10902 *J. Am. Chem. Soc.* **1996,** *118,* 10902−10903

Dodecamethylcarba-*closo*-dodecaboranyl ($CB_{11}Me_{12}^{\bullet}$), a Stable Free Radical

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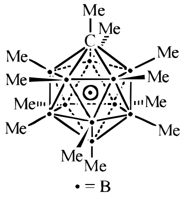
Received July 1, 1996

We report the preparation and characterization of a stable crystalline delocalized boron-based icosahedral free radical, $CB_{11}Me_{12}^{\bullet}$ (**1**), the first isolated neutral metal-free odd-electron boron cluster.[1] The oxidation level of **1** lies halfway between ordinary *closo* compounds and boron subhalides.[2] It is a strong oxidizing agent[3] whose reduced form, the dodecamethylcarba-*closo*-dodecaborate(−) anion[4] (**2**, $CB_{11}Me_{12}^{-}$), is very weakly nucleophilic[5] and thus compatible with numerous normally unstable cationic oxidation products.



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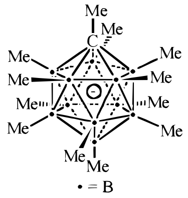

2

Oxidation of Cs^+ **2** either with PbO_2/CF_3COOH (74% yield)[6] or electrochemically[7] yields **1** as shiny black tetrahedral crystals stable to air for a few days, sublimable under reduced pressure but destroyed by heating above 150 °C. It dissolves in oxidation-resistant nonpolar solvents (pentane, carbon tetrachloride, diethyl ether) to deep blue solutions. The pentane solution is stable to prolonged visible irradiation but unstable to air and extended UV irradiation. The stability of **1** is attributable to steric protection of the delocalized free valence carrying centers in the carborane icosahedron by a sheath of methyl groups. Such steric protection of free radicals, albeit often less perfect, is known from numerous examples of persistent organic radicals.[8]

The result of a single crystal X-ray diffraction analysis[9] is shown in Figure 1. The centers of the icosahedra are arranged in a face-centered cubic lattice, with the 12 nearest neighbors 9.023 Å distant. The asymmetric unit is comprised of two atoms of the carborane cage and their attached methyl groups. Application of 3-fold rotations and an inversion completes the icosahedron. The closest intermolecular contact is a 2.85 Å distance between a pair of H atoms.

The icosahedra appear perfectly symmetrical since the location of the carbon vertex within each icosahedron is random. Only the average lengths of the 30 edges of the icosahedron and of the 12 cage atom−methyl carbon bonds can be determined [1.797(6) Å and 1.572(6) Å, respectively]. The anion **2** has an average icosahedral edge length of 1.77(2) Å and average cage atom−methyl carbon bond length of 1.59(2) Å.[4] In radical **1**, the distance between opposite vertices of the icosahedron is 3.417(9) Å, the distance between opposite methyl carbons is 6.561(8) Å, and the distance between opposite hydrogen atoms is 7.54 Å. With 1.2 Å for the van der Waals radius of H, the average "vertex-to-vertex" diameter of **1** is 9.94 Å. These values can be compared with the averaged values for **2**,[4] with opposite vertices of the icosahedra 3.38 Å apart, opposite methyl carbons 6.55 Å distant, opposite hydrogen atoms 7.54 Å distant, and a "vertex-to-vertex" diameter of 9.95 Å.

Solutions and low-temperature glasses containing **1** exhibit a broad EPR signal, $g = 2.0037(3)$ (peak-to-peak width 37 G)[10] and no NMR signals. The IR spectrum (KBr pellet, 916, 1052, 1152, 1313, 1438, 2830, 2900, 2935 cm^{-1}) is nearly identical with that of Cs^+ **2**.[4] The expected isotopic distribution of masses is observed in EI MS (base peak at *m/e* 311). The UV−visible absorption and magnetic circular dichroism of **1** suggest the presence of a series of electronic transitions extending to exceptionally low energies and are compatible with excitation energies and oscillator strengths calculated by the INDO/S method[11] (ROHF, CIS with 25 occupied and four virtual MOs) at the experimental geometry[4] of **2** (Figure 2). All observed spectral features are assigned to transitions from doubly occupied MOs to the SOMO.

The cathodic reduction potential of **1** in acetonitrile is 1.27 V [Bu_4NPF_6, $Ag/AgNO_3$(MeCN); ferrocene, 0.09 V], equal to the anodic oxidation potential of **2**.[4] No oxidation wave for **1** was observed up to 2.6 V. Understandably, the oxidizing power of **1** for neutral substrates is reduced in nonpolar solvents. In pentane, **1** oxidizes Ph_3N to its radical cation, but not perylene, and induces polymerization of styrene. In methylene chloride, it oxidizes perylene as well as tetracene and acenaphthene. In addition to π-electron systems, **1** also oxidizes molecules with only σ electrons, and rapid reactions were observed even in nonpolar solvents with substrates containing C−Sn and Si−Si bonds. Oxidation of $[Fe(CO)_2Cp]_2$ in toluene[12] afforded $Fe(CO)_2Cp^+$ **2**, based on the observation of intense peaks at 2125(2) and 2070(2) cm^{-1}, attributed to CO stretches (cf. 2128 and 2088 cm^{-1} in $Fe(CO)_2Cp^+Br_6CB_{11}H_6^-$).[13] The similarity of the frequencies suggests[13] similarly weak nucleophilicity for

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(1) Charged deltahedral borane radicals with this level of oxidation have been prepared by dianion oxidation and/or neutral reduction: $B_{10}H_{10}^{1-}$: Lewis, J. S.; Kaczmarczyk, A. *J. Am. Chem. Soc.* **1966**, *88*, 1068. Middaugh, R. L.; Farha, F. Jr. *J. Am. Chem. Soc.* **1966**, *88*, 4147. $B_9Hal_9^{1-}$: Wong, H. W.; Kabbani, R. M. *Inorg. Chem.* **1980**, *19*, 451. $B_8H_8^{1-}$: Klanberg, F.; Eaton, D. R.; Gubbenberger, L. J.; Muetterties, E. L. *Inorg. Chem.* **1967**, *6*, 1271. $B_6Hal_6^{1-}$: Heinrich, A.; Keller, H.-L.; Preetz, W. *Z. Naturforsch.* **1990**, *45b*, 184.

(2) Only halogenated and *tert*−butylated boranes are presently known to exist in the B_nX_n oxidation state: Wong, H. W. *Inorg. Chem.* **1981**, *20*, 1300. Massey, A. G. *Chem. Brit.* **1980**, *16*, 588. Morrison, J. A. *Chem. Rev.* **1991**, *91*, 35. Davan, T.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 250. Mennekes, T.; Paetzold, P.; Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *2*, 173.

(3) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(4) King, B. T.; Janoušek, Z.; Grüner, B.; Trammell, M.; Noll, B. C.; Michl, J. *J. Am. Chem. Soc.*, **1996**, *118*, 3313.

(5) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(6) PbO_2 (3.0 g) and Cs^+ **2** (300 mg) were combined with purified acetonitrile (12 mL) and pentane (12 mL) followed by trifluoroacetic acid (3 mL), and the mixture was stirred for 3 min under Ar. The deep blue pentane phase was collected under Ar through a Teflon cannula. Extraction with pentane (10 mL portions) was repeated until the blue color of **1** was no longer evident. The pentane phase was extracted with acetonitrile (10 mL). Solvent was removed by a stream of Ar, giving 186 mg (83%) of pure crystalline **1**. Anal. Calcd for $C_{13}B_{11}H_{36}$: C, 50.15; H,11.65 Found: C, 49.96; H, 11.58.

(7) Crystals of **1** used for X-ray diffraction were electrocrystallized on a Pt anode. Cs^+ **2** (50 mg) was dissolved in 8 mL of 0.1 M Bu_4NF in acetonitrile and oxidized at 1.5 V vs. Ag/AgCl (aq).

(8) Griller, D.; Ingold, K. *Acc. Chem. Res.* **1976**, *9*, 13.

(9) Crystal data: **1**, cubic, $a = 12.7610(8)$ Å, space group $Pa\bar{3}$; $Z = 4$; $\rho_{calc} = 0.995$; $R_1 = 0.1108$ ($F \geq 4\sigma(F)$), $wR_2 = 0.2238$ (all data); 1364 reflections used. Intensity data were collected at 150 K on a Siemens SMART CCD diffractometer with graphite monochromated Mo K_α ($\lambda = 0.71073$ Å).

(10) This is as expected, given the 3 spin of ^{10}B nuclei and 3/2 spin of ^{11}B nuclei (20% and 80% natural abundance, respectively), the presence of four groups of protons (3H, 15 H, 15H, 3H), and effective orbital degeneracy. All attempts to observe ENDOR failed.

(11) Ridley, J.; Zerner, M. *Theor. Chim. Acta* **1973**, *32*, 111.

(12) A toluene solution of $[Fe(CO)_2Cp]_2$ (2 mg/mL) was added dropwise to 4 mg of solid radical **1** under Ar until the blue color was just discharged.

(13) Xie, Z.; Jelínek, T.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1907.

S0002-7863(96)02216-0 CCC: $12.00

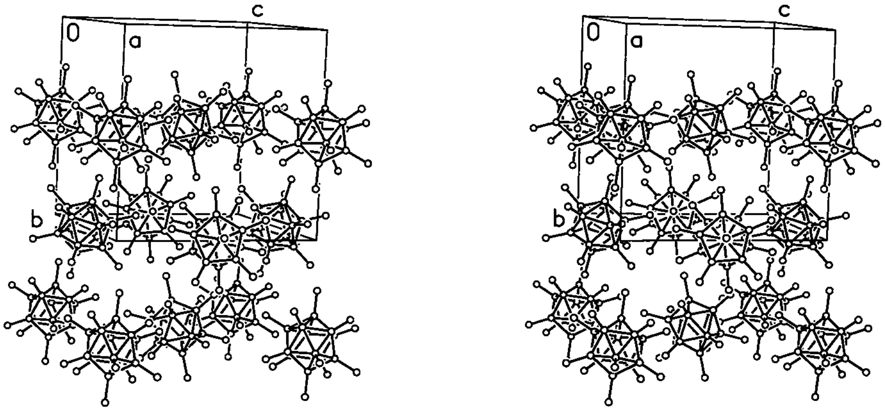

Figure 1. A stereoscopic view of the crystal structure of **1**.

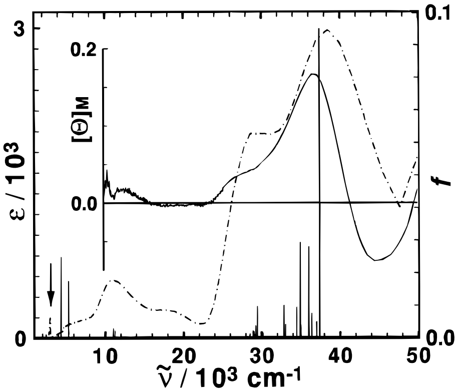

Figure 2. UV−visible-NIR-IR (dashed line, pentane above 4650 and CCl_4 below 4650 cm^{-1}) and MCD (deg cm^2 dmol^{-1} G^{-1}, solid line, pentane) spectra with calculated (INDO/S) transition energies and oscillator strengths *f* (vertical bars). The arrow indicates a peak due to CH stretching vibrations.

2 and $Br_6CB_{11}H_6^-$ or, possibly, ligation of $Fe(CO)_2Cp^+$ with toluene rather than with the anion.

It is likely that **1** is merely a first member of a new family of strongly oxidizing neutral radicals. Thus, a mixture of fluoroundecamethylcarba-*closo*-dodecaborate anions[14] in acetonitrile is reversibly oxidized at 1.37 V [Bu_4NPF_6, Ag/$AgNO_3$(MeCN)] to yield a lavender solution of persistent radicals.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9318469, CHE-9412767, CHE-9505926, and CHE-9423319). We are grateful to Ms. Corie Coe for technical assistance.

Supporting Information Available: Details of the crystallographic analysis of **1** (6 pages). See any current masthead page for ordering and Internet access instructions.

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(14) Predominantly the 12-fluoro compound, containing about 30% of the 7-fluoro (or, much less likely, 2-fluoro) isomer, prepared in 74% yield by action of the neat HF•pyridine complex on Cs^+ **2** at room temperature: MS *m/e* 315. For PPh_4+ salt: Anal. Calcd for $C_{36}B_{11}H_{53}PF$: C, 65.80; H 8.14. Found: C, 66.00; H, 8.05. Nearly pure 12-fluoro compound was isolated by HPLC: ^{1}H NMR (acetone-d_6) δ 0.797 [s, 3H, CH_3(1)], −0.310 [s, 15H], −0.343 [s, 15H]; ^{11}B NMR (2−D COSY) δ 11.76 [bd s, 1B, B(12)], −10.84 [s, 5B, B(7−11)], −13.12 [s, 5B, B(2−6)]; ^{19}F NMR δ −209.0 (q, J_{BF} = 60 Hz). The fluorination reaction is analogous to the conversion of the $CB_{11}H_{12}^-$ anion to the 12-$FCB_{11}H_{11}^-$ anion reported by Ivanov, S. V.; Lupinetti, A. J.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 6419.