$B_{12}(OH)_{12}]$[8] by cation exchange using cation exchange resin and was dried at 60 °C in vacuo for 24 h before use. NMR spectra were obtained on a Bruker ARX 500 spectrometer, electrospray mass spectra on a Perkin-Elmer Sciex API III triple quadrupole mass spectrometer, and FAB mass spectra were obtained on a VG ZAB-SE mass spectrometer.

Cs_2-**1**: A suspension of Cs_2[*closo*-$B_{12}(OH)_{12}$] (48 mg, 0.080 mmol) in acetic acid anhydride (6 mL) was heated with stirring at reflux for three days under argon. The brown reaction mixture was cooled to room temperature and the volatiles were removed in vacuo. The residue was dried in vacuo at 50 °C for 10 h. The solid was dissolved in water (6 mL) at room temperature, the suspension filtered, and the filtrate cooled at 3 °C for 60 min. The resulting suspension was again filtered using a 0.2 µm filter and the water removed in vacuo to give Cs_2-**1** as a light brown solid in sufficient purity for further use (38 mg, 0.034 mmol, 43 %). Further purification can be achieved by recrystallization from acetic anhydride. Single crystals suitable for X-ray structure analysis were obtained from a solution in acetonitrile/water with the addition of a small amount of thiourea. ^{1}H NMR (500 MHz, D_2O): $\delta = 1.9$ (s); ^{13}C NMR (126 MHz, D_2O): $\delta = 22.0$ (Me), 174.0 (CO); ^{11}B NMR (160 MHz, D_2O): $\delta = -16$; ESI-MS (negative mode, water): m/z: 839.2 [$\mathbf{1}^{2-}$+H]$^-$, 419.1 $\mathbf{1}^{2-}$.

$[H_3O]_2$-**2**: To a suspension of $[NBu_4]_2$[*closo*-$B_{12}(OH)_{12}$] (47 mg, 0.058 mmol) in dry acetonitrile (30 mL) were added benzoyl chloride (0.40 mL, 480 mg, 3.5 mmol) and dry triethylamine (2 mL, 1.452 g, 14.3 mmol). The reaction mixture was heated with stirring at reflux for 10 days under argon. The brown suspension was cooled to room temperature, filtered, and the volatiles were removed in vacuo. The resulting dark brown solid was purified by filtration over silica gel by employing CH_2Cl_2, followed by THF, and finally acetonitrile as the mobile phases. The first two mobile phases eluted colored impurities and elution was continued until the eluate was colorless. The mobile phase was then changed to acetonitrile. The acetonitrile fractions were collected, the solvent was removed in vacuo, and the solid was washed with THF and warm water to give pure $[H_3O]_2$-**2** as a white solid (49 mg, 0.030 mmol, 52 %). ^{1}H NMR (500 MHz, $[D_6]$DMSO): $\delta = 8.0$ (m, 24 H), 7.4 (m, 12 H), 7.1 (m, 24 H); ^{13}C NMR (126 MHz, $[D_6]$DMSO): $\delta = 163.6$ (CO), 134.7, 130.7, 130.1, 127.2; ^{11}B NMR (160 MHz, $[D_6]$DMSO): $\delta = -16$; ESI-MS (negative mode, acetonitrile): m/z: 1584.0 [$\mathbf{2}^{2-}$+H]$^-$, 791.5 $\mathbf{2}^{2-}$.

$[Ph_4As]_2$-**2**: To a solution of $[H_3O]_2$-**2** (40 mg, 0.025 mmol) in DMF (2 mL) was added a solution of $[Ph_4As]Cl$ (31 mg, 0.074 mmol) in DMF (2 mL). Subsequent addition of water (4 mL) gave $[Ph_4As]_2$-**2** as a white precipitate which was washed twice with warm water and dried in vacuo (59 mg, 0.025 mmol, 100 %). Single crystals suitable for X-ray structure analysis were obtained from a solution in methanol.

^{1}H NMR (500 MHz, CD_3CN): $\delta = 8.0$ (m, 24 H), 7.8 (m, 8 H), 7.7 (m, 16 H), 7.6 (m, 16 H), 7.4 (m, 12 H), 7.1 (m, 24 H); ^{13}C NMR (126 MHz, CD_3CN): $\delta = 165.1$ (CO), 135.7, 135.4, 134.1, 131.8, 131.7, 131.0, 128.3; ^{11}B NMR (160 MHz, CD_3CN): $\delta = -15$.

Received: October 27, 2000 [Z 16003]

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[1] Closomers are defined as polyhedra whose surfaces support polyatomic substituents. In the formulation below, the first number indicates the total number of cluster vertices potentially available for substitution, while the second number refers to the number of attached substituents. The designation 12(12)-closomer indicates a polyhedron containing 12 vertices and 12 substituents.

[2] A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1999**, *99*, 1665, and references therein.

[3] M. Brettreich, S. Burghardt, C. Böttcher, T. Bayerl, S. Bayerl, A. Hirsch, *Angew. Chem.* **2000**, *112*, 1915; *Angew. Chem. Int. Ed.* **2000**, *39*, 1845.

[4] A. Herzog, A. Hirsch, O. Vostrowsky, *Eur. J. Org. Chem.* **2000**, 171.

[5] R. Elsäßer, G. H. Mehl, J. W. Goodby, D. J. Photinos, *Chem. Commun.* **2000**, 851.

[6] A. R. Pitochelli, M. F. Hawthorne, *J. Am. Chem. Soc.* **1960**, *82*, 3228.

[7] H. C. Miller, N. E. Miller, E. L. Muetterties, *J. Am. Chem. Soc.* **1963**, *85*, 3885.

[8] T. Peymann, A. Herzog, C. B. Knobler, M. F. Hawthorne, *Angew. Chem.* **1999**, *111*, 1130; *Angew. Chem. Int. Ed.* **1999**, 38, 1062.

[9] T. Peymann, C. B. Knobler, S. I. Khan, M. F. Hawthorne, *Angew. Chem.* **2001**, *113*, 1713; *Angew. Chem. Int. Ed.* **2001**, *40*, 1664.

[10] a) Cs_2-$\mathbf{1}\cdot 2\,SC(NH_2)_2$, triclinic, space group $P\bar{1}$ with $a = 10.953(6)$, $b = 11.334(7)$, $c = 11.532(7)$ Å, $\alpha = 91.918(11)°$, $\beta = 113.221(9)°$, $\gamma = 112.575(9)°$, $V = 1185.6(12)$ Å^3, $Z = 1$. Data were collected on a Bruker SMART 1000 using $Mo_{K\alpha}$ radiation, $2\theta_{max} = 56°$, giving 5436 unique reflections and the structure was solved by direct methods. The final discrepancy index was $R = 0.020$, $R_W = 0.048$ for 4914 independent reflections with $I > 2\sigma(I)$. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151203 (Cs_2-$\mathbf{1}\cdot 2\,SC(NH_2)_2$) and CCDC-151204 ($[Ph_4As]_2$-**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] The signal strengths in the negative ion mode for $\mathbf{2}^{2-}$ and [$\mathbf{2}^{2-}$+H]$^-$ relative to the cations observed in the positive ion mode was estimated from the ratio of signal intensities obtained in the two modes under identical scanning and detector settings with the same solution and in the absence of reagents that might enhance ion intensities in either mode and assuming similar ionization efficacy for positive and negative ions. For a salt with the composition AB_2 (A: anion, B: cation) the signal intensities for the negative and the positive ions are expected to be equivalent to the ratio of 1:2. The measured signal intensities of anions and cations in the same sample reveal only a ratio of about 1:0.18.

[12] $[Ph_4As]_2$-**2**, triclinic space group $P\bar{1}$ with $a = 13.873(2)$, $b = 15.680(2)$, $c = 16.280(2)$ Å, $\alpha = 65.368(2)°$, $\beta = 66.727(2)°$, $\gamma = 80.638(2)°$, $V = 2957.2(7)$ Å^3, $Z = 1$. Data were collected on a Bruker SMART ccd diffractometer using $Mo_{K\alpha}$ radiation, $2\theta_{max} = 56.6°$, giving 13 554 unique reflections and the structure was solved by Patterson and heavy atom methods. The final discrepancy index was $R = 0.054$, $R_W = 0.159$ for 7763 independent reflections with $I > 2\sigma(I)$.[10b]

Dodeca(benzyloxy)dodecaborane, $B_{12}(OCH_2Ph)_{12}$: A Stable Derivative of *hypercloso*-$B_{12}H_{12}$**

Toralf Peymann, Carolyn B. Knobler, Saeed I. Khan, and M. Frederick Hawthorne*

In agreement with Wade's rules, the framework of a polyhedral borane requires $2n+2$ (n = number of vertices) skeletal electrons to form a *closo* cage.[1] These rules have been employed to successfully classify and rationalize the structures of the polyhedral boranes.[2] Exceptions to Wade's rules have been reported for species having an apparent *closo* structure in which the number of framework electrons is less than the required $2n+2$. These electron-deficient cages are

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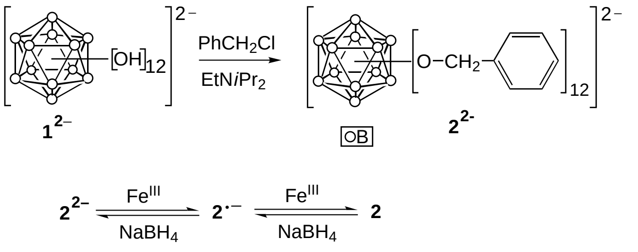
[**] This work was supported by the U.S. Department of Energy (DE-FG02-95ER61975) and the National Science Foundation (NSF CHE 9730006 and NSF CHE 9871332).

designated as *hypercloso* clusters.[3] For cages with a framework composed solely of boron vertices such *hypercloso* species include paramagnetic anions with $2n+1$ electrons, such as $[B_nH_n]^{\bullet -}$, $[B_nX_n]^{\bullet -}$ (X = halogen),[4] $[B_{12}Me_{12}]^{\bullet -}$,[5] and the neutral boron halides B_nX_n with $2n$ electrons.[6] The stability of the persubstituted *hypercloso* polyhedral boranes has been attributed to a combination of both steric protection and electron donation provided by the substituents.[3]

Here we report the per-O-benzylation of [*closo*-$B_{12}(OH)_{12}]^{2-}$ ($\mathbf{1}^{2-}$)[7] to produce [*closo*-$B_{12}(OCH_2Ph)_{12}]^{2-}$ ($\mathbf{2}^{2-}$); the reversible one-electron oxidation of $\mathbf{2}^{2-}$ to paramagnetic [*hypercloso*-$B_{12}(OCH_2Ph)_{12}]^{\bullet -}$ ($\mathbf{2}^{\bullet -}$); and the synthesis and structure of a novel electron-deficient *hypercloso* species: the neutral *hypercloso*-$B_{12}(OCH_2Ph)_{12}$ (**2**), the first characterized derivative of *hypercloso*-$B_{12}H_{12}$.[8] Although the latter borane has not been synthesized, it has been the subject of numerous computational studies.[3, 9]

The precursor for the synthesis of *hypercloso*-**2**, [*closo*-$B_{12}(OH)_{12}]^{2-}$ ($\mathbf{1}^{2-}$)[7] is especially attractive due to its sheath of twelve identical hydroxy functions.[7, 10] The preceding communication[11] reports the synthesis of species in which the twelve hydroxy functions of $\mathbf{1}^{2-}$ have been converted to carboxylic acid esters. These dodecafunctionalized structures in which twelve organic substituents emanate from the vertices of the icosahedral surface have been designated as closomers and differentiated from dendritic structures.[11]

The anion $\mathbf{1}^{2-}$ (PPN salt, PPN: bis(triphenylphosphoranylidene)ammonium) was per-*O*-benzylated in acetonitrile at the reflux temperature employing benzyl chloride in the presence of ethyldiisopropylamine (Scheme 1). After a reaction time of six days the salt Na[PPN][*closo*-$B_{12}(OCH_2Ph)_{12}$] (Na[PPN]-**2**) was obtained in 48% yield. During the product isolation procedure sodium borohydride was added to reduce spurious amounts of the radical species $\mathbf{2}^{\bullet -}$ formed during the reaction. Prolonged reaction times led to lower yields of $\mathbf{2}^{2-}$, presumably due to the decomposition of paramagnetic *hypercloso*-$\mathbf{2}^{\bullet -}$ produced by the oxidation of $\mathbf{2}^{2-}$ with excess benzyl chloride. Shorter reaction times, on the other hand, led to decreased yields because of the incomplete conversion of $\mathbf{1}^{2-}$ to $\mathbf{2}^{2-}$.



Scheme 1. Synthesis of *hypercloso*-$B_{12}(OCH_2Ph)_{12}$ (**2**) by per-O-benzylation of [*closo*-$B_{12}(OH)_{12}]^{2-}$ ($\mathbf{1}^{2-}$) followed by oxidation with two equivalents of Fe^{III}.

An ion with *m*/*z* 708.2 (100%) is observed by electrospray mass spectrometry for $\mathbf{2}^{2-}$; in the positive-ion mode signals ascribed to the two cations, Na^+ and PPN^+, are observed. The ^{11}B, ^1H, and ^{13}C NMR data confirm the icosahedral symmetry of species $\mathbf{2}^{2-}$. The UV/Vis spectrum of K_2-**2**, obtained from Na[PPN]-**2** through metathesis, has absorption bands at 210, 233, and 260 nm. Figure 1 depicts the solid-state structure of $\mathbf{2}^{2-}$ determined by an X-ray diffraction study of Cs[PPN]-**2**.[12] The cage of dianion $\mathbf{2}^{2-}$ has icosahedral symmetry with the B−B bond lengths covering the narrow range of 1.781(4) to 1.824(4) Å and B−O bond lengths of 1.434(3) to 1.451(3) Å. Salts of anion $\mathbf{2}^{2-}$ slowly air-oxidize and develop a purple tint upon exposure to air due to the formation of $\mathbf{2}^{\bullet -}$.

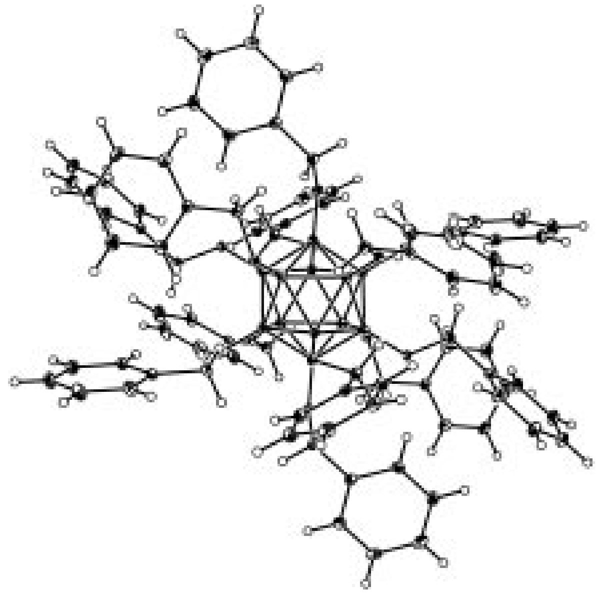


Figure 1. Structure of [*closo*-$B_{12}(OCH_2Ph)_{12}]^{2-}$ ($\mathbf{2}^{2-}$)(ORTEP diagram). The ellipsoids represent a 30% probability level.

Chemical one-electron oxidation of $\mathbf{2}^{2-}$ employing Fe^{III} afforded the purple, paramagnetic monoanion $\mathbf{2}^{\bullet -}$ as its PPN^+ salt in 90% yield (Scheme 1). A broad (200 G) EPR signal with $g = 2.1997$ was observed with [PPN]-**2**. Negative-ion electrospray mass spectrometry of [PPN]-**2** gave a peak at *m*/*z* 1416.0 (100%) corresponding to the formulation [*hypercloso*-$B_{12}(OCH_2Ph)_{12}]^-$. The UV/Vis spectrum of [PPN]-**2** in acetonitrile exhibits an intense band in the visible region at 537 nm accompanied by strong absorption in the UV due to the presence of benzyl groups. The crystal structure of [PPN]-**2**·C_6H_6 confirms the monoanionic nature of $\mathbf{2}^{\bullet -}$.[12b, 13] In contrast to $\mathbf{2}^{2-}$ the boron cage of species $\mathbf{2}^{\bullet -}$ is more distorted from icosahedral symmetry (B−B 1.768(4)–1.840(4) Å) and the B−O distances (1.398(3)–1.419(3) Å) are shortened by about 0.03 Å.

The sequential two-electron oxidation of $\mathbf{2}^{2-}$ with Fe^{III} in ethanol affords **2** as a dark-orange solid (Scheme 1). The purple anion-radical $\mathbf{2}^{\bullet -}$ is observed as an intermediate in this overall reaction. An ion at *m*/*z* 1415.8 (100%) assigned to the formula $[B_{12}(OCH_2C_6H_5)_{12}]^-$ is recorded for **2** by fast atom bombardment mass spectrometry. The ^{11}B NMR spectrum of **2** exhibits a singlet at $\delta = 43.3$, a downfield shift of 58 ppm relative to the singlet observed at $\delta = -14.8$ for $\mathbf{2}^{2-}$. The ^1H and ^{13}C NMR spectra exhibit broad signals, probably due to paramagnetic impurities or spurious reduction of **2** to $\mathbf{2}^{\bullet -}$ in solution. A detailed study concerning the redox stability of **2** is currently under way and will be reported elsewhere. The visible spectrum of orange **2** in acetonitrile solution exhibits a strong absorption at 467 nm.

A crystal of **2** suitable for X-ray diffraction studies was obtained from acetonitrile.[12b, 14] Most importantly, the solid-state structure of **2** reveals a *hypercloso* borane cage with only approximate icosahedral geometry (D_{3d}). A detailed analysis of the bonding parameters demonstrates this departure from icosahedral symmetry. Notably, the B–B distances observed in **2** are in the broad range of 1.755(2) to 1.918(2) Å and should be compared with the corresponding distances of 1.781(4) – 1.824(4) Å in **2**$^{2-}$ and 1.768(4) – 1.840(4) Å in the paramagnetic anion **2**$^{\bullet-}$. Conspicuously, the B–O distances observed in **2** are shortened by about 0.06 Å with respect to those in **2**$^{2-}$ and by about 0.02 Å relative to those in **2**$^{\bullet-}$ (**2**: 1.369(2) – 1.404(2) Å; **2**$^{2-}$: 1.434(3) – 1.451(3) Å; **2**$^{\bullet-}$: 1.398(3) – 1.419(3) Å).

A more detailed examination of the distorted icosahedral geometry of **2** reveals that the six longest B–B bonds (B–B 1.910(2) – 1.918(2) Å) are located in two opposing symmetry-related boron triangles, (B4, B5, B2′, see Figure 2) and (B4′, B5′, B2). The remaining shorter B–B bond lengths (1.755(2) – 1.864(2) Å) are similar to those observed in **2**$^{2-}$ and **2**$^{\bullet-}$. The B–O bond lengths of **2** may be divided into two groups, as well. The six shorter B–O bond lengths (1.369(2) – 1.378(2) Å) are associated with the oxygen atoms attached to the boron vertices of the elongated triangles. The six longer B–O bonds (1.398(2) – 1.404(2) Å) are associated with the remaining boron vertices. All B-O-C bond angles deviate from the ideal sp^3 bond angle by more than 10°. The bond angles associated with the shorter B–O bonds (123.2(1) – 123.4(1)°) are about 2° larger than the corresponding angles about the oxygen atoms of the longer B–O bonds (121.5(1) – 121.7(1)°).

The distorted icosahedron of **2** (Figure 2) has approximate D_{3d} symmetry with the C_3 axis penetrating the centers of the elongated triangles (B4, B5, B2′) and (B4′, B5′, B2). Previously, neutral B_{12} clusters structurally similar to the distorted icosahedron of **2** have been observed in elemental boron. In β-rhombohedral boron, three structural types of B_{12} clusters are present.[15] One of these icosahedra displays D_{3d} symmetry with two triangular faces having elongated edges (long B–B bonds 1.801 Å, short B–B bonds 1.751 – 1.767 Å). Furthermore, a distorted icosahedron with D_{3d} symmetry has been identified as an energy minimum in computations carried out on an HF/6-31G(d) level for [*hypercloso*-$B_{12}H_{12}$].[9] An undistorted icosahedral [*hypercloso*-$B_{12}H_{12}$] structure would have partially occupied fourfold degenerate HOMOs. A Jahn – Teller distortion to the observed D_{3d} structure removes this degeneracy.[9]

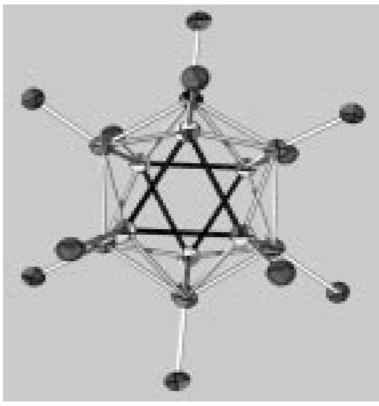


Figure 2. The distorted icosahedron (point group D_{3d}) of *hypercloso*-$B_{12}(OCH_2Ph)_{12}$ (**2**) without the benzyl groups and viewed along the C_3 axis. The boron atoms (B4, B5, B2′, front, and B4′, B5′, B2, rear) form two triangles (dark gray) with elongated B–B distances (see text). The B–O bonds originating at these six B atoms are shortened relative to the other B–O bonds present in **2** due to back-bonding from oxygen.

In a comparison of the structures of the per(benzyloxy) icosahedral boranes $[B_{12}(OCH_2Ph)_{12}]^{n-}$ ($n = 0-2$), it becomes apparent that the range of B–B bond lengths widens with a decrease in the number of skeletal electrons. On the other hand, the B–O bond lengths shorten concomitantly with the loss of cluster electron density suggesting the presence of considerable double-bond character in **2** attributed to enhanced π-backbonding of the exo-oxygen atoms to the electron-deficient *hypercloso*-icosahedron. Indeed, the shortest B–O bonds of **2** are associated with those oxygen atoms attached to the more electron-poor boron triangles (B4, B5, B2′) and (B4′, B5′, B2) having the longest B–B bonds.

The redox chemistry of **2** was studied by cyclic voltammetry. The cyclic voltammogram of **2** (100 mM $(nBu)_4NPF_6$, Ag/AgCl, acetonitrile) shows reversible one-electron transfer processes with $E_{1/2} = 0.46$ and 0.0 V which are attributed to the two couples **2**/**2**$^{\bullet-}$ and **2**$^{\bullet-}$/**2**$^{2-}$, respectively.

In summary, we have presented the per-O-benzylation of **1**$^{2-}$ affording **2**$^{\bullet-}$, the one-electron oxidation of **2**$^{2-}$ to paramagnetic **2**$^{\bullet-}$ and the subsequent one-electron oxidation of **2**$^{\bullet-}$ to **2**. The stability of the neutral *hypercloso*-species **2** is ascribed to both oxygen π-backbonding and steric encumbrance resulting from its twelve benzyloxy substituents. The crystal structure of **2** revealed a Jahn – Teller distortion from icosahedral geometry (point group D_{3d}), similar to one B_{12} cluster observed in β-rhombohedral boron, and shortened B–O bonds characteristic of B–O π-backbonding.

Experimental Section

Na[PPN]-**2**: A solution of $[PPN]_2$-**1**[7] (0.60 g, 0.43 mmol), ethyldiisopropylamine (0.89 mL, 5.1 mmol), and benzyl chloride (2.9 mL, 26 mmol) in acetonitrile (15 mL) was heated at reflux for six days under nitrogen. All volatile materials present in the purple reaction mixture containing **2**$^{\bullet-}$ were removed in vacuo and ethanol (20 mL) was added. The resulting suspension was kept at −18 °C overnight and a grayish purple solid was removed by filtration. This solid was dissolved in warm ethanol, and sodium borohydride (0.04 g, 1 mmol) was added to decolorize the suspension by reducing **2**$^{\bullet-}$ to **2**$^{2-}$. The solvent was removed in vacuo and the residue extracted with acetonitrile. The extracts were combined and evaporated to produce a residue which was recrystallized from ethanol. After seven days at −18 °C, crystals of Na[PPN]-**2** were collected by filtration (m.p. > 250 °C; 0.40 g, 0.20 mmol, 48 % yield). Electrospray MS (MeCN): negative-ion mode: m/z (%): 708.2 (100) $[\mathbf{2}]^{2-}$; positive-ion mode: m/z (%): 22.7 (50) $[Na]^+$, 63.8 (95) $[Na+MeCN]^+$, 104.9 (70) $[Na+2MeCN]^+$, 539.0 (100) $[PPN]^+$; ^{11}B NMR (160 MHz, acetone): $\delta = -14.8$ (s); ^1H NMR (400 MHz, $[D_8]$acetone): $\delta = 7.60-7.52$ (m, 30 H, Ph of PPN^+), 7.38 – 7.02 (m, 60 H, CH_2*Ph*), 5.57 (s, 24 H, C*H*$_2$Ph); ^{13}C NMR (126 MHz, $[D_8]$acetone): $\delta = 145.8$ (C1, CH_2*Ph*); 127.2, 126.7 (2 C2, 2 C3, CH_2*Ph*), 125.0 (C4, CH_2*Ph*), 68.3 (*C*H$_2$Ph).

K_2-**2**: To a warm solution of Na[PPN]-**2** (350 mg, 0.18 mmol) in ethanol (10 mL) was added a solution of CH_3COOK (350 mg, 3.57 mmol) in ethanol (5 mL). The mixture was kept at −18 °C for one week. The formed crystals were separated by filtration and dried to yield K_2-**2** (260 mg, 0.17 mmol, 94 %). No PPN$^+$ resonances were observed by ^{1}H NMR spectroscopy. UV/VIS (MeCN): λ (ε) = 210 (6.8×10^4), 233 (2.1×10^4), 260 nm (6×10^3).

[PPN]-**2**: To a solution of Na[PPN]-**2** (100 mg, 0.050 mmol) in warm ethanol (10 mL) was added a solution of $FeCl_3 \cdot 6H_2O$ (14 mg, 0.050 mmol) in ethanol (5 mL). The purple reaction solution was stirred for 30 min at 25 °C and then kept at −18 °C for 3 h. Dark purple crystals precipitated which were separated by filtration, recrystallized from ethanol, and dried (m.p. 197 °C) to yield [PPN]-**2** (90 mg, 0.046 mmol, 90 %). Electrospray MS (MeCN), negative-ion mode: *m/z* (%): 1416.0 (100) [**2**]$^-$; VIS (MeCN): λ (ε) = 537 nm (1.4×10^4); EPR (solid, 273 K): $g = 2.1997$.

2: A sample of K_2-**2** (100 mg, 0.067 mmol) was dissolved in ethanol (10 mL) and a solution of $FeCl_3 \cdot 6H_2O$ (45 mg, 0.166 mmol) in ethanol (5 mL) was added. The reaction mixture turned purple and then dark red. The suspension was stirred for 1 h at room temperature and the precipitate was removed by filtration. The orange-brown solid was recrystallized from ethanol (m.p. 155 °C) to give **2** (80 mg, 0.057 mmol) in 84 % yield. FAB-MS (acetone), negative-ion mode: *m/z* (%): 1324.7 (25) [**2** − CH_2Ph]$^-$, 1415.8 (100) [**2**]$^-$, 1506.7 (70) [**2**+CH_2Ph]$^-$; ^{11}B NMR (160 MHz, acetone): δ = 43.3 (s); VIS (MeCN): λ (ε) = 467 nm (1.7×10^4).

Received: October 27, 2000
Revised: January 29, 2001 [Z 16004/16005]

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[1] J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry*, 4th ed., HarperCollins College Publishers, New York, **1993**, p. 798.

[2] E. L. Muetterties, W. H. Knoth, *Polyhedral Boranes*, Dekker, New York, **1968**.

[3] M. L. McKee, Z.-X. Wang, P. von R. Schleyer, *J. Am. Chem. Soc.* **2000**, *122*, 4781 – 4793, and references therein.

[4] see [3], ref. 19.

[5] T. Peymann, C. B. Knobler, M. F. Hawthorne, *Chem. Commun.* **1999**, 2039 – 2040.

[6] J. Morrison, *Chem. Rev.* **1991**, *91*, 35 – 48.

[7] a) T. Peymann, A. Herzog, C. B. Knobler, M. F.Hawthorne, *Angew. Chem.* **1999**, *111*, 1130 – 1132; *Angew. Chem. Int. Ed.* **1999**, *38*, 1062 – 1064; b) T. Peymann, C. B. Knobler, S. I. Khan, M. F. Hawthorne, *J. Am. Chem. Soc.* **2001**, *123*, 2182.

[8] In neutral, zwitterionic species such as *closo*-$B_{12}H_{10}(SMe_2)_2$ the B_{12} cluster retains 26 skeletal electrons and thus two negative charges are delocalized throughout the icosahedral cluster.

[9] M. Fujimori, K. Kimura, *J. Solid State Chem.* **1997**, *133*, 178 – 181.

[10] C. E. Housecroft, *Angew. Chem.* **1999**, *111*, 2883 – 2885; *Angew. Chem. Int. Ed.* **1999**, *38*, 2717 – 2719.

[11] A. Maderna, C. B. Knobler, M. F. Hawthorne, *Angew. Chem.* **2001**, *113*, 1710; *Angew. Chem. Int. Ed.* **2001**, *40*, 1661.

[12] a) Cs[PPN]-**2**, triclinic, space group $P\bar{1}$, $a = 9.986(2)$, $b = 14.039(3)$, $c = 18.441(4)$ Å, $\alpha = 90.062(4)$, $\beta = 93.348(3)$, $\gamma = 90.238(4)°$, $V = 2580.6(8)$ Å^3, $Z = 1$, $2\theta_{max} = 56.6°$, $\rho = 1.343$ Mg m^{-3}, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, 100 K. Of the 11868 uniqe reflections measured, 7291 were considered observed ($I > 2\sigma(I)$). Data were corrected for Lorentz and polarization effects but not for absorption, $\mu = 0.455$ mm^{-1}. The structure was solved by statistical methods. $R = 0.042$, $wR = 0.065$.; b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148658 (**2**), CCDC-148659 (Cs[PPN]-**2**) and CCDC-148660 ([PPN]-**2** · C_6H_6). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] [PPN]-**2** · C_6H_6, triclinic, space group $P\bar{1}$, $a = 17.761(8)$, $b = 18.786(8)$, $c = 20.588(9)$ Å, $\alpha = 65.156(7)$, $\beta = 65.725(8)$, $\gamma = 63.417(8)°$, $V = 5360(4)$ Å^3, $Z = 2$, $2\theta_{max} = 56.66°$, $\rho = 1.259$ Mg m^{-3}, $\lambda(Mo_{K\alpha}) = 0.71069$ Å^3, 100 K. Of the 24400 unique reflections measured, 14575 were considered observed ($I > 2\sigma(I)$). Data were corrected for Lorentz and polarization effects but not for absorption, $\mu = 0.106$ mm^{-1}. The structure was solved by statistical methods. $R = 0.073$, $wR = 0.186$.

[14] **2**, triclinic, space group $P\bar{1}$, $a = 10.107(3)$, $b = 15.014(4)$, $c = 15.033(4)$ Å, $\alpha = 114.893(4)$, $\beta = 103.118(5)$, $\gamma = 102.823(5)°$, $V = 1880.8(9)$ Å^3, $Z = 1$, $\rho = 1.25$ Mg m^{-3}, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, 100 K. Of the 11869 unique reflections measured, 8403 were considered observed ($I > 2\sigma(I)$). Data were corrected for Lorentz and polarization effects, and for absorption, $\mu = 0.079$ mm^{-1}. The structure was solved by statistical methods. $R = 0.048$, $wR = 0.118$.

[15] J. Donohue, *The Structures of the Elements*, Wiley, New York, **1974**, pp. 48 – 82.

Parity Violation in Fluorooxirane[**]

Robert Berger, Martin Quack,[*] and Jürgen Stohner

Dedicated to Professor Paul von Ragué Schleyer
on the occasion of his 70th birthday

Van't Hoff pointed out more than a century ago[1] that the heat of formation and the entropy of enantiomers of chiral molecules must be exactly equal for symmetry reasons. Traditional quantum chemistry which only includes the electromagnetic interaction finds just this symmetry.[2] However, electroweak quantum chemistry which includes parity violation predicts an energy and entropy difference. One of the greatest challenges in the current understanding of fundamental aspects of the structure and dynamics of chiral molecules concerns the experimental proof of the role of parity violation because of the weak nuclear interaction.[3] Experimental spectroscopic approaches have been proposed for some time. One of these approaches is to measure directly the heat of reaction $\Delta_r H_0^0$ for the transformation of *S* into *R* enantiomers which is related to the parity violating energy difference $\Delta_{pv}E$[3, 4] as shown in Equation (1).

$$\Delta_r H_0^0 \ (S \rightleftarrows R) \approx N_A \Delta_{pv} E \tag{1}$$

Another approach is measuring certain frequency shifts of the enantiomers, for instance in NMR,[5] microwave,[6] IR,[6–10] or Mößbauer[11] spectra of *R* and *S* enantiomers (see the diagram in Figure 1).

The recent theoretical discovery[12, 13] that parity-violating effects in chiral molecules are typically one to two orders of magnitude larger than previously anticipated[14, 15] has stimulated intensified theoretical[16–22] and experimental interest[6, 10, 11] in this field. Of particular importance are experi-

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[**] This work is supported financially by the Schweizerischer Nationalfonds and ETH Zürich (including C^4 and CSCS)