Carborane Clusters

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Isolation of a Carborane-Fused Triazole Radical Anion**

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Radicals play important roles as reactive intermediates in biological systems, in materials science, and in the construction of conducting polymers, and as spin carriers for solar-cell applications.[1] With the exception of simple inorganic molecules, such as NO and O_2, most radicals are transient species that defy isolation. In 1900, Gomberg,[2] in an attempt to isolate hexaphenylethane, discovered the first persistent organic radical species, triphenylmethylene. Following the pioneering studies of Gomberg, a variety of persistent and stable[3] radical species of the second-row elements were reported.[1b,d,e,3] These species are often stabilized by kinetic protection of the radical center and/or by significant delocalization of the unpaired electron. Further stability can also be bestowed by the incorporation of a heavier main-group element into the spin system.

Among the radicals of interest are those derived from aromatic species. Aromatic N heterocycles, for example, have been the subject of numerous oxidation/reduction studies; however, very few neutral radical species have been isolated.[4] Cationic N-heterocyclic radicals are similarly rare, with only a limited number of isolable species reported.[5] Isolable N-heterocyclic radical anions are even more elusive: only a handful of examples of crystalline solids have been described, most of which are stabilized by adjacent heavy chalcogens (S or Se).[6] Another class of radicals derived from aromatic species that have recently drawn attention[1c] are those of icosahedral boranes (B_{12}^{2-})[7] and carboranes (CB_{11}^{-}).[8] All of these species are produced by one-electron oxidation of the three-dimensional aromatic cluster by the removal of a skeletal electron. Notable examples of isolated species are the stable radical anions $B_{12}Me_{12}^{\bullet -}$[9] and $B_{12}Cl_{12}^{\bullet -}$,[10] as well as the neutral carborane radical $HCB_{11}Me_{11}^{\bullet}$.[11]

Recently, we reported the synthesis of a family of unusual 1,2,3-triazoles that are fused with icosahedral carborane anions.[12] Interestingly, both the carborane and five-membered-triazole portions of these molecules independently feature aromatic characteristics. Herein we report the investigation of the electrochemical properties of one such molecule and its subsequent derivatization, which led to the first isolable triazole radical anion.[13]

It was postulated that because N-heterocyclic carborane anions, such as the *N*-phenyl-substituted derivative **1**, display some degree of *exo*-cluster delocalization,[14] these species might possess interesting redox properties (Figure 1, top). Cyclic voltammetry (CV) experiments indicated that compound **1** undergoes no observable oxidation processes and only irreversible reduction processes at large negative potentials (Figure 1, bottom, A). We postulated that the large potential required to reduce the heterocyclic anion **1** was due to unfavorable electrostatic repulsion associated with the production of a radical dianion. We reasoned that if the negative charge of **1** were masked, by the formation of a zwitterion, its electrochemical properties would be altered in such a way as to enable facile reduction. Hence, anion **1** was alkylated with methyl triflate to afford the zwitterionic species **2** in excellent yield (90%; Figure 1, top). Heterocycle **2** was air-stable and showed no propensity to act as

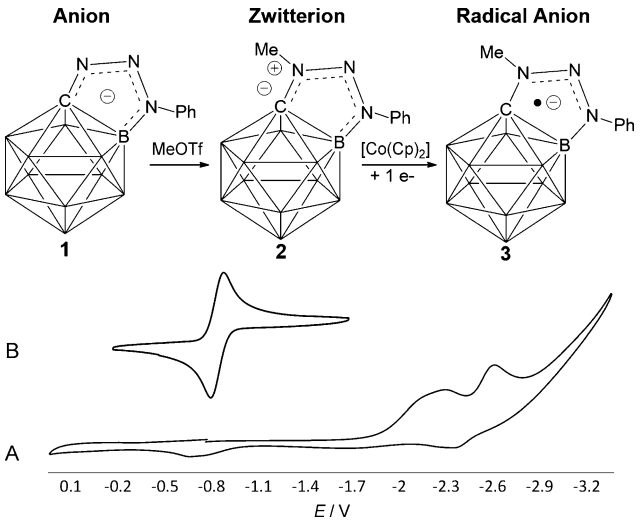

Figure 1. Top: Synthesis of the zwitterionic heterocycle **2** and chemical reduction to the radical anion **3** (unlabeled vertices: B–Cl; Tf = trifluoromethanesulfonyl). Bottom: Cyclic voltammograms of A) **1** and B) **2** in THF (E_o = 0.87 V; supporting electrolyte: 0.1 M Bu_4NPF_6; scan rate: 100 mVs^{-1}; working electrode: Pt wire; reference: Fc/Fc^+ = 0.0 V).

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a methylating agent towards nucleophilic solvents, such as water, methanol, or acetonitrile. This behavior contrasts starkly with that of zwitterionic methylating agents derived from simple halogenated carborane anions,[15] which are strong enough to abstract hydrides from alkanes, and highlights the unusual nucleophilicity of **1**.

To compare the electrochemical properties of the anionic carborane **1** with those of the zwitterionic heterocycle **2**, we carried out CV experiments. In marked contrast to **1**, **2** undergoes a clearly reversible reduction at −0.87 V versus Fc/Fc^+ (Figure 1, bottom, B; Fc = ferrocene). However, at reduction potentials less than −2.50 V, irreversible one-electron-transfer steps are evident. Encouraged by these results, we set out to chemically reduce **2** and isolate the radical species **3**.[13] The CV data indicate that the choice of reducing agent may be extremely important inasmuch as over-reduction appears to be a distinct possibility. With a reduction potential of −1.33 V, which is comfortably higher than the required −0.87 V and well below that of the first irreversible reduction step (−2.50 V), cobaltocene appeared to be an ideal choice of reducing agent. Furthermore, the cobaltocenium cation is generally weakly coordinating, robust, and often good for crystallization. Thus, a solution of cobaltocene in diethyl ether was added to the zwitterionic heterocycle **2**. The mixture was stirred for 12 h, after which time a green/brown precipitate was isolated. NMR spectroscopic analysis of the material revealed the formation of the cobaltocenium cation and thus indicated that electron transfer had occurred. There were no signals for the heterocycle in the NMR spectrum. A radical species was detected by EPR spectroscopy: one broad signal was observed at $g = 2.003$ (the peak-to-peak width of the signal was 28.8 G, or 28.2 G at 120 K), which is in very good agreement with the value calculated for the radical anion **3** ($g = 2.004$).[16] The hyperfine coupling constants could also be calculated (see Figure S18 in the Supporting Information) but were not observed experimentally because of the broad nature of the signal. The broadness of the signal may be attributed to the inherent asymmetry of the five-membered ring.

To confirm the formation of the radical anion **3** and compare its structural features with those of the unreduced zwitterion **2**, we obtained crystals suitable for single-crystal X-ray diffraction studies of both compounds.[17a] In the solid state, the five-membered heterocyclic portions of both **2** and **3** (Figure 2) are perfectly planar (sum of the internal angles: 540°), and the phenyl group remains coplanar (dihedral angle between the two rings: 5.9° in **2** and 1.8° in **3**).[17b] However, an examination of the bond lengths of the radical anion **3** reveals a dramatic elongation of the N1-N2-N3 portion of the heterocycle (N1–N2 1.386(5), N2–N3 1.391(5) Å; Figure 2) with respect to the zwitterionic carborane **2** (N1–N2 1.307(3), N2–N3 1.302(3) Å; see Figure S11). This elongation is consistent with the addition of an electron into an N-N-N π antibonding molecular orbital of **2**. Whereas the N1–C1 distances in **2** and **3** are identical (**2**: 1.413(3), **3**: 1.413(5) Å), a bond contraction between N3 and B1 (N3–B1 1.514(4) in **2**, 1.472(6) Å in **3**) is an indication of enhanced π donation[14] from N3 to the cluster. Additionally, the N3–C2 bond of **3**

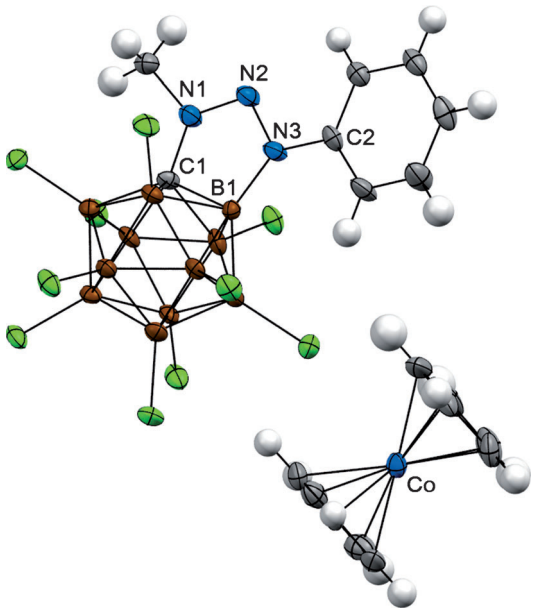

Figure 2. X-ray crystal structure of the radical anion **3**. Solvent of crystallization (THF) in the unit cell of **3** has been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level (H white, C gray, B brown, Cl green).

(1.413(5) Å) is shorter than that in the zwitterion **2** (1.430(4) Å), which suggests some delocalization of the spin density onto C2 of the benzene ring. However, the internal benzene-ring bond lengths are essentially identical in **2** and **3**. Likewise, all bond lengths in the icosahedral core of the radical anion **3** are similar to those in the zwitterion **2** and thus suggest no disruption of the skeletal electrons of the cage.

To gain further insight into the electronic structures of the redox couple **2** and **3**, we carried out DFT calculations[16] at the B3PW91 level of theory. The LUMO of **2** and the SOMO of **3** are nearly identical and are composed of orbital contributions from the three nitrogen atoms and the pendent benzene ring, with very slight mixing of the icosahedral core (Figure 3). A π-bonding interaction between N3 and C2 is evident in the SOMO of **3**, in agreement with the observed bond contraction in the X-ray diffraction study. The spin density is primarily located on the N_3 fragment (86%), with 75% centered on N2 (see Figure S17). The majority of the remaining spin density is distributed through the π system of the pendent benzene ring. The computed and experimental UV/Vis spectra of **2** and **3** ($\lambda_{max}(\mathbf{2}) = 385/360$ nm; $\lambda_{max}(\mathbf{3}) = 347/346$ nm) are in good agreement and thus allow an accurate discussion of the electronic transitions associated with these absorptions. The two absorptions are analogous $\pi \rightarrow \pi^*$ transitions from the HOMO to the LUMO of **2** and from the SOMO-1 to the SOMO of **3** (see Figures S13–S16). The blue-shifted absorbance of radical **3** relative to that of **2** is in line with a higher-energy electron transition to a half-filled antibonding orbital.

Radical **3** is stabilized by a combination of kinetic protection by the chlorinated porcupine-like carborane portion of the molecule and delocalization of the unpaired electron throughout the *exo*-cluster π system. Since the

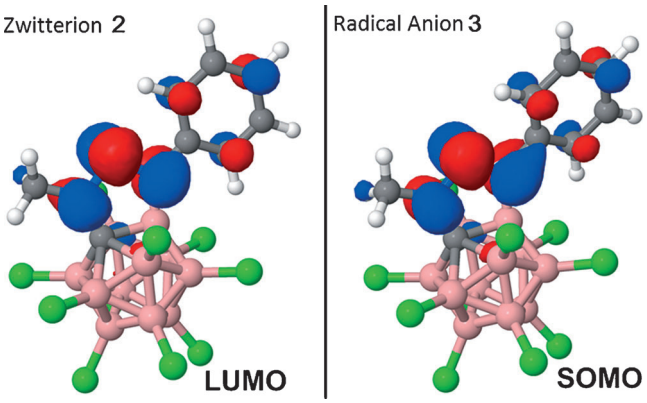

Figure 3. Calculated lowest occupied molecular orbital (LUMO) of **2** and singly occupied molecular orbital (SOMO) of **3**. Calculations were carried out at the B3PW91 level of theory.

synthesis of precursors of type **1** is fairly general,[12] the isolation of **3** paves the way for access to an entirely new series of stable radical heterocycles. Furthermore, our strategy of masking the charge of the carborane anion to render the reduction process more favorable can probably be applied to the isolation of other radical anions that contain the carba-*closo*-dodecaborate structural motif. We are currently investigating electronically distinct derivatives of **3** and exploring the possibility of applying these principles to the preparation of other novel heterocyclic radical anions. Additionally, we are actively exploring the application of these radical anions in functional materials.

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[16] For complete computational details, see the Supporting Information.

[17] a) CCDC 944081 (**2**) and 944082 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. b) This angle was measured as the dihedral angle N2-N3-C2-C3. In the case of **8**, the average value for both structures found in the unit cell is reported (see the Supporting Information for details).

