Inorganic Chemistry

Synthesis of Boron-Iodinated *o*-Carborane Derivatives. Water Stability of the Periodinated Monoprotic Salt

Francesc Teixidor,[†] Gemma Barberà,[†] Clara Viñas,^{*,†} Reijo Sillanpää,[‡] and Raikko Kivekäs[§]

Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, E-08193 Bellaterra, Spain, Department of Chemistry, University of Jyväskylä, FIN-40351 Jyväskylä, Finland, and Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland

Received January 20, 2006

Boron periodination of *o*-carborane has been achieved by taking account of the fact that B atoms in the cluster are of two types, i.e., those adjacent to both C atoms and the remainder. The high number of nonequivalent leaving groups opens the possibility through B–C coupling to materials with novel possibilities and to self-assembling due to the enhanced polarizability of the C–H bond. Periodination has accentuated the acidity of the carborane, and monoprotic salts are stable in water.

Highly iodinated molecular species are of great interest in medical applications¹ as well as in materials science, as demonstrated by the many studies on C_6I_6 for which even superconductivity was found.² Boron cluster compounds would be ideal for incorporating a large number of I atoms. However, whereas substitutions have been achieved with good success with the cluster anions, this was not the case in 1,2-dicarba-*closo*-dodecaborane (*o*-carborane or 1,2-*closo*- $C_2B_{10}H_{12}$; Figure 1). The latter are, nevertheless, the most intensively investigated of the borane and heteroborane clusters.³

The paucity of reported examples is in agreement with the relative rates of halogenation, which decrease in the order $[B_{12}H_{12}]^{2-} > [CB_{11}H_{12}]^{-} > C_2B_{10}H_{12}$.⁴ While perfluorination⁵ and perchlorination⁶ of dicarbaboranes have been obtained, perbromination and periodination of *o*-carborane have never been achieved. Although reference to tetrasubstitution at the

- [†] Institut de Ciència de Materials de Barcelona.
- [‡] University of Jyväskylä.
- [§] University of Helsinki.
- (1) Ell, P. J.; Gambhir, S. Nuclear Medicine in Clinical Diagnosis and Treatment, 3rd ed.; Elsevier: New York, 2004.
- (2) Nakayama, A.; Fujihisa, H.; Aoki, K.; Carlon, R. P. Phys. Rev. B 2000, 62 (13), 8759.
- (3) (a) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970.
 (b) Bregadze, V. I. *Chem. Rev.* 1992, 92, 209.
- (4) Jelínek, T.; Plešek, J.; Mareš, F.; Heřmánek, S.; Štíbr, B. Polyhedron 1987, 6, 1981.
- (5) Kongpricha, S.; Schroeder, H. Inorg. Chem. 1969, 8, 2449.
- (6) (a) Sieckhaus, J. F.; Semenuk, N. S.; Knowles, T. A.; Schroeder, H. Inorg. Chem. 1969, 8, 2452. (b) Schroeder, H.; Heying, T. L.; Reiner, J. R. Inorg. Chem. 1963, 2, 1092.
- 3496 Inorganic Chemistry, Vol. 45, No. 9, 2006



Figure 1. Vertex numbering in 1,2-closo- $C_2B_{10}H_{12}$, o-carborane.

8, 9, 10, and 12 positions had been made on *o*-carboranes,⁷ well-defined synthetic procedures existed only for 9,12-I₂-1,2-*closo*-C₂B₁₀H₁₀.⁸ A major progress was achieved upon the synthesis of 4,5,7,8,9,10,11,12-I₈-1,2-*closo*-C₂B₁₀H₄.⁹

The C's adjacent positions B(3,6) did not iodinate because these are the most electron-deficient sites in the molecule. Calculations on 1,2-*closo*-C₂B₁₀H₁₂, at the B3LYP/6-31G* level,¹⁰ have shown that Mulliken charges are considerably more positive at B(3,6) than at B(8,9,10,12) (+0.017 vs -0.061).¹¹ Therefore, the strongest halogenating agents F⁺ and Cl⁺ are capable of substituting all B atoms, but the weakest, Br⁺ and I⁺, do not.¹² This led us to consider the positive B(3,6) atoms separately from the rest, and in this way, 3,4,5,7,8,9,10,11,12-I₉-1,2-*closo*-C₂B₁₀H₃,¹³ along with 3,6,9-I₃-1,2-*closo*-C₂B₁₀H₉, 3,9,12-I₃-1,2-*closo*-C₂B₁₀H₉, and 3,6,9,12-I₄-1,2-*closo*-C₂B₁₀H₈, B-substituted species were synthesized.¹⁴ There remained the periodinated 1,2-

- (9) Srivastava, R. R.; Hamlin, D. K.; Wilbur, D. S. J. Org. Chem. 1996, 61, 9041.
- (10) Gaussian 98; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (11) Teixidor, F.; Barberà, G.; Vaca, A.; Kivekäs, R.; Sillanpää, R.; Oliva, J.; Viñas, C. J. Am. Chem Soc. 2005, 127, 10158.
- (12) Plešek, J.; Plzák, Z.; Stuchlík, J.; Heřmánek, S. Collect. Czech. Chem. Commun. 1981, 46, 1748.
- (13) (a) Barberà, G.; Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Eur. J. Inorg. Chem.* **2003**, 1511. (b) Barberà, G.; Teixidor, F.; Welch, A. J.; Rosair, G. M.; Viñas, C. *Boron Chemistry at the Beginning of the 21st Century*; Russian Academy of Science: Moscow, 2003; pp 192–197.
- (14) Yamazaki, H.; Ohta, K.; Endo, Y. Tetrahedron Lett. 2005, 46, 3119.

10.1021/ic060124y CCC: \$33.50 © 2006 American Chemical Society Published on Web 03/28/2006

^{*} To whom correspondence should be addressed. E-mail: clara@icmab.es. Tel: 34 93 5801853 (ext. 242). Fax: 34 93 5805729.

^{(7) (}a) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, *3*, 607. (b) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *37*, 2460. (c) Stanko, V. I.; Brattsev, V. A.; Vostrikova, T. N.; Danilova, G. N. Zh. Obshch. Khim. **1968**, *38*, 1300.

^{(8) (}a) Li, J.; Logan, C. M.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 4866.
(b) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, *3*, 575.



Figure 2. Perspective view of **1** with 30% ellipsoids. Selected bond lengths (Å): C1-C2, 1.640(9); B-I, 2.126(8)-2.158(8).

Scheme 1. Synthesis of the Periodinated Carboranes



 $H_2-1,2$ -closo- $C_2B_{10}I_{10}$ (1) to be made. In this paper, we report on this first all iodinated B-substituted o-carborane, its unprecedented acid properties, and the stability of the monoanionic species in water. Starting from [3-I-7,8-nido- $C_2B_9H_{11}$]^{-,15} the first step consists of producing 3,6-I₂-1,2 $closo-C_2B_{10}H_{10}$ (2).^{14,16} The first total boron periodination was achieved by reacting 2 with triflic acid and ICl to yield 1 (Scheme 1). In a typical experiment, 2 (1.00 g, 2.50 mmol) was dissolved in triflic acid (10 g) and ICl (6 mL) and refluxed at 90 °C for 5 days. After workup, a 73% yield of 1 was obtained. The ${}^{11}B{}^{1}H{}$ NMR shows a pattern 2:2:4:2 in which no boron resonance splits in ¹¹B NMR, confirming that all B atoms have one exocluster I. The structure of 1 was confirmed by X-ray diffraction analysis as the 1. 1.350DMSO \cdot 0.650acetone adduct (DMSO = dimethyl sulfoxide).¹⁷ (Figure 2) In the adduct, weak C-H···O interactions, with C····O distances of 2.92-3.01 Å, between the cluster C-H and the disordered solvent molecules are found.



Figure 3. ¹¹B NMR spectra of **1** (A) in DMSO- d_6 and after additions of *t*-BuOK in ratios 1:0.2 (B), 1:0.4 (C), 1:0.8 (D), and 1:1 (E).

This implies that the C-H bond is polarized, a fact that is corroborated by the C-H resonance shifts in the¹H NMR of 2 (4.1 ppm) and 1 (7.4 ppm). A continuous C-Hdownfield chemical shift is observed paralleling an increasing number of I atoms, 1,2-closo-C₂B₁₀H₁₂ (3.6 ppm), 3-I-1,2closo-C₂B₁₀H₁₁ (3.8 ppm), 3,6-I₂-1,2-closo-C₂B₁₀H₁₀ (4.1 ppm), and 1 (7.4 ppm), and an increasing acidity. The C-Hshift of 1,2-*closo*-C₂B₁₀H₁₂ is slightly acid, $pK_a = 22$ but requires strong bases to be removed.¹⁸ Would it then be possible to remove the C-H protons in highly iodinated carborane derivatives with relatively weak bases? Would their conjugate acids not be regenerated in water? In 1963, Schroeder et al. reported^{6b} the preparation of [HNEt₃]₂[1,2 $closo-C_2B_{10}Cl_{10}$, which is stable in aqueous media. They reacted NEt₃ and 1,2-H₂-1,2-closo-C₂B₁₀Cl₁₀ in benzene or ethanol. The existence of this salt was later put in doubt by Zakharkin and Ogorodnikova, who proved that in aqueous ethanol 1,2-H₂-1,2-closo-C₂B₁₀Cl₁₀ behaved as a monoprotic acid and not as a diprotic acid.18 The 1H NMR spectrum of $1,2-H_2-1,2-closo-C_2B_{10}Cl_{10}$ indicating that CH's at 5.9 ppm was given. Additionally, the value of the experimental pK_a was 6.98.¹⁸ According to the ¹H NMR data, the pK_a of 1,2- H_2 -1,2-*closo*- $C_2B_{10}Cl_{10}$ should be more positive than that of 1, and possibly a water-stable salt of a carborane derivative could be produced. Upon dissolution of 1 in CD₃OD and the addition of 1 equiv of t-BuOK, the ¹H NMR C-H resonance originally present at 7.4 ppm was eliminated. The ¹¹B NMR spectrum presented an abrupt change, now showing three peaks at -7.7, -14.9, and -21.1 ppm. A further addition of t-BuOK did not produce any change in the spectrum. The same experiment was run again in DMSO- d_6 with different ratios of **1** to *t*-BuOK, 1:0, 1:0.2, 1:0.4, 1:0.8, and 1:1. The results are presented in Figure 3. Labels A-E refer to the different spectra from 1,2-H₂-1,2-closo-C₂B₁₀I₁₀ (A) to $[1,2-C_2B_{10}I_{10}H]^-$ (E). When water was added to the methanolic or DMSO solution of $[1,2-C_2B_{10}I_{10}H]^-$, the spectrum remained unaltered and protonation did not occur. Subsequent tests were directly performed in water, in which **1** is insoluble, but the addition of $HNEt_2$ (p $K_a = 10.9$) leads

⁽¹⁵⁾ Barberà, G.; Viñas, C.; Teixidor, F.; Welch, A. J.; Rosair, G. M. J. Organomet. Chem. 2002, 657, 217.

⁽¹⁶⁾ Vaca, A.; Barberà, G.; Viñas, C.; Teixidor, F.; Sillanpää, R.; Kivekäs, R.; Oliva, J. M. The 3rd European Meeting on Boron Chemistry, Sept 2004; Abstract 02.

⁽¹⁷⁾ Crystals were obtained from a DMSO/acetone (1:5) mixture. Crystal data: C_{6.650}H₁₄B₁₀I₁₀O₂S_{1.350} or C₂H₂B₁₀I₁₀•1.350DMSO•0.650acetone; orthorhombic; *Pbca* (No. 61); colorless; a = 17.0878(2) Å; b = 19.0063(2) Å; c = 19.9227(2) Å; V = 6470.41(12) Å³; Z = 8; $D_{calcd} = 3.175$ g cm⁻³; μ (Mo K α) = 9.673 mm⁻¹; data collection temperature 173 K; R1 = 0.0318; wR2 = 0.0535 [$I > 2\sigma(I)$]; GOF on $F^2 = 1.023$. Full details are described in the Supporting Information.

 ^{(18) (}a) Zakharkin, L. I.; Ogorodnikova, N. A. J. Organomet. Chem. 1968, 12, 13. (b) Leites, L. A.; Ogorodnikova, N. A.; Zakharkin, L. I. J. Organomet. Chem. 1968, 15, 287.

COMMUNICATION

to gradual dissolution. After total dissolution, the ¹¹B NMR spectrum is identical with that obtained after the addition of 1 equiv of *t*-BuOK in either DMSO or methanol.

The addition of acids with strength higher than or equal to $pK_a = 2.9$, i.e., HCl ($pK_a = -7$), CCl₃COOH ($pK_a = 0.6$), and CH₂ClCOOH ($pK_a = 2.9$), led to insoluble 1. This is not the case for CH₃COOH ($pK_a = 4.7$), which is unable to protonate the species existing in E. Therefore, the pK_a of 1 must lie between 2.9 and 4.7, being a stronger acid than 1,2-H₂-1,2-*closo*-C₂B₁₀Cl₁₀, in agreement with the ¹H NMR C-H resonance. Can the fully deprotonated species be generated? Our experiments show that the addition of more than 1 equiv of a strong base gradually leads to degradation of the cluster. We have tested this with n-BuLi in dimethyl ether and t-BuOK in ethanol. As a last test, [N(PPh₃)₂]Cl was added to the aqueous solution of $[1,2-closo-C_2B_{10}I_{10}H]^-$, and $[N(PPh_3)_2][1,2-closo-C_2B_{10}I_{10}H]$ was precipitated. Similarly, [N(PPh₃)₂]Cl in methanol was added to the methanolic solution of $[1,2-closo-C_2B_{10}I_{10}H]^-$ to produce the same salt.

The MALDI-TOF-MS spectrum showed a peak at m/z 1402.4 (C₂B₁₀I₁₀H⁻), which demonstrates the monoanionic character of the cluster. This work has permitted isolation for the first time of a water-stable salt of the 1,2-*closo*-C₂B₁₀H₁₂ derivative, through the synthesis of the boron-periodinated *o*-carborane **1**. This is more acidic than its chlorinated homologues and permits the isolation of [N(PPh₃)₂][1,2-*closo*-C₂B₁₀I₁₀H]. Our interpretation of Schroeder's salt⁹ is that an adduct C–H···N is generated. It was already treated as an adduct by Zakharkin and Ogoronikova.¹⁸

Acknowledgment. This work was supported by Generalitat de Catalunya (Grant 2001/SGR/00337) and CICYT (Project MAT03-01108).

Supporting Information Available: Experimental data for **1** and **2** and crystallographic data (CIF) for **1**·1.350DMSO·0.650acetone. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060124Y