PREPARATION OF CARBORANYL AND DODECABORATE DERIVATIVES OF COUMARIN

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Received August 29, 2007
Accepted October 20, 2007

A series of derivatives of coumarin (2*H*-chromen-2-one) and 6,7-benzocoumarin (3*H*-benzo-[*f*]chromen-3-one) carrying the *o*-carborane, *m*-carborane, and dodecaborate clusters, has been obtained. X-ray structure analysis has been carried out for three of the products. The addition of *o*-carborane occurs in the 4-position of the coumarin ring, in a stereoselective way, independent of whether the cluster was reacted as the lithium or magnesium salt. *m*-Carborane gives two products, one being the result of 1,2-addition to an exocyclic ester bond and 1,4-addition to the coumarin system, the other resulting from 1,4-addition. The negatively charged dodecaborate derivatives obtained, link the cluster via oxygen or sulfur and an appropriate linker to a 7-hydroxy-substituted coumarin. For the coumarin derivatives, an *o*-carboranecarbonyl derivative could also be obtained.

Keywords: Boron clusters; X-ray diffraction; Coumarins; Carboranes; Dodecaborate; Boron-neutron capture therapy; Carborane conjugates.

Coumarins were found to have a number of different uses. They are biologically interesting, as they can intercalate into DNA [1], are cytotoxic, anti-inflammatory, anticoagulant, and antioxidative[2]. They are also widely used as fluorescent probes, labels and pigments, dyes for lasers, and in sensors[3].

The icosahedral boron clusters of *o*-carborane, *m*-carborane, and dodecahydrododecaborate(2–) are building blocks which have been widely used in boron-neutron capture therapy (BNCT), and in optical devices[4]. The carborane cluster has been successfully used as a very hydrophobic pharmacophore[5]. Therefore, the preparation of coumarins carrying one of these clusters is of interest, both for pharmaceutical aims and for the development of new materials.

Previously, we have described some boron-containing coumarin derivatives[6]. Here we report the preparation of boron-containing coumarins and

Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 12, pp. 1740–1754

doi:10.1135/cccc20071740

the X-ray analysis data of some of the obtained structures. Some of the reactions occur in an unexpected manner.

EXPERIMENTAL

NMR spectra were recorded on a Bruker DPX 200 spectrometer at 200 MHz for ^{1}H, 64.2 MHz for ^{11}B, and 50.3 MHz for ^{13}C NMR. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) are given in Hz. IR spectra (wavenumbers in cm^{-1}) of KBr pellet were collected on a BioRad FTS 155 spectrometer. Electrospray mass spectra were measured on a Bruker Esquire spectrometer. The charge was determined through isotope satellite peaks. For B-containing compounds, the peak with highest intensity is given. The peak multiplicity for B-containing compounds was compared with the theoretical pattern and was found to agree for all B-containing compounds prepared. Melting points were measured on a Büchi 512 melting point apparatus.

4-(2-Isopropyl-*o*-carboran-1-yl)-3,4-dihydrocoumarin (**5**)

To a solution of 10.0 mmol of 1-isopropyl-2-lithium-*o*-carborane (**3a**) (prepared from 1.86 g (10.0 mmol) of *C*-isopropyl-*o*-carborane and 11.0 mmol of BuLi) in a benzene–diethyl ether mixture (50 ml, 4:1), a solution of 1.46 g (10.0 mmol) of coumarin (**1**) in benzene was added dropwise at room temperature and stirred overnight. Diluted HCl was added to the reaction mixture, which then was extracted with diethyl ether. The extract was dried over Na_2SO_4 and filtered, and the solvent was removed. The residue was purified by chromatography over silica gel (eluent diethyl ether–hexane 1:1). Yield 2.32 g (70%), m.p. 192–193 °C. IR (KBr): 3070, 3044, 3002, 2980, 2943, 2914, 2881 (C–H); 2621, 2572 (B–H); 1770 (C=O). ^{1}H NMR ($CDCl_3$): 0.57–3.6 m, br, 10 H (B-H); 1.34 dd, *J* = 11.74 and 6.85, 6 H ((CH_3)$_2$CH); 2.48 sep, *J* = 6.77, 1 H (C**H**(CH_3)$_2$); 2.96 dd, *J* = 16.87 and 7.09, 1 H (CH-C**H**$_2$); 3.19 dd, *J* = 17.12 and 1.47, 1 H (CH-C**H**$_2$); 3.68 d, *J* = 5.38, 1 H (C**H**-CH_2); 7.11–7.19 m, 3 H (Ar); 7.36–7.45 m, 1 H (Ar). ^{11}B NMR ($CDCl_3$): –4.72 (2 B); –9.35 (4 B); –11.79 (4 B). ^{13}C NMR ($CDCl_3$): 25.01 ((CH_3)$_2$CH); 31.81 (CH-CH_3); 36.29 (CH-CH_2); 37.76 (CH-CH_2); 84.67, 89.59 (C-carboranyl); 118.56, 121.48, 124.99, 130.38, 131.14 (Ar); 152.25 (Ar-O-); 165.98 (C=O). MS (EI), *m/z* (rel.%): 147 (100) [M^+ – $CB_{10}H_{10}CCH(CH_3)_2$]; 332 (67) [M^+]$^{\bullet}$.

6,7-Benzo-4-(2-isopropyl-*o*-carboran-1-yl)-3,4-dihydrocoumarin (**6**)

To a solution of 10.0 mmol of **3a** (prepared as for **5**) in benzene–diethyl ether (50 ml, 4:1), a solution of 1.96 g (10.0 mmol) of benzocoumarin (**2**) in THF was added dropwise at room temperature and stirred overnight. 1 M HCl was added to the reaction mixture, which was then extracted with ethyl acetate. The extract was dried over Na_2SO_4 and filtered, and the solvent was removed. The residue was crystallized by the addition of hexane, and then recrystallized from a hexane–benzene mixture. Yield 2.63 g (69%), m.p. 195–197 °C. IR (KBr): 2985, 2932 (C–H); 2622, 2609, 2573 (B–H); 1774 (C=O). ^{1}H NMR ($CDCl_3$): 0.62–3.8 m, br, 10 H (B-H); 1.44 dd, *J* = 10.27 and 6.85, 6 H ((CH_3)$_2$CH); 2.54 sep, *J* = 6.85, 1 H (C**H**(CH_3)$_2$); 2.99 dd, *J* = 16.87 and 6.11, 1 H (CH-C**H**$_2$); 3.21 dd, *J* = 16.63 and 1.96, 1 H (CH-C**H**$_2$); 4.53 dd, *J* = 6.11 and 1.71, 1 H (C**H**-CH_2); 7.33 d, 1 H (Ar); 7.49–7.57 m, 1 H (Ar); 7.61–7.70 m, 1 H (Ar); 7.88–7.95 m, 3 H (Ar). ^{11}B NMR ($CDCl_3$): –3.69 (2 B); –10.53 (4 B); –12.14 (4 B). ^{13}C NMR ($CDCl_3$): 24.79 ((CH_3)$_2$CH); 31.30 (CH-CH_3); 35.29 (CH-CH_2); 37.00

(C**H**-CH_2); 85.09, 87.62 (C-carboranyl); 116.03, 118.50, 122.35, 123.25, 126.09, 128.33, 129.74, 131.67, 132.26 (Ar); 150.01 (Ar-O-); 165.93 (C=O). MS (EI), *m/z* (rel.%): 197 (100) [M^+ – $CB_{10}H_{10}CCH(CH_3)_2$]; 382 (24) [M^+].

6,7-Benzo-4-(2-phenyl-*o*-carboran-1-yl)-3-ethoxycarbonyl-3,4-dihydrocoumarin (**9c**)

A) From 1-lithio-2-phenyl-o-carborane (**3c**). To a solution of **3c** (10.0 mmol) (prepared from 2.2 g (10 mmol) of 1-phenyl-*o*-carborane and 12.0 mmol of BuLi) in benzene, a solution of 2.68 g (10.0 mmol) of 6,7-benzo-3-ethoxycarbonylcoumarin (**7**) in benzene was added dropwise at room temperature. The reaction mixture was stirred for 3 h. Diluted HCl was added, and the reaction mixture was extracted with benzene. The extract was dried with Na_2SO_4, and the benzene was removed. The residue was crystallized by the addition of hexane and recrystallized from a hexane–benzene mixture. Yield 4.39 g (90%), m.p. 140–142 °C.

B) From (1-bromomagnesio)-2-phenyl-o-carborane (**3d**). To a solution of **3d** (10.0 mmol) (prepared from 2.2 g (10.0 mmol) of 1-phenyl-*o*-carborane and 13.0 mmol of EtMgBr) in THF, a solution of 2.68 g (10.0 mmol) of **7** in benzene was added dropwise at room temperature. The reaction mixture was stirred overnight, and then worked up as under *A*). Yield 3.22 g (66%), m.p. 140–142 °C. IR (KBr): 3020, 2976, 2926 (C–H); 2605, 2589 (B–H); 1795, 1723 (C=O); 1623 (Ar). ^{1}H NMR ($CDCl_3$): 0.51–3.6 m, br, 10 H (B-H); 0.74 t, *J* = 7.09, 3 H (C**H**$_3$CH$_2$); 3.77 dq, *J* = 1.47 and 7.17, 2 H (C**H**$_2$CH$_3$); 3.97 d, *J* = 1.47, 1 H (C**H**-CH); 4.55 d, *J* = 1.47, 1 H (CH-C**H**); 7.07 d, *J* = 7.34, 1 H (Ar); 7.26 d, *J* = 8.31, 1 H (Ar); 7.36–7.50 m, 2 H (Ar); 7.60–7.68 m, 3 H (Ar); 7.79–7.90 m, 4 H (Ar). ^{11}B NMR ($CDCl_3$): –1.34 (2 B); –7.79 (4 B); –9.91 (4 B). ^{13}C NMR ($CDCl_3$): 13.95 (**C**H$_3$CH$_2$); 38.60 (BC-**C**H); 53.68 (**C**H-COOC$_2$H$_5$); 63.22 (O**C**H$_2$-CH$_3$); 83.33, 86.22 (C-carboranyl); 114.18, 117.83, 123.28, 126.11, 128.19, 129.37, 130.02, 130.35, 131.48, 131.56, 132.04, 132.57 (Ar); 150.65 (Ar-O-); 163.59 (**C**OOC$_2$H$_5$); 165.22 (C=O). MS (EI), *m/z* (rel.%): 197 (91) [M^+ – $COOC_2H_5$ – $CB_{10}H_{10}CC_6H_5$]; 415 (23) [M^+ – $COOC_2H_5$]; 488 (100) [M^+].

6,7-Benzo-4-(2-isopropyl-*o*-carboran-1-yl)-3-ethoxycarbonyl-3,4-dihydrocoumarin (**9a**)

A) From 1-isopropyl-2-lithio-o-carborane (**3a**). Analogously to **9c** variant *A*) from 10.0 mmol of **3a** and 10.0 mmol of **7**, 4.0 g (88%) of **9a** were obtained, m.p. 186–188 °C (ethyl acetate–hexane).

B) From 1-bromomagnesium-2-isopropyl-o-carborane (**3b**). Analogously to **9c** variant *B*) from 10.0 mmol of **3b** and 10.0 mmol of **7**, 2.93 g (64%) of 6,7-benzo-4-(2-isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydrocoumarin were obtained, m.p. 186–188 °C (ethyl acetate–hexane). IR (KBr): 3022, 2976, 2938 (C–H); 2631, 2619, 2586 (B–H); 1771, 1736 (C=O). ^{1}H NMR ($CDCl_3$): 0.51–3.7 m, br, 10 H (BH); 0.88 t, *J* = 7.09, 3 H (C**H**$_3$CH$_2$); 1.48 dd, *J* = 17.61 and 6.85, 6 H ((C**H**$_3$)$_2$CH); 2.68 sep, *J* = 6.85, 1 H ((CH$_3$)$_2$C**H**); 3.97 q, *J* = 7.17, 2 H (C**H**$_2$CH$_3$); 4.14 d, *J* = 1.47, 1 H (C**H**-CH); 5.02 d, *J* = 1.47, 1 H (CH-C**H**); 7.31 d, *J* = 8.80, 1 H (Ar); 7.49–7.57 m, 1 H (Ar); 7.62–7.71 m, 1 H (Ar); 7.86–7.98 m, 3 H (Ar). ^{11}B NMR ($CDCl_3$): –3.57 (2 B); –10.44 (4 B); –12.17 (4 B). ^{13}C NMR ($CDCl_3$): 14.03 (**C**H$_3$CH$_2$); 14.96, 25.43 ((**C**H$_3$)$_2$CH); 31.44 ((CH$_3$)$_2$**C**H); 39.08 (BC-**C**H); 53.07 (**C**H-COOC$_2$H$_5$); 63.67 (O**C**H$_2$-CH$_3$); 83.49, 88.21 (C-carboranyl); 114.09, 118.06, 123.31, 126.31, 128.64, 129.59, 131.50, 131.98, 132.74 (Ar); 150.40 (Ar-O-); 162.86 (**C**OOC$_2$H$_5$); 165.64 (C=O). MS (EI), *m/z* (rel.%): 197 (100) [M^+ – $COOC_2H_5$ – $CB_{10}H_{10}CCH(CH_3)_2$]; 381 (15) [M^+ – $COOC_2H_5$]; 454 (85) [M^+]$^\bullet$.

6,7-Benzo-4-(7-isopropyl-*m*-carboran-1-yl)-3-ethoxycarbonyl-3,4-dihydrocoumarin (**11**) and 6,7-Benzo-4-(7-isopropyl-*m*-carboran-1-yl)-3-[(7-isopropyl-*m*-carboran-1-yl)carbonyl]-3,4-dihydrocoumarin (**13**)

To a solution of **10** (prepared from 1.86 g (10.0 mmol) of isopropyl-*m*-carborane and 11.0 mmol of BuLi) in benzene, a solution of 1.34 g (5.0 mmol) of **7** in benzene was added dropwise at room temperature and stirred overnight. The work-up was as for **9c**. The residue was crystallized by the addition of isooctane. The crystals (0.56 g of **13**) were filtered off and recrystallized from isooctane. The mother liquor was evaporated, and the residue was chromatographed on silica gel with isooctane–benzene 1:1 as an eluent. Yields were 1.08 g (34%) of **13** (together with the first portion), m.p. 150–152 °C, and 0.72 g (32%) of **11**, m.p. 141–142 °C, after recrystallization from benzene–hexane.

Compound **13**. IR (KBr): 3020, 2970, 2943, 2884 (C–H); 2605 (B–H); 1790, 1710 (C=O). ^{1}H NMR ($CDCl_3$): 0.60–3.9 m, br, 20 H (BH); 0.96 dd, *J* = 19.07 and 6.85, 6 H ((C**H**$_3$)$_2$CH); 2.11 sep, *J* = 6.77, 1 H (C**H**(CH$_3$)$_2$); 4.44 s, 1 H (C**H**-CH); 4.57 s, 1 H (CH-C**H**); 7.30 d, *J* = 6.36, 1 H (Ar); 7.52 t, *J* = 6.85, 1 H (Ar); 7.66 t, *J* = 7.09, 1 H (Ar); 7.78 d, *J* = 8.80, 1 H (Ar); 7.90 t, *J* = 7.09, 2 H (Ar). ^{11}B NMR ($CDCl_3$): –3.79 (2 B); –7.01 (4 B); –10.82 (10 B); –13.99 (4 B). ^{13}C NMR ($CDCl_3$): 24.28 ((**C**H$_3$)$_2$CH); 34.22 (**C**H-CH$_3$); 34.46 (CH-**C**H); 39.70 (**C**H-CH); 56.71, 76.81 (C-carboranyl); 113.45, 117.66, 123.08, 126.03, 128.39, 129.62, 131.59, 131.76, 132.40 (Ar); 150.20 (Ar-O-); 163.20 (C=O); 188.19 (C=O). MS (EI), *m/z* (rel.%): 197 [M^+ – $CB_{10}H_{10}CCH(CH_3)_2$ – $COCB_{10}H_{10}CCH(CH_3)_2$]; 223 (15) [$M^+$ – 2($CB_{10}H_{10}CCH(CH_3)_2$)]; 410 (5) [M^+ – $CB_{10}H_{10}CCH(CH_3)_2$]; 594 (100) [M^+]$^\bullet$.

Compound **11**. IR (KBr): 3072, 2972, 2953, 2912 (C–H); 2605 (B–H); 1783, 1718 (C=O). ^{1}H NMR ($CDCl_3$): 0.70–3.7 m, br, 10 H (BH); 0.88 t, *J* = 7.58, 3 H (C**H**$_3$CH$_2$); 0.93 d, *J* = 6.85, 6 H ((C**H**$_3$)$_2$CH); 2.09 sep, *J* = 6.93, 1 H (C**H**(CH$_3$)$_2$); 3.95 q, *J* = 7.17, 2 H (CH$_3$C**H**$_2$); 4.13 d, *J* = 1.47, 1 H (C**H**-CH); 4.71 d, *J* = 1.47, 1 H (CH-C**H**); 7.28 d, *J* = 9.29, 1 H (Ar); 7.46–7.54 m, 1 H (Ar); 7.60–7.68 m, 1 H (Ar); 7.83–7.89 m, 2 H (Ar); 8.00 d, *J* = 8.31, 1 H (Ar). ^{11}B NMR ($CDCl_3$): –3.78 (1 B); –7.00 (2 B); –10.82 (5 B); –13.99 (2 B). ^{13}C NMR ($CDCl_3$): 14.06 (**C**H$_3$CH$_2$); 24.28 ((**C**H$_3$)$_2$CH); 34.22 (**C**H-CH$_3$); 34.22 (CH-**C**H); 40.39 (**C**H-CH); 53.82, 76.80 (C-carboranyl); 63.27 (O-**C**H$_2$CH$_3$); 115.47, 117.69, 123.72, 126.11, 128.36, 129.29, 131.34, 132.01, 132.21 (Ar); 149.64 (Ar-O-); 163.88 (C=O); 165.89 (C=O). MS (EI), *m/z* (rel.%): 197 (75) [M^+ – $COOC_2H_5$ – $CB_{10}H_{10}CCH(CH_3)_2$]; 381 (20) [M^+ – $COOC_2H_5$]; 454 (100) [M^+]$^\bullet$.

7-[(*o*-Carboran-1-yl)carbonyloxy]-4-methylcoumarin (**17b**)

To a suspension of 1.76 g (10.0 mmol) of 4-methyl-7-hydroxycoumarin (**14b**) in 30 ml of dry THF, 10.0 mmol of NaOEt in 5 ml of dry ethanol were added dropwise and stirred for additional 30 min. To the resulting solution, 2.06 g (10.0 mmol) of *o*-carborane-1-carbonyl chloride (**16**) in 10 ml of dry THF were added, and the reaction mixture was stirred at room temperature for 1 h. A 5% solution of Na_2CO_3 in water was added, and the solution was extracted with benzene. The extract was dried with Na_2SO_4, the solvent was evaporated, and the residue was crystallized by the addition of hexane. The solid was recrystallized from benzene–hexane. Yield 3.03 g (88%), m.p. 220–222 °C. IR (KBr): 3076, 3062, 2925 (C–H); 2635, 2622, 2608, 2585, 2575 (B–H); 1771, 1732 (C=O); 1615 (C=C). ^{1}H NMR ($CDCl_3$): 0.8–3.8 m, br, 10 H (BH); 2.46 s, 3 H (CH$_3$C=C); 4.20 s, 1 H (HC-B); 6.32 s, 1 H (C=CH); 7.07 dd, *J* = 8.80 and 2.45, 1 H (Ar); 7.15 d, *J* = 1.96, 1 H (Ar); 7.65 d, *J* = 8.80, 1 H (Ar). ^{11}B NMR ($CDCl_3$): –2.05 (2 B); –8.47 (2 B); –12.02 (6 B). ^{13}C NMR ($CDCl_3$): 19.20 (**C**H$_3$C=CH); 57.55, 68.58 (C-carboranyl); 110.22, 115.83, 117.24, 126.34 (Ar); 119.46

(C=C-C=O); 138.80 (CH_3C=C); 151.91, 152.28 (Ar-O-); 160.03, 160.31 (C=O). UV/VIS ($CHCl_3$), λ_{max} (log ε): 271 (4.09); 279 (4.06); 312 (3.99). MS (EI), *m/z* (rel.%): 143 (20) [$HCB_{10}H_{10}C$]; 171 (56) [$HCB_{10}H_{10}CCO$]; 346 (100) [M^+].

7-[(*o*-Carboran-1-yl)carbonyloxy]coumarin (**17a**)

Analogously to **17b**, compound **17a** was prepared from 1.62 g (10.0 mmol) of **14a**, 10.0 mmol of C_2H_5ONa and 2.06 g (10.0 mmol) of **16** [7]. Yield 2.74 g (83%), m.p. 147–149 °C (benzene–hexane). IR (KBr): 3073 (C–H); 2633, 2589, 2575 (B–H); 1750, 1727 (C=O). ^{1}H NMR ($CDCl_3$): 0.7–3.9 m, br, 10 H (BH); 4.19 s, 1 H (CH-B); 6.46 d, *J* = 9.78, 1 H (CH=C**H**-CO); 7.06 dd, *J* = 8.31 and 2.45, 1 H (Ar); 7.16 d, *J* = 1.96, 1 H (Ar); 7.55 d, *J* = 8.80 (Ar); 7.71 d, *J* = 9.78, 1 H (C**H**=CH-CO). ^{11}B NMR ($CDCl_3$): –2.11 (2 B); –8.44 (2 B); –11.99(6B). ^{13}C NMR ($CDCl_3$): 57.55, 68.53 (C-carboranyl); 110.22, 117.52, 117.63, 129.48 (Ar); 118.22 (C=C-C=O); 142.90 (C=C-C=O); 152.36, 155.03 (Ar-O-); 160.03, 160.23 (C=O). UV/VIS ($CHCl_3$), λ_{max} (log ε): 274 (4.07); 282 (4.06); 313 (3.95). MS (EI), *m/z* (rel.%): 143 (20) [$HCB_{10}H_{10}C$]; 171 (56) [$HCB_{10}H_{10}CCO$]; 332 (100) [M]$^{\bullet}$.

7-[2-(*closo*-Undecahydrododecaboratylthio)ethoxy]coumarin(2–) Bis(tetramethylammonium) Salt (**21b**)

To a suspension of 0.5 g (1.34 mmol) of bis(tetramethylammonium) *S*-(cyanoethyl)thio-undecahydro-*closo*-dodecaborate(2–) (**18**) in 50 ml of dry CH_3CN at room temperature, 0.85 g (3.0 mmol) of 7-(2-bromoethoxy)-4-methylcoumarin[8] (**19b**) were added as a solid. The reaction mixture was stirred at room temperature for 12 h and then at 70 °C for 2 h. The crystals of NMe_4Br, which precipitated upon cooling, were filtered off, and the solution was evaporated and brought to crystallization by the addition of diethyl ether. The obtained precipitate was dissolved in 10 ml of acetone, and the cyanoethyl group was removed by the addition of NMe_4OH (1.34 mmol, 25% solution in MeOH). The resulting precipitate was filtered off and washed first with MeOH and then with diethyl ether. The product was recrystallized from CH_3CN–MeOH. Yield 0.44 g (63%), m.p. 114 °C (decomp.). IR (KBr): 3029, 2955, 2922 (C–H); 2484 (B–H); 1715 (C=O); 1613 (C=C). ^{1}H NMR (DMSO-d_6): –0.3 to 2.25 m, br, 11 H (BH); 2.39 s, 3 H (CH_3C=C); 2.60 t, *J* = 6.85, 2 H (S-CH_2); 3.09 s, 24 H (N-CH_3); 4.09 t, *J* = 8.07, 2 H (CH_2-O); 6.18 s, 1 H (C=CH); 6.83 d, *J* = 2.45, 1 H (Ar); 6.94 dd, *J* = 8.80 and 2.45, 1 H (Ar); 7.68 d, *J* = 8.80, 1 H (Ar). ^{11}B NMR (DMSO-d_6): –5.92 (1 B); –14.69 (5 B); –15.31 (5 B); –17.33 (1 B). ^{13}C NMR (DMSO-d_6): 18.10 (CH_3C=CH); 30.18 (S-CH_2); 54.41, 54.49 (CH_3-N); 70.08 (O-CH_2); 101.21, 110.87, 112.08, 126.48 (Ar); 112.81 (C=C-C=O); 153.46 (CH_3C=C); 154.70, 160.23 (Ar-O-); 161.85 (C=O). UV/VIS (CH_3CN), λ_{max} (log ε): 321 (4.16). MS (ESI), *m/z* (positive, negative): 74 [cat^+]; 598 [A^{2-} + 3 cat^+]$^+$; 141 [$B_{12}H_{11}$]$^-$; 450 [A^{2-} + cat^+]$^-$.

7-[2-(*closo*-Undecahydrododecaboratylthio)ethoxy]coumarin (2–) Bis(tetramethylammonium) Salt (**21a**)

Analogously to **21b**, compound **21a** was prepared from 0.5 g (1.34 mmol) of **18** with 0.81 g (3 mmol) of **19a** and 1.34 mmol of NMe_4OH (25% solution in MeOH). Yield 0.42 g (61%), m.p. 178 °C (decomp.). IR (KBr): 3025, 2957, 2928 (C–H); 2484 (B–H); 1723 (C=O); 1610 (C=C). ^{1}H NMR (DMSO-d_6): –0.4 to 2.25 m, br, 11 H (BH); 2.60 t, *J* = 7.09, 2 H (S-CH_2); 3.09 s, 24 H (N-CH_3); 4.08 t, *J* = 7.83, 2 H (CH_2-O); 6.25 d, *J* = 9.29 1 H (CH-C=O); 6.84 d, *J* =

2.45, 1 H (Ar); 6.91 dd, *J* = 8.80 and 2.45, 1 H (Ar); 7.61 d, *J* = 8.31, 1 H (Ar); 7.98 d, *J* = 9.29, 1 H (C**H**=CH-CO). ^{11}B NMR (DMSO-d_6): –6.01 (1 B); –14.66 (5 B); –15.25 (5 B); –17.24 (1 B). ^{13}C NMR (DMSO-d_6): 30.18 (S-CH_2); 54.41 (CH_3-N); 70.08 (O-CH_2); 101.15, 112.05, 112.16, 129.51 (Ar); 112.39 (C=C-C=O); 144.39 (CH_3C=C); 155.37, 160.37 (Ar-O-); 161.97 (C=O). UV/VIS (CH_3CN), λ_{max} (log ε): 323 (4.19). MS (ESI), *m/z* (positive, negative): 74 [cat$^+$]; 584 [A^{2-} + 3 cat$^+$]$^+$; 141 [$B_{12}H_{11}$]$^-$; 436 [A^{2-} + cat$^+$]$^-$.

Bis[2-(4-methylcoumarin-7-yl)oxyethyl]sulfonio-*closo*-undecahydrododecaborate(1–) Tetramethylammonium Salt (**24**)

To a solution of 0.272 g (1.24 mmol) of disodium sulfanylundecahydro-*closo*-dodecaborate(2–) (**22**) in 10 ml of degassed water, 1 equivalent of aqueous 0.01 M NaOH solution was added dropwise. The reaction mixture was stirred at room temperature for 30 min. The water was removed, and the residue was dried under vacuum. The residue was dissolved in 50 ml of CH_3CN, and 1.13 g (4.0 mmol) of **19b** were added. The reaction mixture was stirred at room temperature for 12 h and then at 70 °C for 2 h. The mixture was cooled, and the solvent was removed. The residue was washed with cold H_2O and then air-dried. The dry residue was suspended in $CHCl_3$, the solid was recovered by filtration and dissolved in hot water. To this solution, 0.272 g (2.48 mmol) of NMe_4Cl were added. The immediately formed precipitate was filtered off and air-dried. Yield 0.59 g (73%), m.p. 155–157 °C. IR (KBr): 3098, 3042, 2933, 2918 (C–H); 2499 (B–H); 1712 (C=O); 1615 (C=C). ^{1}H NMR (DMSO-d_6): –0.05 to 2.20 m, br, 11 H (BH); 2.33, s, 6 H (CH_3C=C); 3.07 s, 12 H (N-CH_3); 3.39–3.58 m, 4 H (S-CH_2); 4.44 s, 4 H (CH_2-O); 6.15 s, 1 H (C=CH); 6.79–7.04 m, 4 H (Ar); 7.55–7.71 m (Ar). ^{11}B NMR (DMSO-d_6): –14.49 (6 B); –15.78 (6 B). ^{13}C NMR (DMSO-d_6): 18.05 (CH_3C=CH); 54.29, 54.38, 54.46 (CH_3-N); 64.18 (S-CH_2); 68.66 (O-CH_2); 101.44, 111.43, 112.13, 112.44, 126.42 (Ar); 113.53 (C=C-C=O); 153.18 (CH_3C=C); 154.41, 160.31 (Ar-O-); 162.83 (C=O). MS (ESI), *m/z* (positive, negative): 74 [cat]$^+$; 727 [A^- + 2 cat$^+$]$^+$; 579 [A]$^-$.

Reaction of Tetrahydrofuran and Dioxane Derivatives of $[B_{12}H_{12}]^{2-}$ with **14a** and **14b**. General Procedure

To a solution of 0.85 mmol of oxonium compounds **25** or **26**, as an NBu_4 salt in 50 ml of dry CH_3CN, 0.90 mmol of **14a** or **14b**, 0.90 mmol of NBu_4Br and 1.0 mmol of K_2CO_3 were added. The reaction mixture was refluxed for 48 h, cooled, and the solvent was removed. The residue was dissolved in MeOH and deprived of solids by filtration. To the resulting solution in MeOH, 2.55 mmol of CsF in MeOH were added. The precipitated Cs salt was filtered and recrystallized from H_2O.

1-(4-Methylcoumarin-7-yl)-6-(closo-undecahydrododecaboratyl)-1,6-dioxahexane dicesium salt (**27b**). IR (KBr): 3073, 2947, 2872 (C–H); 2481 (B–H); 1701 (C=O); 1618 (C=C). ^{1}H NMR (D_2O): –0.3 to 2.20 m, br, 11 H (BH); 1.62–1.82 m, 4 H (O-CH_2-(C**H**$_2$)$_2$-CH_2-O); 2.42 s, 3 H (C**H**$_3$-C=CH); 3.59 t, *J* = 6.60, 2 H (CH_2-O-B); 4.14 t, *J* = 6.11, 2 H (Ar-O-C**H**$_2$); 6.18 s, 1 H (CH-C=O); 6.90–7.01 m, 2 H (Ar); 7.66 d, *J* = 8.80, 1 H (Ar). ^{11}B NMR (DMSO-d_6): 6.84 (1 B); –16.60 (5 B); –18.12 (5 B); –23.02 (1 B). ^{13}C NMR (DMSO-d_6): 18.16 (CH_3-C=CH); 25.86, 28.05 (OCH_2-(CH_2)$_2$-CH_2O); 67.55, 68.70 (O-CH_2-(CH_2)$_2$-CH_2-O); 101.24, 110.92, 112.30, 126.48 (Ar); 112.89 (C=C-C=O); 153.52 (CH_3C=C); 154.75, 160.28 (Ar-O-); 161.97 (C=O). UV/VIS (H_2O), λ_{max} (log ε): 323 (4.23). MS (ESI), *m/z* (positive, negative): 133 [cat$^+$]; 787 [A^{2-} + 3 cat$^+$]$^+$; 141 [$B_{12}H_{11}$]$^-$; 521 [A^{2-} + cat$^+$]$^-$.

1-(Coumarin-7-yl)-6-(closo-undecahydrododecaboratyl)-1-6-dioxyhexane dicesium salt (**27a**). IR (KBr): 2966, 2934, 2905, 2863 (C–H); 2481 (B–H); 1732 (C=O); 1616 (C=C). ^{1}H NMR (D_2O): –0.4 to 2.30 m, br, 11 H (BH); 1.57–1.72 m, 4 H (O-CH_2-(C**H**$_2$)$_2$-CH_2-O); 3.45 t, *J* = 6.36, 2 H (CH_2-O-B); 4.03 t, *J* = 6.36, 2 H (Ar-O-C**H**$_2$); 6.19 d, *J* = 9.78, 1 H (CH-C=O); 6.86–6.90 m, 2 H (Ar); 7.45 d, *J* = 9.29, 1 H (Ar); 7.84 d, *J* = 9.29, 1 H (C**H**=CH-CO). ^{11}B NMR (DMSO-d_6): 6.87 (1 B); –16.57 (5 B); –18.10 (5 B); –22.88 (1 B). ^{13}C NMR (DMSO-d_6): 25.80, 28.02 (OCH_2-(CH_2)$_2$-CH_2O); 67.58, 68.70 (O-CH_2-(CH_2)$_2$-CH_2-O); 101.18, 112.16, 112.24, 129.51 (Ar); 112.61 (C=C-C=O); 144.45 (CH_3C=C); 155.40, 160.42 (Ar-O-); 162.02 (C=O). UV/VIS (H_2O), λ_{max} (log ε): 325 (4.22). MS (ESI), *m/z* (positive, negative): 133 [cat$^+$]; 773 [A^{2-} + 3 cat$^+$]$^+$; 141 [$B_{12}H_{11}$]$^-$; 507 [A^{2-} + cat$^+$]$^-$.

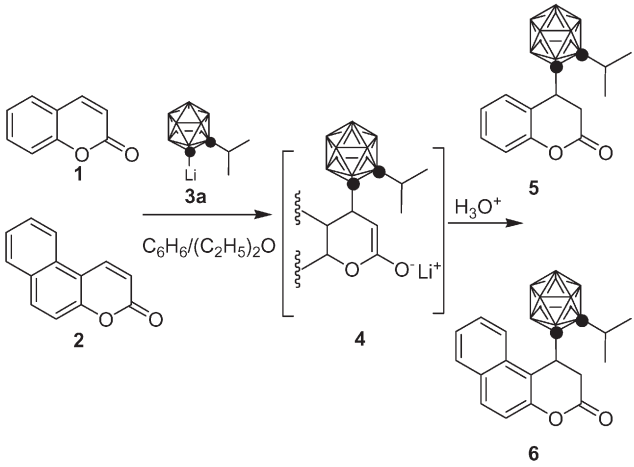
1-(4′-Methylcoumarin-7′-yl)-7-(closo-undecahydrododecaboratyl)-1,4,7-trioxaheptane dicesium salt (**28b**). IR (KBr): 3064, 2939, 2905, 2867 (C–H); 2472 (B–H); 1701 (C=O); 1616 (C=C). ^{1}H NMR (DMSO-d_6): –0.35 to 1.97 m, br, 11 H (BH); 2.40 s, 3 H (C**H**$_3$-C=CH); 3.44 s, 4 H (-C**H**$_2$-O-CH_2-); 3.73 t, *J* = 4.65, 2 H (CH_2-O-B); 4.20 t, *J* = 4.65, 2 H (Ar-O-C**H**$_2$); 6.20 s, 1 H (CH-C=O); 7.01–7.06 m, 2 H (Ar); 7.69 d, *J* = 9.29, 1 H (Ar). ^{11}B NMR (DMSO-d_6): 6.67 (1 B); –16.63 (5 B); –17.95 (5 B); –22.79 (1 B). ^{13}C NMR (DMSO-d_6): 19.03 (CH_3C=CH); 68.00 (B-O-CH_2); 68.84, 69.18 (-CH_2-O-CH_2-); 73.27 (Ar-O-CH_2-); 102.28, 111.99, 113.28, 127.38 (Ar); 114.04 (C=C-C=O); 154.36 (CH_3-C=C); 155.56, 161.10 (Ar-O-); 162.42 (C=O). UV/VIS (H_2O), λ_{max} (log ε): 321 (4.19). MS (ESI), *m/z* (positive, negative): 133 [cat$^+$]; 803 [A^{2-} + 3 cat$^+$]$^+$; 141 [$B_{12}H_{11}$]$^-$; 202 [A]$^{2-}$; 537 [A^{2-} + cat$^+$]$^-$.

7-[2-(Ethyleneoxyundecahydro-closo-dodecaboratyl)ethyleneoxy]coumarin dicesium salt (**28a**). IR (KBr): 3075, 2945, 2911, 2882, 2854 (C–H); 2466 (B–H); 1716 (C=O); 1614 (C=C). ^{1}H NMR (DMSO-d_6): –0.63 to 1.97 m, br, 11 H (BH); 3.43 s, 4 H (-C**H**$_2$-O-C**H**$_2$-); 3.71 t, *J* = 4.16, 2 H (CH_2-O-B); 4.17 t, *J* = 4.65, 2 H (Ar-O-C**H**$_2$); 6.25 d, *J* = 9.78, 1 H (CH-C=O); 6.98–7.30 m, 2 H (Ar); 7.60 d, *J* = 9.29, 1 H (Ar); 7.99 d, *J* = 9.29, 1 H (C**H**=CH-CO). ^{11}B NMR (DMSO-d_6): 6.70 (1 B); –16.69 (5 B); –17.95 (5 B); –22.76 (1 B). ^{13}C NMR (DMSO-d_6): 67.97 (B-O-CH_2-); 68.84, 69.12 (-CH_2-O-CH_2-); 73.25 (Ar-O-CH_2-); 102.25, 113.28, 113.37, 130.41 (Ar); 113.54 (C=C-C=O); 145.29 (CH_3C=C); 156.21, 161.24 (Ar-O-); 162.47 (C=O). UV/VIS (H_2O), λ_{max} (log ε): 324 (4.19). MS (ESI), *m/z* (positive, negative): 133 [cat$^+$]; 789 [A^{2-} + 3 cat$^+$]$^+$; 141 [$B_{12}H_{11}$]$^-$; 195 [A]$^{2-}$; 523 [A^{2-} + cat$^+$]$^-$.

CCDC 658165 (for **9a**), 658166 (for **11**), and 658167 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

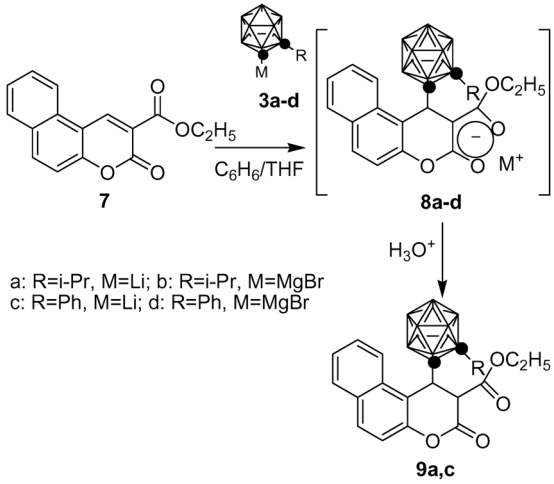
RESULTS AND DISCUSSION

The lithium derivative of *C*-isopropyl-*o*-carborane **3a** reacts, in a mixture of benzene and diethyl ether, with coumarin **1** and 6,7-benzocoumarin **2** in a 1,4-addition according to Scheme 1. The reaction starts with the formation of adduct **4**, and 4-(2-isopropyl-*o*-carboranyl)-3,4-dihydrocoumarin (**5**) and 6,7-benzo-4-(2-isoproyl-*o*-carboranyl)-3,4-dihydrocoumarin (**6**) are formed in the yields of 70 and 69%, respectively.



SCHEME 1

6,7-Benzo-3-ethoxycarbonylcoumarin **7** reacts in a benzene–THF mixture with the Li and Mg derivatives of *C*-isopropyl-*o*-carborane (**3a** and **3b**, respectively) and *C*-phenyl-*o*-carborane (**3c** and **3d**, respectively) regioselectively to give the resonance-stabilized intermediates **8a**, **8b** and **8c**, **8d**, respectively (Scheme 2), which hydrolyze with aqueous mineral acid to form the 6,7-benzo-4-(2-isopropyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydrocoumarin (**9a**) and 6,7-benzo-4-(2-phenyl-*o*-carboranyl)-3-ethoxycarbonyl-3,4-dihydrocoumarin (**9b**), respectively. When using Li as metal, the yields are 88–90%, with Mg only 64–66%. While the 1,4-additions are



SCHEME 2

normally characteristic of Mg derivatives, they are very uncommon for lithiumorganic compounds (such as butyllithium or phenyllithium)[9], which preferentially give a 1,2-addition product. In the case of a 1,2-addition, reaction at the exocyclic ester group or the lactone of the coumarin would have been observed.

When increasing the molar ratio of the *C*-metallic *o*-carborane derivatives over the coumarin to two or three, no formation of other products was found. The addition leads to a racemate of only one diastereomer, probably because steric hindrance of the ester group by the cluster prevents the formation of the other diastereomer.

X-ray structure analysis of **9a** (Fig. 1) shows that the two bulky substituents of the lactone ring are *trans* with respect to each other, and axial, minimizing the steric stress. The tetrahedral angle between C15 of the cluster, C4 and C3 is widened to 117°, probably due to a close contact between H3 of the coumarin ring and H17 of the isopropyl group (2.14 Å). The isopropyl group of the *o*-carborane cluster pointing away from the ring system, also minimizes sterically demanding interactions.

The *C*-lithium derivative of *C*-isopropyl-*m*-carborane **10** reacts also with **7**, giving two products, which are obtained by two different reaction paths (Scheme 3). One of the products, compound **11**, is obtained as expected from the reaction of **7** with Li-*o*-carborane. The other product, compound **13**, contains two *m*-carborane units.

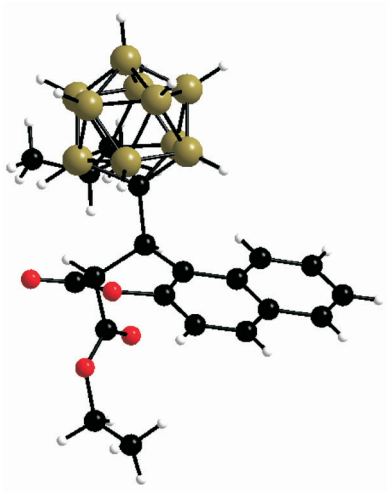
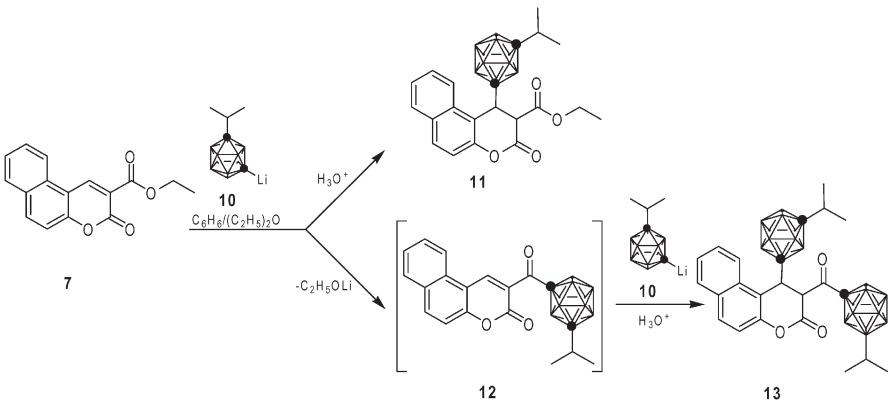


FIG. 1
Result of the X-ray structure analysis of **9a**



SCHEME 3

We think that **13** might have arisen by an initial 1,2-addition to the exocyclic ester group resulting in the intermediate **12**, which subsequently reacts, at a much higher rate, with an additional Li-*m*-carborane to form **13** in a 1,4-addition. When the ratio of **7** to **10** is 1:1, the yields of **11** and **13** each are not more than 20%, but **12** is not observed. When the molar ratio **7** to **10** is 1:2, the yields of **11** and **13** increase to 32 and 34%, respectively. The fact, that **11** and **13** are found in approximately equal ratios independent of the amount of **10** added, indicates that **11** and **13** result from parallel reactions, and that **13** is not formed from **11**. Coumarin **11** arises from **7** through a 1,4-addition. In contrast to the the intermediate **12**, **11** does not undergo an additional 1,4-addition.

Crystals suitable for the X-ray structure analysis could be obtained of **11** and **13**. The result of the X-ray analysis of **11** is shown in Fig. 2. The cluster is again *trans* to the ester group, as already observed for **9a**, relieving any possible steric hindrance. Again, probably for the same reason, the lactone ring is puckered, and the two bulky substituents are pseudo-axial with respect to the ring.

As in the other structures, the lactone ring of **13** has a boat conformation (Fig. 3). The two clusters are *trans* oriented, as observed also for the monosubstituted coumarins **6** and **11**, where the ester groups are *trans* positions to the cluster at the 4-position of the coumarin.

The difference in the reaction paths in Schemes 2 and 3 might be explained by the different nucleophilicity of the *o*- and *m*-carboranyl anions. The *o*-carboranyl anion, which is generated by the treatment of *o*-carborans

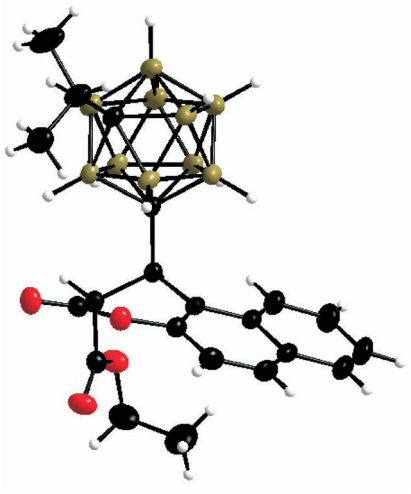


FIG. 2
Structure of **11** based on X-ray analysis. The ellipsoids of 50% probability are shown

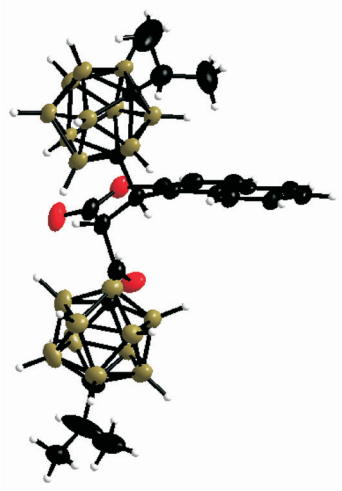
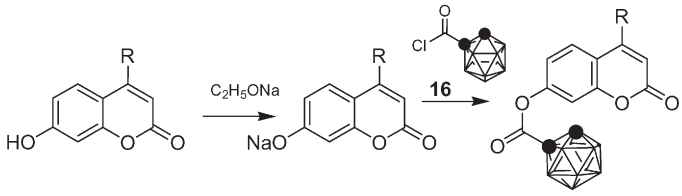


Fig. 3
Structure of **13** based on X-ray analysis. The ellipsoids of 50% probability are shown

with butyllithium, has a higher basicity and lower nucleophilicity, due to higher electronegativity of the cluster and resonance stabilization[10]. Therefore, the *o*-carboranyl anions **3a** and **3b** attack the soft electrophilic center (position 4) of **7** giving intermediates **8a** and **8d** (Scheme 2). The *m*-carboranyl anion, due to the lower electronegativity of the cluster and the higher localization of the charge density on the reactive *C*-atom, shows a higher nucleophilicity than the *o*-carborane one. The *m*-carborane anion **10**, as a hard nucleophile, preferentially attacks the hard reaction center (the ester group) in **7** and gives a carboranylated oxocoumarin as an intermediate, which further reacts to give **13**.

The 7-hydroxycoumarins **14a** and **14b** react in dry THF with carboranecarbonyl chloride **16** to form the carboranyl-containing esters **17a** and **17b** (Scheme 4). Compounds **14a**, **14b** were activated with 1 equivalent of sodium ethoxide. An excess of sodium ethoxide leads to the destruction of the *closo*-carborane and formation of the *nido* cluster[11]. The use of stronger bases such as NaOH and KOH leads to a side reaction, in which the coumarin ring is opened. The sodium derivatives **15a** and **15b** react fast with **16** to give **17a** and **17b**, in the yields of 83 and 88%, respectively.



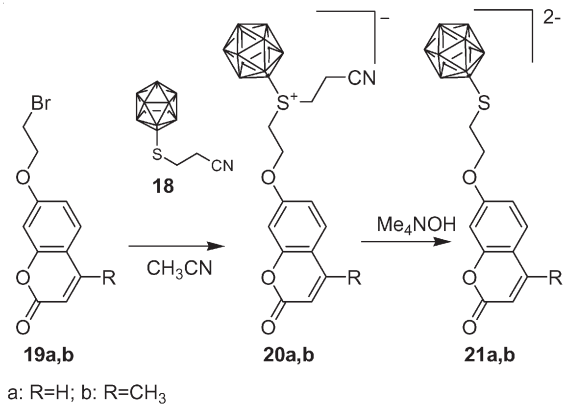
14a, b
a: R=H b:R=CH_3

15a, b

17a, b

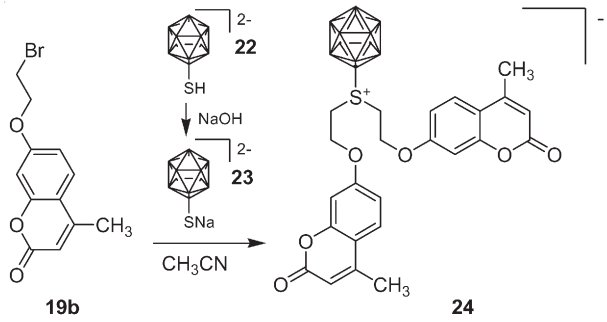
SCHEME 4

The coumarin bromoalkyl derivatives **19a** and **19b** react with *S*-(cyanoethyl)thioundecahydro-*closo*-dodecaborate(2–) (**18**) in dry CH_3CN to the expected *S,S*-dialkyl derivatives **20** (Scheme 5)[12]. Their formation was demonstrated by MS analysis (**20a** (ESI, *m/z* (positive, negative)): 74 [cat^+], 564 [$A^- + 2\ cat^+]^+$, 141 [$B_{12}H_{11}]^-$, 416 [A]$^-$; **20b** (ESI, *m/z* (positive, negative)): 74 [cat^+], 578 [$A^- + 2\ cat^+]^+$, 141 [$B_{12}H_{11}]^-$, 430 [A]$^-$). Further treatment of **20**, without prior purification, with 1 equivalent of NMe_4OH (25% solution in MeOH) led to the deprotection and the desired products **21a** and **21b**, in the yields of 61 and 63%, respectively. With the analogous chloroalkyl derivatives, no reaction was observed, indicating that Cl is an unsuitable leaving group for these reactions.



SCHEME 5

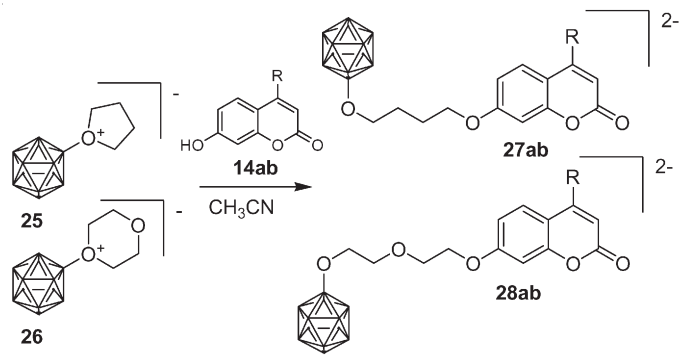
4-Methyl-7-(2-bromoethoxy)coumarin (**19b**) reacts with thiolate **23** (obtained from disodium mercaptoundecahydro-*closo*-dodecaborate(2–) (**22**) and 1 equivalent NaOH in water) in dry CH_3CN at 70 °C to form the sulfonium derivative **24** (Scheme 6). In situ deprotonation of **22** was not successful, as the unwanted opening of the coumarin ring occurred.



SCHEME 6

The 7-hydroxycoumarins **14a** and **14b** reacted as nucleophiles very well with the tetrahydrofuran and dioxane derivatives **25** and **26** of dodecahydro-*closo*-dodecaborate (described by Peymann[13] and Sivaev[14]), as shown in Scheme 7. Deprotonation of **14** could be achieved with K_2CO_3. The phenolates could open the oxonium rings of **25** and **26** in dry CH_3CN under re-

flux with NBu_4 as counter ion (similar reactions with phenols have been described by Semioshkin[15]). The final products could be precipitated as Cs salts with CsF in dry MeOH, to yield **27a**, **27b**, and **28a**, **28b**, respectively. The Cs salts are well soluble in water.



SCHEME 7

In conclusion, we synthesized compounds containing the *o*-carborane, *m*-carborane and dodecaborate clusters. The addition reactions of Li-carboranes with the coumarin backbone yielded unexpectedly 1,4-addition products. The establishment of suitable routes to such derivatives opens the possibilities to explore their use.

Supplemental Information

^1H, ^{13}C NMR and MS spectra, as well as information of the results from the X-ray diffraction are available online (doi:10.1135/cccc20071740).

E. Justus acknowledges support from the Otto Benecke Foundation. Dodecaborate has been supplied by BASF.

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