Synthesis of Schiff Bases Derived from the Ammoniaundecahydro-*closo*-dodecaborate(1−) Anion, $[B_{12}H_{11}NH{=}CHR]^-$, and Their Reduction into Monosubstituted Amines $[B_{12}H_{11}NH_2CH_2R]^-$: A New Route to Water Soluble Agents for BNCT

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The reaction of $[B_{12}H_{11}NH_3]^-$, the amino derivative of the *closo*-dodecaborate anion, with aldehydes in methanol in the presence of catalytic amounts of alkali gives N-protonated Schiff bases $[B_{12}H_{11}NH{=}CHR]^-$ (R = C_6H_5, 2-C_6H_4OMe, 4-C_6H_4OMe, 4-C_6H_4SMe, 4-$C_6H_4NMe_2$, 4-$C_6H_4NHCOMe$, 4-C_6H_4CN, 4-C_6H_4Br, 4-C_6H_4Cl, 3,4-$C_6H_3O_2CH_2$, 1-$C_{10}H_7$, 2-$C_{10}H_7$, CH=CHMe, CH=CHPh). Reduction of the Schiff bases with $NaBH_4$ in aqueous 2-propanol gives quantitatively the corresponding monoalkylamino derivatives $[B_{12}H_{11}NH_2CH_2R]^-$ (R = 2-C_6H_4-OMe, 3,4-$C_6H_3O_2CH_2$, 4-$C_6H_4NHCOMe$, 4-C_6H_4CN). *closo*-Dodecaborate derivatives containing amino, carboxy, and isothiocyanate functions on aromatic rings, $[B_{12}H_{11}NH_2CH_2C_6H_4$-4-$NH_2]^-$, $[B_{12}H_{11}NH_2CH_2C_6H_4$-4-$COOH]^-$, and $[B_{12}H_{11}NH_2CH_2C_6H_4$-4-$NCS]^-$, were prepared. Functionalized derivatives of the $[B_{12}H_{12}]^{2-}$ anion can be used in BNCT and as a linker for iodination and astatination of biomolecules for radioimmunodetection and for radioimmunotherapy. The structures of Schiff bases $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-$NMe_2]$*$CHCl_3$ (**I**) and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-2-OMe] (**II**) were determined by single-crystal X-ray diffraction. **I** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ and unit cell dimensions $a = 11.465(6)$ Å, $b = 21.314(7)$ Å, $c = 16.625(6)$ Å, $\beta = 101.38(3)°$. Crystals **II** belong to the monoclinic space group $P2_1/c$ system, $a = 10.282(2)$ Å, $b = 20.272(5)$ Å, $c = 17.052(3)$ Å, $\beta = 105.31(2)°$, $Z = 4$. The trans configuration of the protonated imino group was established (B−N = 1.517(7) and 1.525(4) Å, $N-C_{im}$ = 1.274(6) and 1.274(3) Å, $C_{im}-C_{ar}$ = 1.421(7) and 1.437(4) Å, for **I** and **II**, respectively). A strong intramolecular hydrogen bond between the imine hydrogen and the methoxy oxygen in the ortho position of the benzene ring (N···O = 2.714(4) Å, N−H = 0.93(2) Å, H_N···O = 1.98(2) Å, N−H···O = 135(2)°) was found in **II**.

Introduction

Dodecahydro-*closo*-dodecaborate(2−) anion $[B_{12}H_{12}]^{2-}$ and carboranes $C_2B_{10}H_{12}$ have been considered for a long time as promising boron moieties for boron neutron capture therapy.[1,2] The main advantages of the $[B_{12}H_{12}]^{2-}$ anion and its derivatives are their high water solubility as sodium salts and simple methods of the parent anion synthesis from ^{10}B-enriched raw material. The main problems of the $[B_{12}H_{12}]^{2-}$ synthetic chemistry compared to that of carborane are the absence of a distinguished reaction center due to its high, close to spherical, symmetry and high reactivity with respect to electrophiles that often give mixtures of products with various substitution degrees. To avoid this complication, the primary introduction of a reaction center (−OH,[3,4] −SH,[3,5,6] $-NH_2$,[7] or −I[8,9]) is necessary.

Study of the $[B_{12}H_{11}OH]^{2-}$ chemistry[10,11] showed that $[B_{12}H_{11}OH]^{2-}$ is a very weak nucleophile and its alkylation requires basic conditions. Alkylation of the $[B_{12}H_{11}SH]^{2-}$ anion generally results in disubstituted sulfonium derivatives $[B_{12}H_{11}SR_2]^-$ that require the use of a special technique to protect the sulfur atom.[12] The possibility of formation of a B−C bond by the palladium-catalyzed coupling of $[B_{12}H_{11}I]^{2-}$ with Grignard reagents was demonstrated recently.[13]

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Alkylation of the $[B_{12}H_{11}NH_3]^-$ anion was also studied.[7,14−16] It was shown that the use of short-chain alkylating agents results in the formation of trialkyl derivatives $[B_{12}H_{11}NR_3]^-$ (R = CH_3, C_2H_5). An increase of the substituent size leads to the appearance of sterical hindrance and formation of dialkyl derivatives $[B_{12}H_{11}NHR_2]^-$ (R = $CH(CH_3)_2$, $CH_2C_6H_5$, $CH_2C_{10}H_7$, $C_{12}H_{25}$, $C_{16}H_{33}$, CH_2-18-crown-6; R_2 = $-CH_2CH_2(OCH_2CH_2)_4-$). Synthesis of the monoalkylated derivatives is problematic. Using the reaction of $[B_{12}H_{11}NH_3]^-$ with 2-chloro-10-(3-bromopropyl)-phenothiazine as an example, it was shown that formation of the mixture of mono- and disubstituted derivatives takes place even at a 1:1 stoichiometric ratio of reagents.

In this paper we report a synthesis of Schiff bases derived from ammoniaundecahydro-*closo*-dodecaborate anion $[B_{12}H_{11}NH{=}CHR]^-$ and their reduction into monosubstituted amines $[B_{12}H_{11}NH_2CH_2R]^-$ which enables a convenient preparation of BNCT agents on the base of the $[B_{12}H_{12}]^{2-}$ anion.

Experimental Section

General Considerations. Tetrabutylamonium ammoniaundecahydro-*closo*-dodecaborate(1−) was prepared by addition of tetrabutylammonium bromide in water to a hot aqueous solution of $(Me_4N)[B_{12}H_{11}NH_3]$ obtained as described in the literature.[7] The ^{1}H and ^{13}C NMR spectra were collected using a Varian Gemini 200 spectrometer and referenced to TMS. Infrared spectra were obtained on Perkin-Elmer 1600 and 1760 FTIR spectrometers. Elemental analyses were performed in the Laboratory of Microanalysis of the Institute of Organo-Element Compounds (Moscow).

Synthesis of the Schiff Bases $(Bu_4N)[B_{12}H_{11}NH{=}CHR]$. In a typical experiment, four drops of 5% aqueous solution of sodium hydroxide was added to a stirred solution of 0.40 g (1.0 mmol) of $(Bu_4N)[B_{12}H_{11}NH_3]$ and 1.1 mmol of aldehyde in 6 mL of methanol. The solution became yellow, and the reacton mixture was stirred for 1−4 h. The formed precipitate of the Schiff base was filtered, washed with diethyl ether, and dried in air. The additional portion of the product was obtained by the addition of 80 mL of diethyl ether to the filtrate.

$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-$N(CH_3)_2]$. Yield: 84%. ^{1}H NMR ($CDCl_3$, ppm): 8.60 (1H, d, J = 19.0 Hz), 8.32 (1H, d, J = 19.0 Hz), 7.47 (2H, d, J = 9.1 Hz), 6.68 (2H, d, J = 9.1 Hz), 3.22 (8H, m), 3.12 (6H, s), 1.61 (8H, m), 1.44 (8H, m), 0.97 (12H, t); (DMSO-d_6, ppm): 10.78 (1H, d, J = 18.9 Hz), 8.14 (1H, d, J = 18.9 Hz), 7.95 (2H, d, J = 8.8 Hz), 6.73 (2H, d, J = 8.8 Hz), 3.14 (8H, m), 3.06 (6H, s), 1.54 (8H, m), 1.28 (8H, m), 0.91 (12H, t). ^{13}C NMR ($CDCl_3$, ppm): 166.6, 154.9, 132.1, 115.9, 111.8, 58.8, 40.2, 24.1, 19.7, 13.8. IR ($CHCl_3$, cm^{-1}): 3290, 3000, 2964, 2932, 2486, 1630, 1593, 1534, 1471, 1444, 1381, 1358, 1320, 1252, 1218, 1190, 1116, 1098, 1046, 1017, 996, 944, 910, 881, 853, 924, 799, 751, 716, 664. Anal. Calcd for $C_{25}H_{59}B_{12}N_3$: B, 24.41; N, 7.91. Found: B, 24.24; N, 8.05.

$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-$NHCOCH_3]$. Yield: 84%. ^{1}H NMR (DMSO-d_6, ppm): 11.75 (1H, d, J = 19.0 Hz), 10.48 (1H, s), 8.44 (1H, d, J = 19.0 Hz), 8.17 (2H, d, J = 8.8 Hz), 7.46 (2H, d, J = 8.8 Hz), 3.17 (8H, m), 2.12 (3H, s), 1.57 (8H, m), 1.34 (8H, m), 0.94 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 169.3, 167.9, 145.3, 132.7, 123, 7, 118.5, 57.5, 24.3, 23.1, 19.2, 13.5. IR ($CHCl_3$, cm^{-1}): 3352, 3283, 3256, 3139, 3112, 3074, 3019, 3002, 2963, 2931, 2873, 2487, 1688, 1638, 1604, 1588, 1514, 1472, 1443, 1419, 1378, 1366, 1454, 1323, 1260, 1232, 1216, 1183, 1138, 1126, 1109, 1091, 1059, 1048, 1011, 927, 912, 886, 850, 821, 758, 718, 668, 655, 645, 618. Anal. Calcd for $C_{25}H_{57}B_{12}N_3O$: C, 55.05; H, 10.15; B, 23.78; N, 7.70. Found: C, 54.99; H, 10.75; B, 23.45; N, 7.96.

$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_5]$. Yield: 72%. ^{1}H NMR (DMSO-d_6, ppm): 12.20 (1H, d, J = 19.2 Hz), 8.63 (1H, d, J = 19.2 Hz), 8.24 (2H, d, J = 7.4 Hz), 7.74 (1H, t, J = 7.4 Hz), 7.60 (2H, t, J = 7.4 Hz), 3.17 (8H, m), 1.57 (8H, m), 1.31 (8H, m), 0.94 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 169.4, 135.1, 131.1, 129.4, 106.6. IR ($CHCl_3$, cm^{-1}): 2189, 3253, 3052, 3018, 2962, 2933, 2874, 2490, 1647, 1598, 1582, 1471, 1456, 1381, 1344, 1313, 1217, 1184, 1171, 1103, 1044, 1013, 929, 885, 845, 819, 754, 717, 682, 669. Anal. Calcd for $C_{23}H_{54}B_{12}N_2$: C, 56.56; H, 11.14; B, 26.56; N, 5.74. Found: C, 56.93; H, 11.22; B, 26.59; N, 6.02.

$(Bu_4N)[B_{12}H_{11}NH{=}CH$-1-$C_{10}H_7]$. Yield: 48%. ^{1}H NMR (DMSO-d_6, ppm): 12.59 (1H, d, J = 18.6 Hz), 9.50 (1H, d, J = 18.6 Hz), 8,36 (2H, t), 8.13 (2H, d), 7.75 (3H, m), 3.13 (8H, m), 1.54 (8H, m), 1.29 (8H, m), 0.91 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 166.7, 135.4, 133.0, 131.0, 129.4, 129.0, 127.1, 125.4, 124,9, 121.4, 57.5, 23.1, 19.2, 13.5. IR ($CHCl_3$, cm^{-1}): 3283, 3248, 3061, 3019, 3002, 2961, 2934, 2876, 2491, 1637, 1623, 1592, 1574, 1512, 1465, 1372, 1358, 1325, 1266, 1247, 1216, 1180, 1107, 1045, 1014, 925, 881, 857, 797, 754, 669. Anal. Calcd for $C_{27}H_{56}B_{12}N_2$: C, 60.23; H, 10.48; B, 24.09; N, 5.20. Found: C, 60.19; H, 10.35; B, 24.02; N, 5.53.

$(Bu_4N)[B_{12}H_{11}NH{=}CH$-2-$C_{10}H_7]$. Yield: 67%. ^{1}H NMR (DMSO-d_6, ppm): 12.22 (1H, d), 8.79 (1H, s), 8.74(1H, d), 8.38 (1H, d), 8.07 (3H, t), 7.72 (2H, m), 3.16 (8H,m), 1.57 (8H, m), 1.31 (8H, m), 0.93 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 169.0, 136.1, 135.5, 132.1, 129.9, 129.7, 129.2, 127.9, 127.6, 123.4, 57.5, 23.1, 19.2, 13.5. IR ($CHCl_3$, cm^{-1}): 3280, 3248, 3019, 3001, 2964, 2932, 2876, 2490, 1637, 1622, 1598, 1470, 1446, 1386, 1366, 1328, 1316, 1270, 1216, 1180, 1128, 1045, 1016, 925, 882, 860, 812, 754, 669. Anal. Calcd for $C_{27}H_{56}B_{12}N_2$: C, 60.23; H, 10.48; B, 24.09; N, 5.20. Found: C, 60.07; H, 10.24; B, 23.54; N, 5.30.

$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-2-$OCH_3]$. Yield: 68%. ^{1}H NMR (DMSO-d_6, ppm): 11.58 (1H, d, J = 19.0 Hz), 8.85 (1H, d, J = 19.0 Hz), 8.18 (1H, d), 7.74 (1H, t), 7.28 (1H, d), 7.14 (1H, t), 3.98 (3H, s), 3.17 (8H, m), 1.57 (8H, m), 1.31 (8H, m), 0.94 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 164.7, 160.2, 137.3, 130.7, 120.9, 116.9, 112.4, 57.2, 56.1, 22.8, 18.9, 13.2. IR ($CHCl_3$, cm^{-1}): 3317, 3002, 2962, 2875, 2482, 1649, 1604, 1578, 1496, 1472, 1458, 1381, 1341, 1316, 1268, 1252, 1219, 1180, 1169, 1131, 1044, 1014, 893, 880, 836, 754, 718, 683, 666. Anal. Calcd for $C_{24}H_{56}B_{12}N_2O$: B, 25.02; N, 5.40. Found: B, 24.95; N, 5.67.

$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-$OCH_3]$. Yield: 64%. ^{1}H NMR (DMSO-d_6, ppm): 11.64 (1H, s), 8.44 (1H, s), 8.17 (2H, d, J = 9.1 Hz), 7.10 (2H, d, J = 9.1 Hz), 3.86 (3H, s), 3.15 (8H, m), 1.55 (8H, m), 1.29 (8H, m), 0.91 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 168.0, 164.8, 133.8, 122.4, 115.0, 57.5, 55.9, 23.0, 19.2, 13.4. IR ($CHCl_3$, cm^{-1}): 3336, 3298, 3269, 3003, 2965, 2876, 2491, 1643, 1601, 1576, 1515, 1480, 1466, 1455, 1432, 1381, 1351, 1313, 1270, 1217, 1176, 1046, 1019, 881, 839, 808, 758, 666.

$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-$SCH_3]$. Yield: 73%. ^{1}H NMR (DMSO-d_6, ppm): 11.85 (1H, s), 8.48 (1H, s), 8.10 (2H, d, J = 8.4 Hz), 7.40 (2H, d, J = 8.4 Hz), 3.16 (8H, m), 2.55 (3H, s), 1.56 (8H, m), 1.29 (8H, m), 0.91 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 168.0, 148.6, 131.3, 125.8, 125.3, 57.5, 23.0, 19.2, 13.7, 13.4. IR ($CHCl_3$, cm^{-1}): 3333, 3289, 3246, 3003, 2965, 2876, 2490, 1639, 1590, 1558, 1495, 1480, 1449, 1438, 1413, 1381, 1346, 1324, 1307, 1284, 1267, 1216, 1192, 1175, 1091, 1049, 1017, 971, 954, 926, 909, 881, 801, 758, 666.

$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-Br]. Yield: 74%. ^{1}H NMR (DMSO-d_6, ppm): 12.31 (1H, s), 8.61 (1H, s), 8.10 (2H, d, J = 8.4 Hz), 7.76 (2H, d; J = 8.4 Hz), 3.17 (8H, m), 1.57 (8H, m), 1.31 (8H, m), 0.94 (12H, t). IR ($CHCl_3$, cm^{-1}): 3299, 3259, 3086, 3019, 2957, 2872, 2481, 1644, 1600, 1587, 1486, 1470, 1407, 1394, 1338, 1330, 1290, 1216, 1184, 1170, 1120, 1070, 1047, 1007, 925, 912, 882, 848, 808, 754, 720, 669.

$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-Cl]. Yield: 65%. ^{1}H NMR (DMSO-d_6, ppm): 12.24 (1H, s), 8.61 (1H, s), 8.18 (2H, d, J = 8.1 Hz), 7.64 (2H, d; J = 8.1 Hz), 3.15 (8H, m), 1.56 (8H, m), 1.30 (8H, m), 0.92 (12H, t). IR ($CHCl_3$, cm^{-1}): 3287, 3258, 3088, 3002, 2958, 2873, 2485, 1643, 1595, 1584, 1490, 1471, 1411, 1390, 1341, 1328, 1286, 1216, 1182, 1170, 1121, 1105, 1088, 1048, 1012, 925, 911, 883, 839, 811, 754, 718, 668.

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$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-CN]. Yield: 57%. ^{1}H NMR (DMSO-d_6, ppm): 12.60 (1H, s), 8.75 (1H, s), 8.37 (2H, d, J = 8.0 Hz), 8.05 (2H, d, J = 8.0 Hz), 3.12 (8H, m), 1.55 (8H, m), 1.29 (8H, m), 0.92 (12 H, t). IR ($CHCl_3$, cm^{-1}): 3287, 3230, 3003, 2963, 2875, 2490, 2235, 1706, 1646, 1608, 1560, 1470, 1412, 1384, 1343, 1278, 1215, 1168, 1109, 1046, 1011, 926, 899, 880, 847, 835, 815, 760, 720, 666.

$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_3$-3,4-$OCH_2O$]. Yield: 73%. ^{1}H NMR (DMSO-d_6, ppm): 11.58 (1H, d, J = 18.6 Hz), 8.39 (1H, d, J = 18.6 Hz), 7.97 (1H, s), 7.71 (1H, d, J = 7.9 Hz), 7.11 (1H, d, J = 7.9 Hz), 6.19 (2H, s), 3.15 (8H, m), 1.55 (8H, m), 1.29 (8H, m), 0.92 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 168.0, 153.4, 148.6, 131.4, 123.8, 108.9, 107.2, 102.7, 57.5, 23.1, 19.2, 13.5. IR ($CHCl_3$, cm^{-1}): 3332, 3305, 3004, 2965, 2934, 2877, 2489, 1643, 1619, 1605, 1505, 1492, 1479, 1459, 1378, 1317, 1266, 1217, 1150, 1112, 1045, 1038, 1016, 931, 881, 854, 801, 756, 720, 667.

$(Bu_4N)[B_{12}H_{11}$-$NH{=}CH{-}CH{=}CH{-}CH_3$]. Yield: 38%. ^{1}H NMR (DMSO-d_6, ppm): 11.44 (1H, d, J = 18.0 Hz), 8.07 (1H, dd, J = 18.0 Hz, J = 10.0 Hz), 7.12 (1H, dq, J = 15.2 Hz, J = 6.5 Hz), 6.46 (1H, ddd, J = 15.2 Hz, J = 10.0 Hz, J ~ 1 Hz), 3.17 (8H, m), 1.96 (3H, d, J = 6.5 Hz), 1.58 (8H, m), 1.32 (8H, m), 0.94 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 169.6, 155.7, 126.4, 57.5, 23.1, 19.2, 13.5. IR ($CHCl_3$, cm^{-1}): 3274, 3256, 3230, 3006, 2964, 2934, 2876, 2494, 1708, 1646, 1483, 1382, 1351, 1260, 1218, 1183, 1154, 1057, 1074, 964, 929, 889, 751, 666.

$(Bu_4N)[B_{12}H_{11}$-$NH{=}CHCH{=}CH{-}C_6H_5$]. Yield: 59%. ^{1}H NMR (DMSO-d_6, ppm): 11.63 (1H, s), 8.26 (1H, dd, J = 9.8 Hz), 7.85 (1H, d, J = 15.9 Hz), 7.54 (5H, m), 7.12 (1H, dd, J = 15.9, J = 9.8), 3.16 (8H, m), 1.56 (8H, m), 1.30 (8H, m), 0.92 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 169.3, 152.3, 134.2, 131.7, 129.4, 128.7, 121.6, 57.6, 23.0, 19.2, 13.4. IR ($CHCl_3$, cm^{-1}): 3265, 3242, 3054, 3005, 2964, 2935, 2876, 2487, 1630, 1595, 1575, 1482, 1467, 1453, 1316, 1381, 1360, 1323, 1296, 1252, 1218, 1170, 1106, 1052, 1020, 974, 967, 926, 893, 882, 852, 838, 807, 751, 688, 666.

Reduction of the Schiff Bases into Amines. In a typical experiment, a solution of 0.12 g (3.2 mmol) of sodium borohydride in 2 mL of water was added to a stirred suspension of 1.0 mmol of Schiff base in 6 mL of 2-propanol. The reaction mixture was stirred for 4−6 h until the solid became white. The precipitate was filtered, washed with water, and dried in a vacuum. The additional portion of the product can be obtained by evaporation of the filtrate to dryness and extraction with dichloromethane.

$(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-$NHCOCH_3$]. Yield: 96%. ^{1}H NMR (DMSO-d_6, ppm): 9.92 (1H, s), 7.49 (2H, d, J = 8.5 Hz), 7.31 (2H, d, J = 8.5 Hz), 6.52 (2H, s), 3.75 (2H, m), 3.17 (8H, m), 2.03 (3H, s), 1.58 (8H, m), 1.31 (8H, m), 0.94 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 168.2, 138.6, 129.5, 118.4, 57.5, 51.0, 24.0, 23.1, 19.2, 13.5. IR ($CHCl_3$, cm^{-1}): 3355, 3288, 3151, 3002, 2964, 2876, 2493, 1675, 1598, 1522, 1480, 1471, 1455, 1414, 1380, 1318, 1289, 1260, 1217, 1183, 1052, 1011, 881, 834, 754, 666.

$(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-2-$OCH_3$]. Yield: 90%. ^{1}H NMR (DMSO-d_6, ppm): 7.35 (1H, d), 7.29 (1H, t), 6.99 (1H, d), 6.90 (1H, t), 6.27 (2H, s), 3.85 (2H, s), 3.81 (3H, s), 3.18 (8H, m), 1.58 (8H, m), 1.32 (8H, m), 0.94 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 157.1, 130.1. 129.2, 123.6, 120.0, 110.5, 57.5, 55.4, 46.9, 23.1, 19.2, 13.5. IR ($CHCl_3$, cm^{-1}): 3355, 3262, 3200, 3001, 2963, 2876, 2486, 1648, 1604, 1578, 1495, 1484, 1466, 1440, 1379, 1340, 1248, 1219, 1169, 1118, 1047, 1010, 946, 893, 880, 824, 756, 665.

$(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_3$-3,4-$OCH_2O$]. Yield: 91%. ^{1}H NMR (DMSO-d_6, ppm): 7.04 (1H, s), 6.81 (2H, s), 6.56 (2H, s), 5.97 (2H, s), 3.71 (2H, s), 3.15 (8H, m), 1.55 (8H, m), 1.29 (8H, m), 0.92 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 146.9, 146.6, 129.8, 122.7, 109.6, 107.7, 100.9, 57.5, 51.3, 23.1, 19.2, 13.5. IR ($CHCl_3$, cm^{-1}): 3284, 3225, 3189, 3127, 3004, 2965, 2934, 2870, 2490, 1640, 1603, 1579, 1505, 1489, 1481, 1468, 1448, 1381, 1344, 1288, 1270, 1255, 1216, 1198, 1117, 1106, 1042, 1008, 976, 930, 896, 878, 865, 820, 757, 720, 666.

$(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-CN]. Yield: 85%. ^{1}H NMR (MeOH-d_4, ppm): 7.72 (2H, d, J = 8.2 Hz), 7.58 (2H, d, J = 8.2 Hz), 4.08 (2H, s), 3.24 (8H, m), 1.67 (8H, m), 1.41 (8H, m), 1.02 (12H, t). ^{1}H NMR (acetone-d_6, ppm): 7.77 (4H, s), 6.25 (2H, s), 4.27 (2H, m), 3.44 (8H, m), 1.82 (8H, m), 1.44 (8H, m), 0.98 (12H, t). IR ($CHCl_3$, cm^{-1}): 3282, 3176, 3113, 3003, 2964, 2875, 2495, 2231, 1610, 1570, 1470, 1416, 1380, 1266, 1217, 1169, 1130, 1108, 1052, 1004, 946, 882, 846, 819, 754, 715, 666.

$(Bu_4N)_2[B_{12}H_{11}NHCH_2C_6H_4$-4-CN]. The reduction was carried out as described above except that 1.2 g (32 mmol) of $NaBH_4$ was taken. Yield: 48%. ^{1}H NMR (DMSO-d_6, ppm): 7.76 (2H, d, J = 8.2 Hz), 7.60 (2H, d, J = 8.2 Hz), 5.60 (1H, s), 3.88 (2H, s), 3.15 (16H, m), 1.55 (16H, m), 1.29 (16 H, m), 0.92 (24 H, t). ^{13}C NMR (DMSO-d_6): 140.4, 130.6, 128.7, 117.6, 108.9, 56.2, 49.4, 21.7, 17.9, 12.1. IR ($CHCl_3$, cm^{-1}): 3330, 3222, 3124, 3003, 2964, 2886, 2490, 2231, 1610, 1576, 1480, 1359, 1217, 1151, 1108, 1055, 1010, 881, 845, 817, 754, 666.

$(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-$NH_2$]. A solution of 1.1 g (2.0 mmol) of $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-$NHCOCH_3]$ in 150 mL of a 2 M ethanolic solution of sodium hydroxide was refluxed overnight under nitrogen. The solution was cooled to room temperature and neutralized by the addition of hydrochloric acid. The reaction mixture was evaporated to dryness. The residue was treated with 100 mL of water and extracted twice with 200 mL of dichloromethane. The organic layer was dried over $MgSO_4$, and the solvent was distilled off, giving 0.87 g (95%) of the light yellow product. ^{1}H NMR (DMSO-d_6, ppm): 7.02 (2H, d, J = 8.4 Hz), 6.46 (2H, d, J = 8.4 Hz), 6.34 (2H, s), 5.04 (2H, s), 3.63 (2H, t), 3.16 (8H, m), 1.57 (8H, m), 1.31 (8H, m), 0.93 (12H, t). ^{13}C NMR (DMSO-d_6, ppm): 148.2, 130.1, 122.8, 113.2, 57.5, 51.4, 23.1, 19.2, 13.5. IR ($CHCl_3$, cm^{-1}): 3370, 3208, 3003, 2964, 2932, 2876, 2491, 1623, 1520, 1480, 1469, 1381, 1287, 1217, 1182, 1051, 1010, 882, 830, 754, 666.

$(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-COOH]. A solution of 8.0 g of sodium hydroxide in 25 mL of water was added to solution of 0.80 g (1.55 mmol) of $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-CN] in 75 mL of methanol, and the reaction mixture was refluxed overnight. The solution was cooled to room temperature and adjusted to pH 3 by the addition of hydrochloric acid. The reaction mixture was evaporated to dryness. The residue was treated with 200 mL of water and extracted twice with 200 mL of dichloromethane. The organic layer was dried over $MgSO_4$, and the solvent was distilled off, giving 0.77 g (93%) of the product. ^{1}H NMR (acetone-d_6, ppm): 8.01 (2H, d, J = 8.2 Hz), 7.65 (2H, d, J = 8.0.2 Hz), 6.19 (2H, s), 4.25 (2H, m), 3.44 (8H, m), 1.82 (8H, m), 1.48 (8H, m), 0.98 (12H, t). ^{13}C NMR (acetone-d_6, ppm): 167.4, 141.8, 131.2, 130.6, 130.0, 59.4, 52.5, 24.4, 20.3, 13.8. IR (Nujol, cm^{-1}): 3281, 3190, 3120, 2922, 2484, 1682, 1616, 1575, 1515, 1469, 1427, 1372, 1345, 1313, 1290, 1262, 1218, 1182, 1130, 1006, 1051, 1002, 986, 968, 903, 883, 864, 833, 792, 761, 739, 716, 706, 652, 638. Anal. Calcd for $C_{24}H_{56}B_{12}N_2O_2$: B, 24.27; N, 5.24. Found: B, 24.39; N, 5.07.

$(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-NCS]. Thiophosgene (65 μL, 0.85 mmol) was added to a vigorously stirred mixture of 0.55 g (4.0 mmol) of K_2CO_3 in a solution of 0.40 g (0.80 mmol) of $(Bu_4N)[B_{12}H_{11}NH_2$-$CH_2C_6H_4$-4-$NH_2]$ in 30 mL of dichloromethane, and the reaction mixture was stirred overnight. Water (10 mL) was added to the reaction mixture, and stirring was continued for 1 h. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness, giving 0.38 g (89%) of the product. ^{1}H NMR (DMSO-d_6, ppm): 7.48 (2H, d, J = 8.5 Hz), 7.36 (2H, d, J = 8.5 Hz), 6.76 (2H, s), 3.83 (2H, t), 3.15 (8H, m), 1.55 (8H, m), 1.29 (8H, m), 0.92 (12H, t). IR ($CHCl_3$, cm^{-1}): 3284, 3199, 3125, 3066, 3004, 2965, 2934, 2873, 2493, 2109, 1608, 1577, 1507, 1479, 1472, 1460, 1420, 1378, 1372, 1309, 1288, 1256, 1217, 1166, 1108, 1050, 1008, 978, 926, 899, 886, 845, 798, 757, 720, 666.

Crystal Structure Determination of $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-$NMe_2]$*$CHCl_3$ and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-OMe]. Yellow needlelike crystals of $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-$NMe_2]$*$CHCl_3$ (**I**) were grown from chloroform/hexane at ambient temperature. Light yellow crystals of $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4$-4-OMe] were grown from methanol. X-ray data (Table 1) were collected at 25 °C on a Siemens P3/PC diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and the $\theta-2\theta$ scan technique (θ_{max} = 28°).

The structures were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms of the substituted *closo*-dodecaborate anions were located from the difference Fourier synthesis and refined in the isotropic approximation. Hydrogen atoms of the tetrabutylammonium cations, and the dimethylamino and methoxy

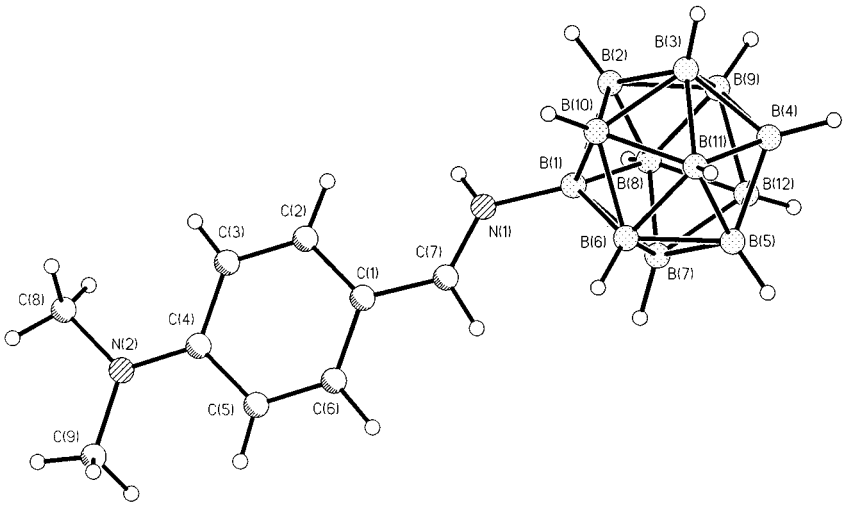
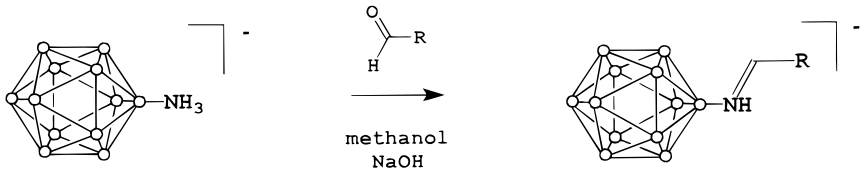


Figure 1. Molecular structure of the $[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]^-$ anion.

Scheme 1



o = BH(B)

R = C_6H_5
$2\text{-}C_6H_4OMe$
$4\text{-}C_6H_4OMe$
$4\text{-}C_6H_4SMe$
$4\text{-}C_6H_4NMe_2$
$4\text{-}C_6H_4NHCOMe$
$4\text{-}C_6H_4CN$
$4\text{-}C_6H_4Br$
$4\text{-}C_6H_4Cl$
$3,4\text{-}C_6H_3O_2CH_2$
$1\text{-}C_{10}H_7$
$2\text{-}C_{10}H_7$
CH=CH-Me
CH=CH-Ph

groups of the substituted anions were fixed in positions of ideal geometry and refined using the riding model. In the chloroform solvate molecule, chlorine atoms disordered in two positions with equal occupancy 1:1 (the hydrogen atom was not found). All calculations were performed on IBM PC/AT-586 using SHELXTL PLUS and SHELXL-93 programs. The final refinements were converged to R1 = 0.078 (from 2813 unique reflections with $I > 2\sigma(I)$) and wR2 = 0.261 (from 4788 unique reflections) for **I** and R1 = 0.076 (from 3230 unique reflections with $I > 2\sigma(I)$) and wR2 = 0.189 (from 6169 unique reflections) for **II**.

Results and Discussion

Synthesis of Schiff Bases. The reactions of $(Bu_4N)[B_{12}H_{11}NH_3]$ with aldehydes HC(O)R (R = C_6H_5, $4\text{-}C_6H_4Cl$, $4\text{-}C_6H_4Br$, $4\text{-}C_6H_4CN$, $4\text{-}C_6H_4OCH_3$, $4\text{-}C_6H_4SCH_3$, $4\text{-}C_6H_4N(CH_3)_2$, $4\text{-}C_6H_4NHCOCH_3$, $2\text{-}C_6H_4OCH_3$, $3,4\text{-}C_6H_3O_2CH_2$, $1\text{-}C_{10}H_7$, $2\text{-}C_{10}H_7$, CH=CHCH$_3$, CH=CHC_6H_5) were carried out in methanol in the presence of catalytic amounts of sodium hydroxide (Scheme 1). The presence of the base is necessary to deprotonate the ammonium nitrogen atom. After addition of sodium hydroxide solution to a methanolic solution of $[B_{12}H_{11}NH_3]^-$ and aldehyde, the color of the solution turned yellow, and after stirring for 20−120 min at room temperature, the corresponding Schiff bases $(Bu_4N)[B_{12}H_{11}NH{=}CHR]^-$ precipitated. In some cases addition of ether to the filtrate gave additional portions of the products. The Schiff bases obtained had a color from yellowish to lemon-yellow.

In the synthesis of $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OCH_3]$ it was shown that dichloromethane could replace MeOH as solvent. After 4 h dichoromethane was evaporated to dryness, and the residue was washed with a small amount of methanol to give the desired product.

The ^{1}H NMR spectra of the Schiff bases in dimethyl sulfoxide-d_6 contain signals of the N−H protons of the protonated imine group in the range of 10.7−12.6 ppm and of the C−H hydrogens of the imine group at 8.0−9.5 ppm. The signals normally appear as doublets ($J \sim 19$ Hz); however,

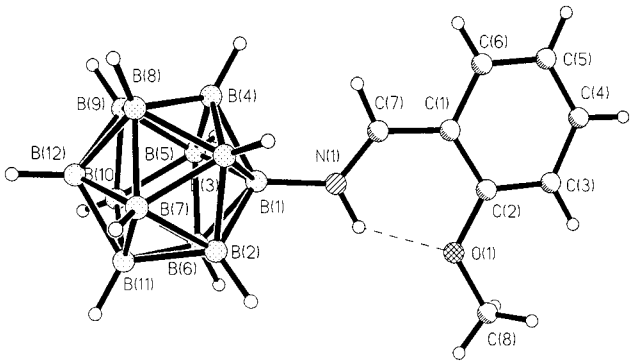


Figure 2. Molecular structure of the $[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]^-$ anion.

Table 1. Crystallographic Data for $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]{*}CHCl_3$ (**I**) and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]$ (**II**)

	$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]{*}CHCl_3$	$(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]$
chemical formula	$C_{26}H_{60}B_{12}Cl_3N_3$	$C_{24}H_{56}B_{12}N_2O$
a, Å	11.465(6)	10.282(2)
b, Å	21.314(7)	20.272(5)
c, Å	16.625(6)	17.052(3)
β, deg	101.38(3)	105.31(2)
V, Å^3	3983(3)	3427.9(13)
Z	4	4
fw	650.84	518.43
space group	*P*2(1)/*c*	*P*2(1)/*c*
T, °C	25	25
λ, Å	0.710 73	0.710 73
ρ(calcd), g/cm^3	1.085	1.005
μ, cm^{-1}	2.52	0.54
R [$I > 2\sigma(I)$][a]	0.0777	0.0756
R_w (all data)[b]	0.2916	0.2058

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w(F_o^2)^2]^{1/2}$.

sometimes they appear as broadened singlets. The signal of the protonated imine N−H hydrogen rapidly disappears after addition of D_2O (the doublet of the imine C−H hydrogen transforms into the singlet) and is solvent dependent (for $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}N(CH_3)_2]$, the N−H proton signal appears at 10.78 and 8.60 ppm in DMSO-d_6 and $CDCl_3$, respectively). The ^{13}C NMR spectra contain a signal of the imine carbon atom in the range 164−170 ppm. The IR spectra of the Schiff bases contain a strong band of the C=N stretching at 1630−1650 cm^{-1} and bands of the N−H proton stretch vibrations in the range 3240−3340 cm^{-1}. The N−H protons usually appear as two sharp bands (approximately at 3250 and 3280 cm^{-1}), but sometimes as a single sharp band ($(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OCH_3]$) or as three weak bands ($(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}OCH_3]$ and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}SCH_3]$). This can be explained by the existence of intra- and intermolecular hydrogen bonds, respectively, between the imine proton and the electronegative atom (oxygen, sulfur) of the substituent on the aromatic ring. The formation of the intramolecular hydrogen bond in $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OCH_3]$ was revealed by single-crystal X-ray analysis.

On the basis of the ^{1}H NMR data, $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}Cl]$, $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}Br]$, and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}CN]$ were found to be unstable in DMSO solution and undergo partial decomposition to the parent $(Bu_4N)[B_{12}H_{11}NH_3]$ and the corresponding aldehyde.

Structure of $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]$ and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]$. Molecular crystal structures of $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]{*}CHCl_3$ and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]$ were determined using the method of single-crystal X-ray analysis. Crystal **I** consists of tetrabutylammonium cations, $[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]^-$ anions (Figure 1), and solvate molecules of chloroform. Crystal **II** consists of tetrabutylammonium cations and $[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]^-$ anions (Figure 2). Both anions have the trans configuration. Selected bond lengths and angles for the $[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]^-$ and $[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]^-$ anions are given in Tables 2 and 3, respectively. The lengths of the B−N bond are 1.517(7) and 1.525(4) Å, respectively, for **I** and **II**, which are slightly shorter than in known alkylammonium derivatives of dodecahydro-*closo*-dodecaborate(2−) anion ($K[B_{12}H_{11}NEt_3]$[17] 1.64(1) Å, $(Me_4N)[B_{12}H_{11}NEt_3]$[18] 1.632(11) Å, $(Bu_4N)[B_{12}H_{11}NEt_3]$[15] 1.637(6) Å, $[(PPh_3)_2ClRuB_{12}H_{11}NEt_3]$[19] 1.631(15) Å, $(PPN)[B_{12}H_{11}NHBz_2]$[15] 1.585(5) Å, $(PPN)[B_{12}H_{11}NH(i\text{-}Pr)_2]$[15] 1.600(3) Å, $(PPN)[B_{12}H_{11}NH_2(i\text{-}Pr)]$[15] 1.578(2) Å), its *N*-pyridinium derivative $(Ph_4As)[(2,2'\text{-}Bipy)B_{12}H_{11}]{*}CH_3CN$[20] (1.562(11) Å), and the parent $Cs[B_{12}H_{11}NH_3]{*}2CH_3OH$[21] (1.535(11) Å) and of the same order as in arylammonium derivative $(Ph_4As)[B_{12}H_{11}NH\text{-}4\text{-}C_5H_4N]{*}2CH_3CN$[22] (1.513(12) Å). The imine N=C bonds in **I** and **II** are 1.274(6) and 1.274(3) Å, respectively, which is typical for the C=N double bonds.[23] The conformation of the substit-

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the $[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]^-$ Anion

Bond Lengths			
B(1)−N(1)	1.517(7)	C(1)−C(2)	1.393(6)
N(1)−C(7)	1.274(6)	C(1)−C(6)	1.388(6)
N(2)−C(4)	1.347(6)	C(2)−C(3)	1.358(7)
N(2)−C(8)	1.446(7)	C(3)−C(4)	1.389(7)
N(2)−C(9)	1.436(7)	C(4)−C(5)	1.419(7)
C(1)−C(7)	1.421(7)	C(5)−C(6)	1.341(7)
B−B	1.716(8)−1.770(8)		
mean of all B−B	1.750		

Bond Angles			
B(1)−N(1)−C(7)	128.7(5)	C(1)−C(2)−C(3)	120.9(5)
N(1)−C(7)−C(1)	128.4(5)	C(1)−C(6)−C(5)	122.4(5)
N(2)−C(4)−C(3)	122.8(5)	C(2)−C(1)−C(7)	123.7(5)
N(2)−C(4)−C(5)	121.1(5)	C(2)−C(3)−C(4)	122.4(5)
C(4)−N(2)−C(8)	120.7(5)	C(3)−C(4)−C(5)	116.2(5)
C(4)−N(2)−C(9)	121.4(5)	C(4)−C(5)−C(6)	121.0(5)
C(8)−N(2)−C(9)	117.9(5)	C(6)−C(1)−C(7)	119.2(4)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the $[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]^-$ Anion

Bond Lengths			
B(1)−N(1)	1.525(4)	C(1)−C(6)	1.391(4)
N(1)−C(7)	1.274(3)	C(2)−C(3)	1.382(5)
O(1)−C(2)	1.362(4)	C(3)−C(4)	1.383(5)
O(1)−C(8)	1.435(4)	C(4)−C(5)	1.361(5)
C(1)−C(7)	1.437(4)	C(5)−C(6)	1.356(5)
C(1)−C(2)	1.395(4)		
B−B	1.752(4)−1.795(5)		
mean of all B−B	1.773		

Bond Angles			
B(1)−N(1)−C(7)	126.8(3)	C(1)−C(6)−C(5)	122.1(3)
N(1)−C(7)−C(1)	129.5(3)	C(2)−C(1)−C(7)	124.2(3)
O(1)−C(2)−C(1)	115.8(3)	C(2)−C(3)−C(4)	119.3(4)
O(1)−C(2)−C(3)	124.2(3)	C(3)−C(4)−C(5)	121.5(4)
C(2)−O(1)−C(8)	118.6(3)	C(4)−C(5)−C(6)	119.0(4)
C(1)−C(2)−C(3)	120.0(3)		

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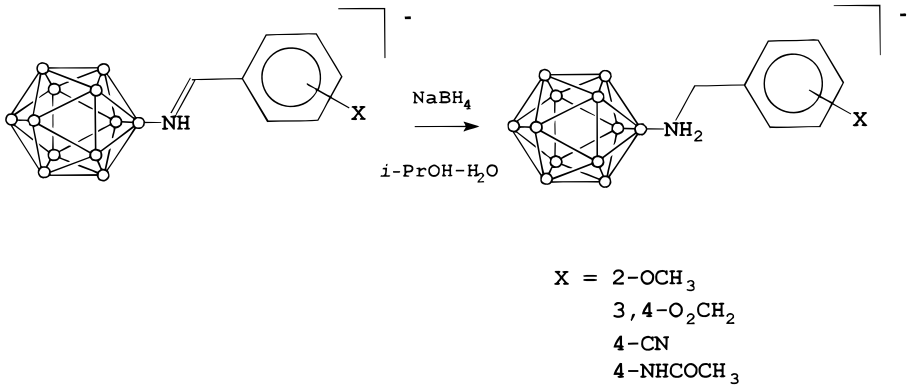
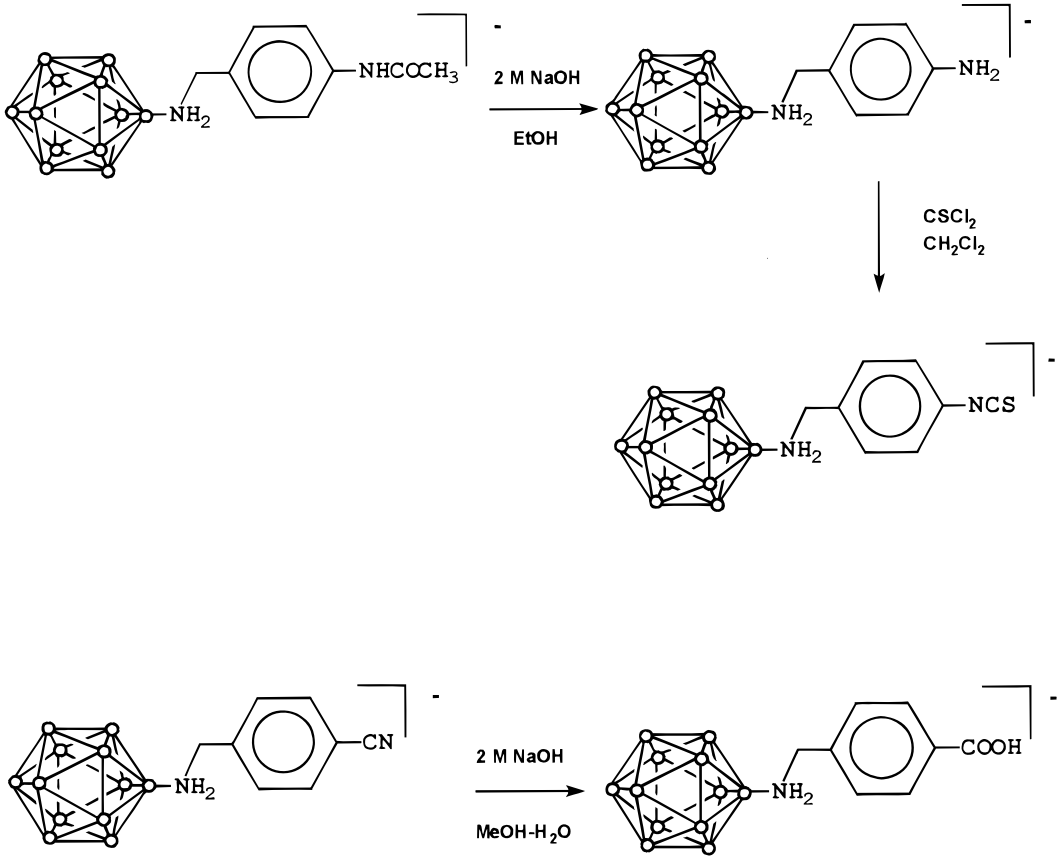
Scheme 2



Scheme 3



uents in the anions studied is close to planar. The nonvalent H(N1)···H(2) interaction with distance 2.13(2) Å, which is comparable with double the van der Waals radius of a hydrogen atom,[24] was found in structure **I**. The formation of a strong intramolecular hydrogen bond between the imine hydrogen atom and the methoxy oxygen atom in the ortho position of the benzene ring takes place in the case of structure **II**. The hydrogen bond parameters are the following: N(1)···O(1) 2.714(4) Å, N(1)−H(N1) 0.93(2) Å, H(N1)···O(1) 1.98(2) Å, N(1)−H(1N)···O(1) 135(2)°, which is close to those found in the N-protonated tautomeric form of 2-hydroxy-1-naphthaldimines.[25,26]

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Reduction of the Schiff Bases. Reduction of the Schiff bases $[B_{12}H_{11}NH{=}CHAr]^-$ (Ar = 2-$C_6H_4OCH_3$, 3,4-$C_6H_3O_2CH_2$, 4-C_6H_4CN, 4-$C_6H_4NHCOCH_3$) into amines $[B_{12}H_{11}NH_2CH_2Ar]^-$ was performed with sodium borohydride in aqueous 2-propanol (Scheme 2). Usually, a suspension of the Schiff base in a solution containing 3 equiv of $NaBH_4$ in aqueous 2-propanol (1:3) was stirred at room temperature until the color of the solid became white. It was found that the use of a large excess of sodium borohydride results in the alkalinization of the solution and, as a consequence, in the deprotonation of the ammonium nitrogen. Here, the product isolated was found to be $(Bu_4N)_2$-$[B_{12}H_{11}NHCH_2C_6H_4$-4-CN] and the yield was half that in a typical experiment (it was assumed that the second half of the amine was in the filtrate as the disodium salt).

Functionalized Derivatives of the $[B_{12}H_{12}]^{2-}$ Anion. Using the mild method of synthesis of monoalkylamino derivatives of the *closo*-dodecaborate anion described above and aiming to synthesize water-soluble functionalized compounds, we prepared some functionalized boron compounds containing functional groups on the aromatic ring (Scheme 3). Amine $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-$NH_2]$ was prepared by deprotection of $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-$NHCOCH_3]$ in a refluxing 2 M ethanolic sodium hydroxide. Alkaline hydrolysis of $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-CN] in refluxing 2 M solution of sodium hydroxide in aqueous methanol (1:3) gave the corresponding acid $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-COOH]. Reaction of the amine $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-$NH_2]$ with thiophosgene in dichloromethane resulted in the formation of the corresponding isothiocyanate $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4$-4-NCS].

The derivatives prepared can be transformed into water-soluble sodium salts using an ion-exchange procedure.

Conclusions

The method described for the attachment of the $[B_{12}H_{11}NH_3]^-$ anion to aldehydes followed by the reduction of the imines formed enables the mild introduction of the $[B_{12}]$ cage into more complex organic molecules including biologically active ones. Moreover, considering the recently described methods of mild synthesis of *closo*-1,2-$C_2B_{10}H_{12}$ and *nido*-[7,8-$C_2B_9H_{12}]^-$ carborane derivatives by the reactions of 1,2-$C_2B_{10}H_{12}$[27] or 1-Bu_3-Sn-1,2-$C_2B_{10}H_{11}$[28,29] and $[B_{10}H_{13}OH]^{2-}$,[30] respectively, with aldehydes, it is now possible to prepare a series of boron-containing compounds with different types of boron cages starting from the same aldehydes. Water-soluble derivatives of the $[B_{12}H_{12}]^{2-}$ anion can be used not only for BNCT but also as a linker for iodination and astatination of biomolecules for radioimmunodetection and for radioimmunotherapy.[31−34]

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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