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Dodecamethylcarba-*closo*-dodecaborate(−) Anion, $CB_{11}Me_{12}^-$

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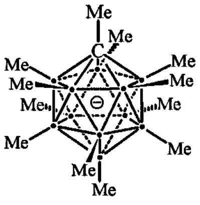
Very weakly nucleophilic anions[1] have been of interest for many applications, such as optimization of solid ionic electrolytes,[2] stabilization of unusual cations,[3,4] production of weakly ligated ("naked") cations in solution for Lewis acid catalysis of polymerization,[5] pericyclic,[6,7] and other[7] reactions, etc. A minimally nucleophilic anion should presumably have a structure that guarantees a firmly bound highly dispersed charge and contains no exposed lone pairs, aromatic rings, multiple bonds, or electron-rich termini of single bonds. Preferably, it should be reasonably stable to fragmentation and to acids, bases, oxidants, and UV radiation, and it should induce solubility in low-polarity solvents. Even the least nucleophilic anions known presently,[1] such as various tetraarylborates,[8,9] tetraalkylaluminates,[10] and deltahedral carba-*closo*-borate(−)s,[4,11] do not meet all of these requirements. We report a simple two-step synthesis of the icosahedral dodecamethylcarba-*closo*-dodecaborate(−) anion (**1**, $CB_{11}Me_{12}^-$),[12] which meets the structural criteria, but still falls a little short in terms of oxidizability and acid resistance.



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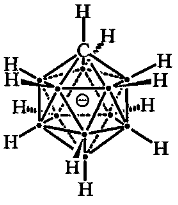

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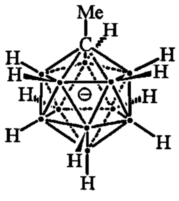

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Trimethylammonium carba-*closo*-dodecaborate(−) (**2**, $CB_{11}H_{12}^-$)[13,14] was methylated on carbon in 92% yield using the general procedure for C-alkylation.[15] The $(CH_3)_4N^+$ salt of the resulting 1-methylcarba-*closo*-dodecaborate(−) anion[16,17] (**3**, $MeCB_{11}H_{11}^-$) was permethylated with excess methyl triflate in the presence of 2,6-di-*tert*-butylpyridine and CaH_2, then converted to a Ph_4P^+ salt of **1** by ion exchange[18] (after a crystallization from MeOH, >98% purity,[19] 48% yield). It was converted into the Ag^+, Li^+, Cs^+, $PhMe_2NH^+$, and Me_3NH^+ salts of **1** by ion exchange on the acidic form of the resin and neutralization and/or precipitation. The presence of a hindered base[20] in the methylation reaction is essential for preventing side reactions and securing an acceptable yield of pure **1**.

We are not aware of prior reports of successful electrophilic alkylation of deltahedral carborane anions. Electrophilic alkylation of the neutral *o*-carborane under Friedel−Crafts conditions using other reagents was reported some time ago but did not lead to persubstitution.[21] An independent communication of a successful permethylation of BH vertices in a neutral *p*-carborane ($1,12-Me_2C_2B_{10}H_{10}$) with a methyl triflate−triflic acid mixture appeared[22] soon after our conference report.[12] However, under such conditions, the much more reactive **2** is converted into products other than **1**. We have also prepared several partially methylated derivatives of **2** and **3** by the recently modified[12] monoiodination procedure[23] or by polyiodination,[12] followed by coupling[24] of the iodo derivatives with CH_3MgI under Pd catalysis.

The structure of **1** follows from an X-ray diffraction analysis of a single crystal of the salt $\mathbf{1}\cdot PhMe_2NH\cdot CH_3OH$, which contains a solvent of crystallization hydrogen bonded to the cation (Figure 1).[25] The closest intermolecular contact between

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

(2) MacCullum, J. R.; Vincent, C. A., Eds. *Polymer Electrolyte Reviews*; Elsevier Applied Science: New York, Vol. 1, 1987; Vol. 2, 1989.

(3) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191.

(4) Xie, Z.; Bau, R.; Reed, C. A. *Inorg. Chem.* **1995**, *34*, 5403. Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* In press.

(5) Jordan, R. F. In *Advances in Organometallic Chemistry*; Academic Press: New York, 1991; Vol. 32, p 325. Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728.

(6) Braun, R.; Sauer, J. *Chem. Ber.* **1986**, *119*, 1269. Föhlisch, B.; Krimmer, D.; Gerlach, E.; Kashammer, D. *Chem. Ber.* **1988**, *121*, 1585. Forman, M. A.; Dailey, W. P. *J. Am. Chem. Soc.* **1991**, *113*, 2761. Grieco, P. A. *Aldrichim. Acta* **1991**, *24*, 59. Jiao, H.; von Ragué Schleyer, P. *Angew. Chem., Int. Ed. Engl.* **1993,** *32*, 1760. Pagni, R. M.; Kabalka, G. W.; Bains, S.; Plesco, M.; Wilson, J.; Bartmess, J. *J. Org. Chem.* **1993**, *58*, 3130. Jiao, H.; von Ragué Schleyer, P. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1559. Jiao, H.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1995**, *117*, 11529.

(7) Santelli, M.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC Press: Boca Raton, 1996.

(8) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430.

(9) Boudjouk, P.; Bahr, S. R. *J. Org. Chem.* **1992**, *57*, 5545. Bahr, S. R.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 4514.

(10) Medley, J. H.; Ahmad, N.; Day, M. C. *Can. J. Chem.* **1985**, *63*, 2906.

(11) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402. Xie, Z.; Liston, D. J.; Jelínek, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384.

(12) Janoušek, Z.; Grüner, B.; Trammell, M.; Michl, J. *Book of Abstracts*, 209th ACS National Meeting, Anaheim, CA, April 2−6; American Chemical Society: Washington, DC, 1995; ORGN 315.

(13) Knoth W. H. *J. Am. Chem. Soc.***1967**, *89*, 1274. Plešek, J.; Jelínek, T.; Drdáková, E.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1559.

(14) Purchased from Katchem, Ltd., El. Krásnohorské 6, 11000 Praha 1, Czech Republic.

(15) Jelínek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, 1982.

(16) $^1H\{^{11}B\}$ NMR (acetone-d_6) δ 3.42 [s, 12H, $N(CH_3)_4$], 1.74 [s, 5H], 1.54 [s, 5H], 1.50 [s, 3H, $CH_3(1)$], 1.46 [s, 1H, H(12)]; $^{11}B\{^1H\}$ NMR δ −11.09 [s, B(12)], −12.83 [s, 10B, B(2−11)]; ^{13}C δ 55.84 [t, $N(CH_3)_4$], 27.68 [s, $CH_3(1)$]; IR (Cs^+ salt, KBr pellet) 487, 728, 938, 1039, 1194, 1311, 1383, 1458, 2544, 2875, 2938 cm^{-1}. For PPh_4^+ salt: Anal. Calcd for $C_{26}B_{11}H_{34}P$: C, 62.91; H, 6.90. Found: C, 63.20; H, 6.84.

(17) ^{11}B referenced to the $B(OMe)_3$ signal at δ 18.1.

(18) CaH_2 (4.5 g, 108 mmol), 2,6-di-*tert*-butylpyridine (17.9 g, 93.7 mmol), $\mathbf{3}\cdot N(CH_3)_4$ (1.65 g, 7.14 mmol), and methyl triflate (27.9 g, 170 mmol) were stirred under Ar at 0 °C for 10 h and then at 25 °C for 36 h, filtered, quenched with 5% NaOH, extracted with Et_2O-Me_2CO (70/30), and dried over $MgSO_4$. 2,6-Di-*tert*-butylpyridine was recovered by vacuum distillation and the residue was dissolved in MeOH, passed through methanolic Amberlyst XN-1010 (acid form), treated with methanolic PPh_4Cl (4 g, 10.7 mmol), and crystallized from MeOH.

(19) After three recrystallizations from MeOH: Anal. Calcd for $C_{37}B_{11}H_{56}P$: C, 68.29; H, 8.68. Found: C, 68.15; H, 8.74.

(20) Arnap, J.; Kenne, L.; Lindberg, B.; Lönngren, J. *Carbohydr. Res.* **1975**, *44*, C5.

(21) The reaction produced complex mixtures from which several alkyl derivatives were isolated by HPLC: Plešek, J.; Plzák, Z.; Stuchlík, J.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1981**, *46*, 1748.

(22) Jiang, W.; Knobler, C. B.; Mortimer, M. D.; Hawthorne, M. F. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1332.

(23) Jelínek, T.; Plešek, J.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1986**, *51*, 819.

(24) Analogous to the known conversion of B-iodo-*o*-carboranes to alkyl- and aryl-*o*-carboranes: Zakharkin L. I.; Kovredov, A. I.; Ol'shevskaya, V. A.; Shaugumbekova, Zh. S. *J. Organomet. Chem.* **1982**, *226*, 217. Li, J.; Logan, C. F.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 4866. Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095.

(25) Crystal data: $[C_6H_5NH(CH_3)_2^+]\cdot\mathbf{1}\cdot CH_3OH$: orthorhombic, a = 13.1241 (10) Å, b = 13.2373(10) Å, c = 17.0648(13) Å, space group $P2_12_12_1$; $Z = 4$; $\rho_{calc} = 1.043$; $R_1 = 0.0690$ ($F \geq 4\sigma(F)$), $wR_2 = 0.1660$ (all data); 11821 reflections used. Intensity data were collected at 123 K on a Siemens SMART CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å).

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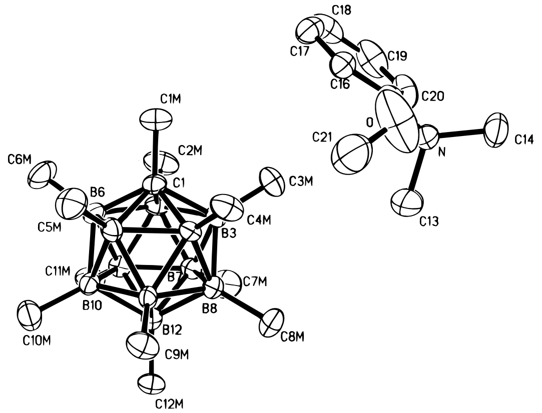

Figure 1. Structure of $[C_6H_5NH(CH_3)_2{}^+]\cdot\mathbf{1}\cdot CH_3OH$. Hydrogen atoms are omitted for clarity. The minor component of disordered methanol is not shown.

Table 1. Selected Interatomic Distances in **1** (Å)[a]

bond type	distance	bond type	distance
C1−B2	1.73(2)	C1−C1M	1.520(5)
B2−B3	1.78(2)	B2−C2M	1.59(2)
B2−B7	1.773(14)	B7−C7M	1.59(2)
B7−B8	1.786(14)	B12−C12M	1.601(6)
B7−B12	1.786(9)		

[a] Averaged over the 5-fold symmetry.

the anion **1** and its counterion is a 2.42-Å distance between an H atom of **1** and an H atom of one of the $PhMe_2NH^+$ methyl groups.

The positions of the C and B atoms in **1** fit the expected 5-fold symmetry nearly perfectly. Among interatomic distances (Table 1), the average $B-CH_3$ bond length of 1.59 Å can be compared to the 1.58 Å reported for neutral permethylated *p*-carborane.[22] The C1 and the B2−B12 atoms lie on the surface of a slightly flattened sphere, with a C(1)−B(12) diameter of 3.27 Å and an average B−B diameter of 3.39 Å, compared with 3.21 and 3.39 Å for **2**.[26] For the methyl carbon atoms, the diameters are 6.39 and 6.56 Å, and for the methyl hydrogen atoms, they are 7.39 and 7.56 Å. With 1.2 Å for the van der Waals radius of H, the short "vertex-to-vertex" diameter of **1** is 9.79 Å and the long one is 9.96 Å. These can be compared with the diameters of the spheres defined by the carbon atoms of C_{60} and by the outer van der Waals radii of its C atoms, 7.02 and 10.7 Å, respectively.[27]

Room temperature spectral properties of **1** reflect an effective pentagonal symmetry, as shown by the NMR of the Ph_4P^+ salt in acetone-d_6: ^{1}H NMR δ 0.802 [s, 3H, $CH_3(1)$], −0.330 [s, 15H, $CH_3(2-6)$], −0.400 [s, 15H, $CH_3(7-11)$], −0.505 [s, 3H, $CH_3(12)$]; ^{11}B NMR[17] δ −0.60 [s, 1B, B(12)], −8.67 [s, 5B-(7−11)], −10.70 [s, 5B(2−6)]; ^{13}C{H} δ −3 [vb, $CH_3(2-12)$], 13.31 [s, $CH_3(1)$]. The assignments are based on 2-D COSY and $^{11}B-^{1}H$ HETCOR spectra. Vibrational spectra were obtained on the Cs^+ salt: IR (KBr pellet) 913, 1150, 1304, 1438, 2827, 2893, 2928 cm^{-1}, Raman (powder) 418, 433, 458, 2831, 2903 cm^{-1}. The expected isotopic distribution of masses is observed in electrospray MS (base peak at *m/e* 311). In the UV (10^{-3} M Li salt in H_2O), **1** shows only end absorption, starting slowly at about 240 nm (under these conditions, **3** shows similar end absorption starting only below 200 nm). The anodic oxidation potential of **1** in acetonitrile is 1.6 V (Bu_4NF, Ag/AgCl; ferrocene, 0.45 V), whereas **2**[15,28] and **3** show no oxidation wave up to 2.0 V (BPh_4^-: 1.0 V,[29] $B(C_6F_5)_4^-$: 2.5 V[1]). Both the shifted end absorption in the UV and the easier oxidation are attributed to the cumulative electron donor effect of the methyl groups.

Salts of **1** appear to be very stable to air, bases (several days in saturated KOH/EtOH), and dilute acids (overnight in 5% H_2SO_4/Et_2O), but are destroyed after several hours in concentrated H_2SO_4 or CF_3SO_3H. The solubility of the hydrated Li^+ salt of **1** is extreme in polar solvents, very high in chloroform, and fair in carbon tetrachloride and toluene.

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Supporting Information Available: Details of the crystallographic analysis of **1** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[26] Shelly K.; Finster D. C.; Young J. L.; Scheidt W. R.; Reed C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.

[27] Gorun, S. M.; Greaney, M. A.; Day, V. W.; Day, C. S.; Upton, R. M.; Briant, C. E. In *Fullerenes*; Hammond, G. S., Kuck, V. J., Eds; ACS Symposium Series 481; American Chemical Society: Washington, DC, 1992; p 41. Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S. in *Fullerenes*; Hammond, G. S., Kuck, V. J. Eds; ACS Symposium Series 481; American Chemical Society: Washington, DC, 1992; p 91.

[28] Wiersema, R. J.; Hawthorne, M. F. *Inorg. Chem.* **1973**, *12*, 785.

[29] In MeCN, 0.92 V vs. SCE: Bancroft, E. E.; Blount, H. N.; Janzen, E. G. *J. Am. Chem. Soc.* **1979**, *101*, 3692. Under these conditions, the oxidation potential of ferrocene is 0.38 V: Chang, D.; Malinski, T.; Ulman, A.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 817.