoes monodeprotonation at a cage C–H location to generate $Li^+Cp^*CoC_2B_4H_5^-$, which reacts with 1 equiv of alkyl halide (RX) to form $Cp^*CoRC_2B_4H_5$ (**4**). Deprotonation of the latter species followed by reaction with R'X affords the *C,C'*-dialkyl complexes $Cp^*CoRR'C_2B_4H_4$ (**5**), thereby furnishing a controlled route to both symmetrical and unsymmetrical C,C'-disubstituted derivatives. For example, the *C*-ethyl and *C*-ethyl-*C'*-benzyl derivatives (**4a** and **5a**, respectively) have been prepared in essentially quantitative yields.[11] Base-induced removal

---

(1) Part 19: Fessenbecker, A.; Stephan, M.; Grimes, R. N.; Pritzkow, H.; Zenneck, U.; Siebert, W. *J. Am. Chem. Soc.* **1991**, *113*, 3061.

(2) Recent reviews: (a) Grimes, R. N. *Pure Appl. Chem.* **1991**, *63*, 369. (b) Grimes, R. N. In *Electron-Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; John Wiley and Sons: New York, 1991; Chapter 11, pp 261–285. See also: (c) Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1990**, *9*, 1171. (d) Attwood, M. D.; Davis, J. H., Jr.; Grimes, R. N. *Organometallics* **1990**, *9*, 1177 and references therein.

(3) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776, 4784.

(4) Piepgrass, K. W.; Davis, J. H., Jr.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1991**, *113*, 681.

(5) The practical synthesis of $RR'C_2B_4H_6$ carboranes[6] utilizes base-promoted reactions of R—C≡C—R' alkynes with B_5H_9 in the absence of solvent, a procedure not viable with H—C≡C—H itself.

(6) (a) Boyter, H. A, Jr.; Swisher, R. G.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1985**, *24*, 3810. (b) Maynard, R. B.; Borodinsky, L.; Grimes, R. N. *Inorg. Synth.* **1983**, *22*, 211.

(7) Hosmane, N. S.; Islam, M. S.; Burns, E. G. *Inorg. Chem.* **1987**, *26*, 3236.

(8) In vacuo, anhydrous $CoCl_2$ (217 mg, 1.67 mmol) in 30 mL of THF was combined with LiCp* (prepared from C_5Me_5H (262 mg, 1.67 mmol) and excess *n*-butyllithium in 50 mL of THF) and stirred for 45 min. $Na^+(Me_3Si)_2C_2B_4H_5^-$ (1.67 mmol, prepared from 383 mg of $(Me_3Si)_2C_2B_4H_6$ and excess NaH in 50 mL of THF) was added, the mixture was stirred for 16 h and opened in the air, and the THF was removed by rotary evaporation. The product was dissolved in CH_2Cl_2 and filtered through silica gel, the filtrate evaporated to dryness, and the residue taken up in 2:1 hexane/CH_2Cl_2 and eluted from a silica gel column. The second band obtained was orange **1** (532 mg, 77%). MS (70 ev): *m/z* 412 (base peak), parent ion; 396 (–CH_3); 194 (Cp*Co). Exact mass: calcd for $^{59}Co^{28}Si_2{}^{12}C_{18}{}^{11}B_4{}^{1}H_{37}^+$, 412.2138; found, 412.2147. ^1H NMR (δ, ppm, $CDCl_3$): 0.4 (s, 18 H, Me_3Si), 1.8 (s, 15 H, Cp*). ^{11}B NMR (δ, ppm relative to $BF_3{\cdot}OEt_2$, CH_2Cl_2; H–B coupling constants (Hz) given in parentheses): 10.1 (1 B), 9.1 (2 B), –3.1 (158) (1 B). IR (neat, cm^{-1}): 2956 s, 2919 s, 2854 m, 2536 vs, 1453 m, 1376 m, 1247 s, 1099 w, 1026 m, 838 vs, 757 m, 690 m.

(9) The C_5H_5 analogue of **1** has been characterized as a minor (~1 mg) byproduct of the reaction of B_6H_{10} with $(Me_3Si)_2C_2$ and Co vapor; see: Briguglio, J. J.; Sneddon, L. G. *Organometallics* **1985**, *4*, 721.

(10) A solution of 154 mg (0.374 mmol) of **1** in 30 mL of THF was cooled to 0 °C, 0.04 mL of 1.0 M TBAF in THF was added via microsyringe, and the solution was stirred for 5 min. After removal of volatiles in vacuo at 0 °C, the dry product was dissolved in a minimal volume of 2:1 hexane/CH_2Cl_2 and passed through a 25-cm silica column, affording two orange bands. Rotary evaporation of each band gave orange crystalline solids, of which the first was recovered **1** (23 mg, 14%) while the second was **2** (109 mg, 85%). MS (70 ev): *m/z* 339 (base peak), parent ion; 324 (–CH_3); 194 (Cp*Co). Exact mass: calcd for $^{59}Co^{28}Si^{12}C_{15}{}^{11}B_4{}^{1}H_{29}^+$, 340.1743; found, 340.1766. ^1H NMR (δ, ppm, $CDCl_3$): 0.3 (s, 9 H, Me_3Si), 1.8 (s, 15 H, Cp*), 5.1 s (1 H, cage CH). ^{11}B NMR (CH_2Cl_2): 12.8 (141) (1 B), 5.9 (1 B), 4.5 (1 B), –2.0 (156 (1 B). IR (neat, cm^{-1}): 2961 s, 2919 s, 2854 m, 2536 vs, 2343 w, 1475 m, 1377 s, 1247 s, 1172 w, 1127 w. When the above procedure was followed by using only 15 mL of THF, with all other quantities unchanged, two bands were obtained of which the first was **2** (0.152 mg, 59%), and the second was the parent species **3** (82 mg, 41%). Data for **3** are as follows. MS (70 ev): *m/z* 267 (base peak), parent ion; 194 (Cp*Co). Exact mass: calcd for $^{59}Co^{12}C_{12}{}^{11}B_4{}^{1}H_{21}^+$, 268.1347; found, 268.1337. ^1H NMR (δ, ppm, $CDCl_3$): 1.8 (s, 15 H, Cp*), 5.1 s (2 H, cage CH). ^{11}B NMR (CH_2Cl_2): 13.0 (141) (1 B), 3.6 (152) (2 B), –0.6 (142) (1 B). IR (neat, cm^{-1}): 3040 w, 2965 m, 2917 s, 2849 m, 2540 vs, 1473 s, 1376 s, 1261 m, 1180 w, 1090 w, 1013 m, 820 m, 679 m.

(11) The *C*-ethyl derivative was prepared as follows. THF (50 mL) was distilled in vacuo onto 97 mg (0.36 mmol) of **3**. *n*-Butyllithium (0.145 mL, 0.36 mmol) was added through a septum cap via syringe, and the solution was stirred for at least 15 min. Iodoethane (0.058 mL, 0.72 mmol) was added via syringe, and the mixture was stirred for 3.5 h. The workup was conducted as in the synthesis of **1** described above, affording a quantitative yield (105 mg, 0.36 mmol) of $Cp^*Co(EtC_2B_4H_5)$ (**4a**). MS (70 ev): *m/z* 295 (base peak), parent ion; 194 (Cp*Co). Exact mass: calcd for $^{59}Co^{12}C_{14}{}^{11}B_4{}^{1}H_{25}^+$, 296.1660; found, 296.1647. ^1H NMR (δ, ppm, $CDCl_3$): 1.1 (t, 3 H, ethyl CH_3), 1.8 (s, 15 H, Cp*), 2.4, 2.8 (d of t, ethyl CH_2), 4.8 (s, 1 H, cage CH). ^{11}B NMR (CH_2Cl_2): 12.9 (116) (1 B), 4.2 (1 B), 2.5 (1 B), 0.5 (1 B). IR (neat, cm^{-1}): 2966 s, 2917 s, 2873 m, 2533 vs, 2360 w, 1737 w, 1475 m, 1453 m, 1382 s, 1118 w.

(12) Although fluoride-promoted C–Si cleavage is well-known in organic chemistry,[13] it is invariably stoichiometric, not catalytic.

(13) Furin, G. G.; Vyazankina, O. A.; Gostevsky, B. A.; Vyazankin, N. S. *Tetrahedron* **1988**, *44*, 2675.

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.

Acknowledgment. This work was supported in part by the National Science Foundation (Grant No. CHE 87-21657) and the U.S. Army Research Office. We thank James H. Davis, Jr., Kevin Chase, and Xiangsheng Meng for assistance in recording some of the NMR and mass spectra.

Department of Chemistry
University of Virginia
Charlottesville, Virginia 22901

Mark A. Benvenuto
Russell N. Grimes*

Received February 12, 1991

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%.

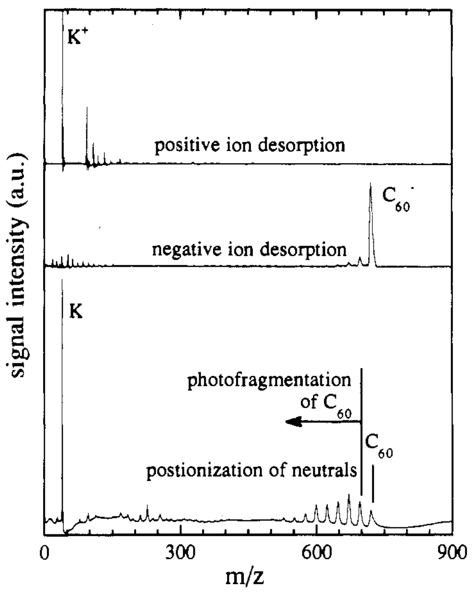


Figure 1. Laser-desorption TOF mass spectra of the K_xC_{60} sample from a stainless steel substrate with 50-ps 266-nm laser radiation. The top panel shows positive ion desorption, the center panel negative ion desorption, and the bottom panel postionization of desorbed neutrals with 308-nm 10-ns laser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

---

(1) Williams, J. M.; Schultz, A. J.; Geiser, U.; Carlson, K. D.; Kini, A. M.; Wang, H. H.; Kwok, W.-K.; Whangbo, M.-H.; Schirber, J. E. *Science*, in press.

(2) Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M.; Kwok, W.-K.; Vandervoort, K. G.; Thompson, J. E.; Stupka, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 2555.

(3) Williams, J. M.; Kini, A. M.; Wang, H. H.; Carlson, K. D.; Geiser, U.; Montgomery, L. K.; Pyrka, G. J.; Watkins, D. M.; Kommers, J. M.; Boryschuk, S. J.; Strieby Crouch, A. V.; Kwok, W.-K.; Schirber, J. E.; Overmyer, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 3262.

(4) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kartan, A. R. *Nature* **1991**, *350*, 600.

(5) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548.

(6) Parker, D. H.; Wurz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. Submitted for publication in *J. Am. Chem. Soc.*

(7) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.

(8) Hare, J. P.; Kroto, H. W.; Taylor, R. *Chem. Phys. Lett.* **1991**, *177*, 394.

(9) Hunt, J. E.; Lykke, K. R.; Pellin, M. J. In *Methods and Mechanisms for Producing Ions from Large Molecules*; Plenum Press: Minaki, Canada, 1991.

0020-1669/91/1330-2838$02.50/0