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The first carborane triflates: synthesis and reactivity of 1-trifluoromethanesulfonylmethyl- and 1,2-bis(trifluoromethanesulfonylmethyl)-*o*-carborane†

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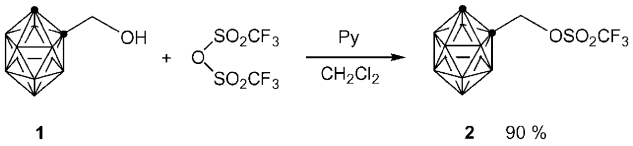
The first carborane triflates, namely, 1-trifluoromethanesulfonylmethyl-*o*-carborane (**2**) and 1,2-bis(trifluoromethanesulfonylmethyl)-*o*-carborane (**7**), were obtained in high yields in the reactions of 1-hydroxymethyl-*o*-carborane (**1**) or 1,2-bis(hydroxymethyl)-*o*-carborane (**6**) with triflic anhydride (Tf_2O) in CH_2Cl_2 in the presence of pyridine. When an excess of pyridine is employed, 1-*o*-carboranylmethylpyridinium triflate (**3**), which retains a *closo*-icosahedral structure, or a pyridinium salt (**4**) with a zwitterionic *nido*-dicarbaundecaborate anion are obtained from **1**, while the *nido* compound **8** is formed from **6**. The reaction of compound **2** or **7** with excess pyridine also gave **3** or **8**, respectively. Compound **2** proved to be a convenient carboranylmethylating agent which reacts with nucleophiles (*e.g.*, potassium phthalimide, PPh_3 or KCN) to give the corresponding substitution products *N*-[(*o*-carboranyl-1-yl)methyl]phthalimide (**9**), *o*-carboranylmethylphosphonium salt **10**, and 1-cyanomethyl-*o*-carborane (**11**). All compounds were characterized by ^1H and ^{11}B NMR spectroscopy. The structures of compounds **4**, **7** and **8** were established by X-ray analysis.

Introduction

The synthesis of carboranylmethylating agents which allow the introduction of a carboranylmethyl group into organic and natural compounds is of major interest in the medicinal chemistry of carboranes,[2] as this generates compounds suitable for boron neutron capture therapy of tumors.[3] A simple solution of this problem would be the application of 1-halomethyl-*o*-carborane, but the carborane cage does not allow their use in Friedel–Crafts reactions, even with activated aromatic hydrocarbons. Thus, prolonged heating of 1-bromomethyl-*o*-carborane with sodium iodide in acetone at 170 °C results only in partial replacement of bromide by iodide.[4] An example of a compound that is more reactive than 1-halomethyl-*o*-carboranes is 1-tosyloxymethyl-*o*-carborane, which in some cases reacts with secondary amines to give carboranylmethylamines,[5] while attempts to react 1-mesyloxymethyl-*o*-carborane with triethyl phosphite and sodium diethylphosphide failed.[6] With the aim of synthesizing a more efficient carboranylmethylating reagent, we prepared previously unknown carboranylmethyl triflates. We expected that the strong electron-withdrawing effect of the triflate group [σ_i (CF_3SO_3) = +0.84[7] would enhance the reactivity of carboranylmethyl triflates in nucleophilic substitution reactions compared to 1-mesyloxymethyl-*o*-carborane [σ_i ($MeSO_3$) = +0.61], and 1-tosyloxymethyl-*o*-carborane [σ_i ($MeC_6H_4SO_3$) = +0.54].[7] Being a good leaving group, triflate is widely used in organic syntheses in nucleophilic substitution reactions.[8–10]

Results and discussion

Hydroxymethyl-*o*-carborane (**1**)[11] reacts smoothly with Tf_2O in the presence of pyridine (1 : 1 : 1 molar ratio) at −5 to 0 °C to give *o*-carboranylmethyl triflate (**2**) (Scheme 1).



1 **2** 90 %

Scheme 1

The reaction of **1** with Tf_2O and an excess of pyridine can give different compounds, namely 1-*o*-carboranylmethylpyridinium triflate (**3**), which retains a *closo*-icosahedral structure, or the pyridinium salt **4** with a zwitterionic *nido*-dicarbaundecaborate anion. The latter is obtained when aqueous pyridine is employed (Scheme 2). The introduction of a strongly electron withdrawing substituent into the carborane cage facilitates deboronation and formation of the dicarbaundecaborate anion;[12] thus, the polyhedral framework in substituted *closo*-carboranyl triflates will be less stable toward the action of bases.

The unusual course of the reaction of compound **1** with Tf_2O in the presence of an excess of pyridine is due to the strong electron-acceptor effect of the triflate group in **2**, which is formed in the early stages of the reaction and immediately reacts with excess pyridine with replacement of the triflate group by pyridine to afford **3**. The reaction between the pyridinium salt **3** and aqueous pyridine (strong nucleophile) results in deboronation of the carborane polyhedron of **3** to produce the *nido* zwitterionic salt **4**, which is also favored by the strong electron-withdrawing effect of the pyridinium group. The reaction of **2** with pyridine gives **3**, which was isolated and in turn reacted with aqueous pyridine to form **4**. This confirms the reaction pathway discussed above (Scheme 3). Compound **4** was previously obtained as a mixture with the boron-substituted pyridinium derivatives in the reaction of 1-bromomethyl-*o*-carborane with pyridine in boiling toluene but was only characterized by elemental analyses.[13]

To confirm the assumption of a decisive role of the electron-withdrawing effect of the triflate group in the stability of

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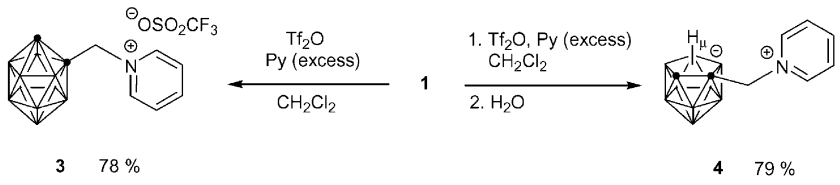
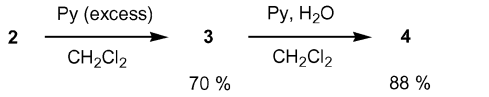
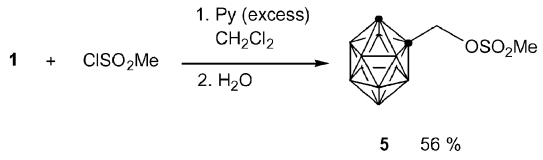


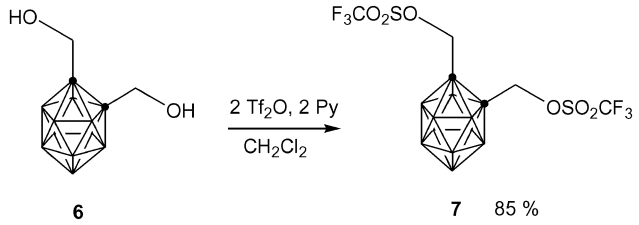
Scheme 2



Scheme 3



Scheme 4



Scheme 5

the carborane cage in **2**, we synthesized 1-mesyloxymethyl-*o*-carborane (**5**)[6] under conditions identical to those for the synthesis of **4** (Scheme 4). In contrast to **3**, the carborane **5** is not transformed into the corresponding *nido* analogue under the action of aqueous pyridine nor is a pyridinium salt formed.

The pattern established during the synthesis of the triflate **2** clearly manifests itself in the synthesis of bis-triflates. Thus, 1,2-bis(hydroxymethyl)-*o*-carborane (**6**)[11] smoothly reacts with Tf_2O in the presence of pyridine (1 : 2 : 2 molar ratio) to give the bis-triflate **7** in good yield (Scheme 5).

In contrast to **2**, the reaction of compound **7**, which contains two electron-withdrawing OSO_2CF_3 groups, with an excess of pyridine in anhydrous CH_2Cl_2 at 20 °C afforded the *nido* compound **8** (Scheme 6). The latter is also obtained directly from **6**, Tf_2O and an excess of pyridine.

The reactivity of the triflate group in **2** is typical for triflates in substitution reactions. The carboranylmethyl triflate **2** smoothly reacts with potassium phthalimide or PPh_3 to give *N*-[(*o*-carboranyl-1-yl)methyl]phthalimide (**9**)[14] or the *o*-carboranylmethylphosphonium salt **10**, respectively (Scheme 7). Another example of nucleophilic substitution of the triflate group is the synthesis of 1-cyanomethyl-*o*-carborane (**11**)[15,16] by the Pd-catalyzed reaction of **2** with KCN in acetonitrile. No replacement of the triflate group in **2** by the CN group occurs in the uncatalyzed reaction.

The carborane triflates and their derivatives obtained in this work were characterized by ^1H and ^{11}B NMR spectroscopy. The ^{11}B NMR spectra confirmed the *closo*-carborane structures of **2**, **3**, **5**, **7**, **9**, **10** and **11**. For all these compounds, changes in the ^{11}B chemical shifts of the ten boron atoms in the corresponding ^{11}B NMR spectra are insignificant compared to the spectrum of unsubstituted *o*-$C_2B_{10}H_{12}$[17] and lie in the range δ −1.48 to 12.88 ppm. The ^{11}B NMR spectrum of the zwitterion **4** exhibits eight signals at δ −9.31 to 35.40 ppm corresponding to nine boron atoms of the *nido* polyhedron compared to five signals for the unsubstituted *nido*-7,8-$C_2B_9H_{12}^-$ anion.[17] The spectrum also contains a dd signal corresponding to B10, which also couples to the bridging H10 atom of the polyhedron (δ −31.31 ppm, J_{BH} = 135 Hz, $J_{B(\mu-H)}$ = 41 Hz). The ^{11}B NMR spectrum of **8** also confirmed the *nido* structure of the carborane polyhedron and is similar to the spectrum of the unsubstituted *nido*-7,8-$C_2B_9H_{12}^-$ anion. Changes in the chemical shifts of the nine boron atoms of the polyhedron are also small.[18] The ^1H NMR spectra of compounds **2**, **3**, **5**, **7**, **9** and **11** exhibit singlets for the CH_2 protons. The ^1H NMR spectrum of compound **3** also exhibits three groups of pyridinium proton resonances at δ 8.07, 8.56 and 8.92 ppm with a relative intensity ratio of 2 : 1 : 2. In the ^1H NMR spectra of the *nido* derivatives **4** and **8** the methylene protons are magnetically inequivalent and manifest themselves as doublets with $^2J_{HH}$ = 14 Hz. Apparently, this is due to the zwitterionic structure of these compounds. The expected signals of the pyridinium protons in **4** and **8** also appear as three groups of resonances with a relative intensity ratio of 2 : 1 : 2.

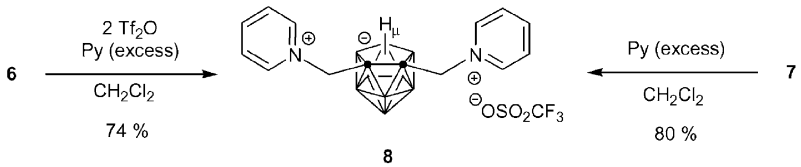
The structures of compounds **4**, **7** and **8** were established by X-ray analysis (Fig. 1) and selected geometrical data (bond lengths and torsion angles) are given in Table 1.

The triflate substituents in **7** and pyridine rings in **8** have different orientations relative to the carborane cage. The dissimilarity in the conformations of the S1–O1–C13–C1–C2–C15–O4–S2 and CH_2Py moieties can be seen from the values of the corresponding torsion angles in **7** (C1–C2–C15–O4 105.6(2), C2–C1–C13–O1 92.9(2), C1–C13–O1–S1 125.4(1), C2–C15–O4–S2 165.2(1), C15–C2–C1–C13 0.4(2)°) and **8** (C8–C7–C6–N1 146.9(2), C7–C8–C6′–N1′ 76.7(3), C7–C6–N1–C5 92.1(3), C8–C6′–N1′–C5′ 116.4(2), C6–C7–C8–C6′ 10.2(3)°). The geometric parameters of the carborane cage in the molecules of **4** and **8** are very similar.

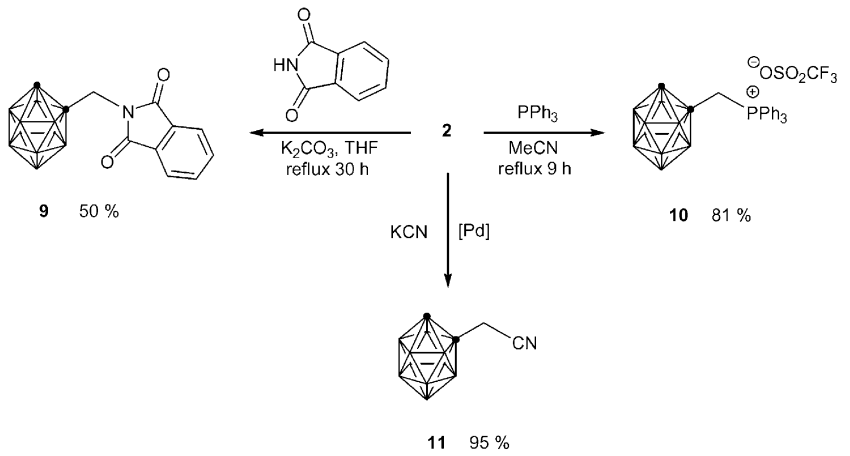
The most important difference in the geometry of the carborane cage of **7** and those of **4** and **8** is the shortening of the C7–C8 bond in **4** and **8** (1.562(2) and 1.592(3) Å, respectively) in comparison to the C1–C2 bond in **7** (1.682(2) Å). This can be regarded as a characteristic feature of a *nido* carborane cage.

Conclusion

We have synthesized and characterized the first carborane triflates. The high reactivity of these compounds toward nucleophilic reagents provides the possibility of performing



Scheme 6



Scheme 7

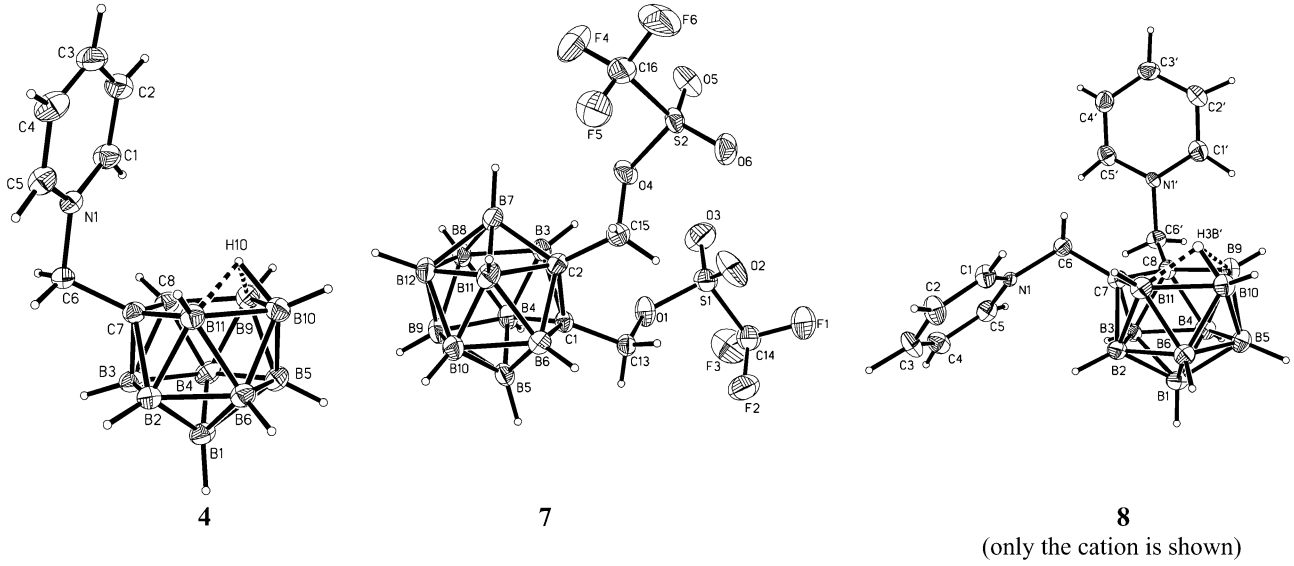


Fig. 1 X-Ray structures of compounds **4**, **7** and **8**.

Table 1 Selected geometrical data (bond lengths and torsion angles) in **4**, **7** and **8**

4		**7**		**8**	
C7–C8	1.562(2)	C1–C2	1.682(2)	C7–C8	1.592(3)
C7–C6	1.512(2)	C2–C15	1.512(2)	C7–C6	1.518(3)
		C1–C13	1.511(2)	C8–C6′	1.514(3)
C6–N1	1.496(2)	O1–S1	1.554(1)	C6–N1	1.491(3)
		O4–S2	1.560(1)	C6′–N1′	1.504(3)
C7–B11	1.617(2)	C1–B4	1.697(2)	C7–B11	1.619(3)
C8–B9	1.620(2)	C1–B6	1.729(2)	C8–B9	1.623(3)
		C2–B3	1.725(2)		
		C2–B11	1.712(2)		
C8–C7–C6–N1	90.6(1)	C1–C2–C15–O4	105.6(2)	C7–C8–C6′–N1′	76.7(3)
		C2–C1–C13–O1	92.9(2)	C8–C7–C6–N1	146.9(2)
C7–C6–N1–C5	117.3(1)	C2–C15–O4–S2	165.2(1)	C7–C6–N1–C5	92.1(3)
		C1–C13–O1–S1	125.4(1)	C8–C6′–N1′–C5′	116.4(2)
		C15–C2–C1–C13	0.4(2)	C6–C7–C8–C6′	10.2(3)

previously impracticable transformations leading to various functional derivatives of carboranes in a simple and selective manner. Further research in this area is currently in progress.

Experimental

General remarks

All experiments were carried out under dry argon. ^{1}H (400.13 MHz), ^{31}P (161.9 MHz) and ^{11}B NMR spectra (128.38 MHz) were recorded with a Bruker AMX-400 spectrometer. $BF_3{\cdot}Et_2O$ was used as external standard for ^{11}B NMR, 85% H_3PO_4 for ^{31}P NMR. The residual proton signals of the deuterated solvents were used as internal references for ^{1}H NMR spectra. 1-Hydroxymethyl-*o*-carborane (**1**),[11] 1,2-bis(hydroxymethyl)-*o*-carborane (**6**)[11] and $[PdCl_2(PPh_3)_2$[19] were synthesized by literature methods.

1-Trifluoromethanesulfonylmethyl-*o*-carborane (2). A solution of Tf_2O (4.23 g, 15 mmol) in CH_2Cl_2 (5 mL) was added

dropwise to a mixture of carborane **1** (2.4 g, 13.8 mmol) and pyridine (1.1 g, 14 mmol) in CH_2Cl_2 (10 mL) at 0–3 °C. The mixture was stirred for 3 h at 20 °C and then water (20 mL) was added. The organic layer was separated, washed with water, and dried over Na_2SO_4. After removal of the solvent the oil-like residue was dissolved in hexane and the solution was cooled to 4 °C. The resulting colourless crystals were filtered off. Yield: 3.8 g (89.9%); mp 25–26 °C. ^{1}H NMR ($CDCl_3$, δ/ppm): δ 4.79 (s, 2 H, CH_2), 3.80 (s, 1 H, CH carborane), 3.3–1.4 (m, 10 H, BH). ^{11}B NMR ($CDCl_3$, δ/ppm): δ −1.58 (d, J_{BH} = 159 Hz, 1 B), −3.41 (d, J_{BH} = 161 Hz, 1 B), −8.69 (d, J_{BH} = 164 Hz, 2 B), −11.67 (d, J_{BH} = 159 Hz, 2 B), −12.84 (d, J_{BH} = 161 Hz, 4 B). Calc. for $C_4H_{13}B_{10}F_3O_3S$ (306.30): C 15.70, H 4.28, B 35.31, F 18.60. Found: C 16.06, H 4.46, B 35.51, F 18.30%.

[(*o*-Carboran-1-yl)methyl]pyridinium trifluoromethanesulfonate (3). A solution of Tf_2O (3.4 g, 12 mmol) in CH_2Cl_2 (5 mL) was added to a mixture of carborane **1** (1.7 g, 10 mmol) and pyridine (3.5 mL, 43 mmol) in CH_2Cl_2 (10 mL) at 0–3 °C. The mixture was stirred for 4 h at 20 °C. The solvent was removed to dryness *in vacuo*. The residue was dissolved in CH_2Cl_2 (20 mL), and the solution thus obtained was washed with 10% HCl (2 × 20 mL) and then with water. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and crystallization from CH_2Cl_2 gave 3 g (77.9%) of **3**, mp 166–167 °C. ^{1}H NMR ($CDCl_3$, δ/ppm): δ 8.92 (d, $^3J_{HH}$ = 5.6 Hz, 2 H-*ortho*, C_5H_5N), 8.56 (t, $^3J_{HH}$ = 7.6 Hz, 1 H-*para*, C_5H_5N), 8.07 (dd, $^3J_{HH}$ = 5.6 Hz, $^3J_{HH}$ = 7.6 Hz, 2 H-*meta*, C_5H_5N), 5.58 (s, 2 H, CH_2), 4.72 (s, 1 H, CH carborane), 3.3–1.4 (m, 10 H, BH). ^{11}B NMR ($CDCl_3$, δ/ppm): δ −2.30 (d, J_{BH} = 159 Hz, 1 B), −3.39 (d, J_{BH} = 144 Hz, 1 B), −8.38 (d, J_{BH} = 150 Hz, 2 B), −12.42 (d, J_{BH} = 130 Hz, 6 B). Calc. for $C_9H_{18}B_{10}F_3NO_3S$ (385.11): C 27.89, H 4.69, B 28.43. Found: C 27.59, H 4.84, B 28.14%.

***nido*-7-[(*N*-Pyridinium)methyl]-7,8-dicarbaundecaborate (4).** A solution of Tf_2O (6.8 g, 24 mmol) in CH_2Cl_2 (5 mL) was added to a mixture of carborane **1** (3.5 g, 20 mmol) and pyridine (7 mL, 86 mmol) in CH_2Cl_2 (15 mL) at 0–3 °C. The reaction mixture was stirred for 6 h at 20 °C. Then water (10 mL) was added and the mixture was stirred for an additional 2 h. The precipitate formed was filtered off and successively washed with 10% HCl (20 mL) and water. Recrystallization from MeCN gave **4** (3.6 g, 79.3%), mp 231–232 °C. Compound **4** was reported in 1973 but was not fully characterized.[13] H NMR ([D$_6$]acetone, δ/ppm): δ 9.05 (d, $^3J_{HH}$ = 6.0 Hz, 2 H-*ortho*, C_5H_5N), 8.76 (t, $^3J_{HH}$ = 8.0 Hz, 1 H-*para*, C_5H_5N), 8.31 (dd, $^3J_{HH}$ = 6.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2 H-*meta*, C_5H_5N), 4.87 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2), 4.77 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2), 2.84 (s, 1H, CH carborane), −3.10 (br s, 1 H, H_μ *nido* carborane). ^{11}B NMR ([D$_6$]acetone, δ/ppm): δ −9.31 (d, J_{BH} = 123 Hz, 1 B), −10.18 (d, J_{BH} = 126 Hz, 1 B), −12.84 (d, J_{BH} = 146 Hz, 1 B), −14.11 (d, J_{BH} = 167 Hz, 1 B), −18.86 (d, J_{BH} = 112 Hz, 2 B), −19.68 (d, J_{BH} = 177 Hz, 1 B), −31.31 (dd, J_{BH} = 135 Hz, $J_{B(\mu-H)}$ = 41 Hz, 1 B), −35.40 (d, J_{BH} = 142 Hz, 1 B). Calc. for $C_8H_{18}B_9N$ (225.53): C 42.25, H 7.98, B 43.61, N 6.16. Found: C 42.11, H 8.08, B 43.68, N 6.19%.

Reaction of 2 with pyridine. Pyridine (1.29 g, 16.31 mmol) was added to a solution of **2** (1.00 g, 3.26 mmol) in CH_2Cl_2 (8 mL) with stirring. The reaction mixture was stirred for 1 h at 20 °C. The solvent was removed to dryness *in vacuo*. The residue was dissolved in CH_2Cl_2 (10 mL) and the solution thus obtained was washed with 10% HCl (2 × 5 mL) and then with water. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*. The residue was recrystallized from CH_2Cl_2 to give 0.88 g (70%) of **3**, mp 166–167 °C. Analytical and spectroscopic date are identical to those given above.

Reaction of 3 with pyridine and H_2O. Water (1 mL) was added to a stirred mixture of **3** (0.39 g, 1 mmol) and pyridine (0.4 mL, 5 mmol) in CH_2Cl_2 (10 mL) at 20 °C. A suspension formed after 0.5 h. After stirring for 6 h at 20 °C the reaction mixture was filtered. The precipitate was washed with 10% HCl (5 mL) and water and then recrystallized from MeCN to give 0.2 g (88.1%) of **4**, mp 229–230 °C. Analytical and spectroscopic date are identical to those given above.

1-Mesyloxymethyl-*o*-carborane (5). A solution of mesyl chloride (1.1 g, 10 mmol) in CH_2Cl_2 (5 mL) was added to a mixture of carborane **1** (1.7 g, 10 mmol) and pyridine (3.5 mL, 43 mmol) in CH_2Cl_2 (10 mL), at 0 to 3 °C. The reaction mixture was stirred for 5 h at 20 °C. Then water (10 mL) was added and the mixture was stirred for an additional 4 h at 20 °C. The organic layer was separated, successively washed with 10% HCl (20 mL) and water, and dried over Na_2SO_4. The mixture was then filtered and the solvent removed. The residue was recrystallized from CH_2Cl_2–hexane to give 1.85 g (55.9%) of **5**, mp 61–62 °C. Analytical and spectroscopic date are identical to those published in ref. 6.

1,2-Bis(trifluoromethanesulfonylmethyl)-*o*-carborane (7). A solution of Tf_2O (6.71 g, 24 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a mixture of carborane **6** (2.04 g, 10 mmol) and pyridine (1.7 g, 21 mmol) in CH_2Cl_2 (15 mL) at 0 to 3 °C. The mixture was stirred for 2 h at 20 °C and then water (15 mL) was added. The organic layer was separated, washed with water and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was recrystallized from hexane to give 4.0 g (85%) of **7**, mp 66–67 °C. ^{1}H NMR ($CDCl_3$, δ/ppm): δ 4.94 (s, 4 H, CH_2), 3.3–1.4 (m, 10 H, BH). ^{11}B NMR ($CDCl_3$, δ/ppm): δ −1.48 (d, J_{BH} = 153 Hz, 2 B), −9.60 (d, J_{BH} = 155 Hz, 4 B), −10.32 (d, J_{BH} = 170 Hz, 3 B), −11.87 (d, J_{BH} = 174 Hz, 1 B). Calc. for $C_6H_{14}B_{10}F_6O_6S_2$ (468.38): C 15.39, H 3.01, B 23.08, F 24.34. Found: C 15.54, H 3.25, B 22.49, F 24.04%.

***nido*-7,8-[Bis(*N*-pyridinium)methyl]-7,8-dicarbaundecaboranyl trifluoromethanesulfonate (8).** A solution of Tf_2O (6.71 g, 24 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a mixture of carborane **6** (2.04 g, 10 mmol) and pyridine (8 mL, 99 mmol) in CH_2Cl_2 (15 mL) at 0 to 3 °C. The mixture was stirred for 2 h at 20 °C. The white precipitate that formed was filtered off, washed with water and recrystallized from ethanol/water (2:1) to give **8** (3.5 g, 74%), mp 232–233 °C. ^{1}H NMR ([D$_6$]acetone, δ/ppm): δ 9.09 (d, $^3J_{HH}$ = 6.0 Hz, 2 H-*ortho*, C_5H_5N), 8.76 (t, $^3J_{HH}$ = 8.0 Hz, 1 H-*para*, C_5H_5N), 8.28 (dd, $^3J_{HH}$ = 6.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2 H-*meta*, C_5H_5N), 5.48 (d, $^2J_{HH}$ = 14.0 Hz, 2 H, CH_2), 5.10 (d, $^2J_{HH}$ = 14.0 Hz, 2 H, CH_2), −2.5 (br s, 1 H, H_μ *nido* carborane). ^{11}B NMR ([D$_6$]acetone, δ/ppm): δ −8.60 (d, J_{BH} = 136 Hz, 2 B), −11.16 (d, J_{BH} = 160 Hz, 1 B), −15.42 (d, J_{BH} = 140 Hz, 2 B), −18.87 (d, J_{BH} = 154 Hz, 2 B), −31.28 (dd, J_{BH} = 140 Hz, $J_{B(\mu-H)}$ = 40 Hz, 1 B), −34.68 (d, J_{BH} = 142 Hz, 1 B). Calc. for $C_{15}H_{24}B_9F_3N_2O_3S$ (466.71): C 38.60, H 5.18, B 20.85, F 12.21, N 6.00. Found: C 38.45, H 5.17, B 21.08, F 11.37, N 5.92%.

Reaction of 7 with pyridine. Pyridine (0.2 g, 2.5 mmol) was added to a stirred solution of **7** (0.2 g, 0.43 mmol) in CH_2Cl_2 (5 mL) at 20 °C. Over 5 min a suspension formed. After stirring for 12 h at 20 °C the reaction mixture was filtered. The solid was washed with CH_2Cl_2 (5 mL) and recrystallized from ethanol–water to give 0.16 g (80%) of **8**, mp 231–232 °C. Analytical and spectroscopic date are identical to those given above.

***N*-[(*o*-Carboran-1-yl)methyl]phthalimide (9).** Phthalimide (0.48 g, 3.3 mmol) and K_2CO_3 (0.46 g, 3.3 mmol) were added to a solution of carborane **2** (1.0 g, 3.3 mmol) in THF (30 mL), and the mixture was refluxed with stirring for 30 h. The solvent was removed *in vacuo* and the residue was purified by chromatography on SiO_2 (15 × 3 cm column) with heptane–ethyl acetate as eluent. The yield of compound **9** was 0.49 g (50%), mp 203–205 °C. Analytical and spectroscopic date are identical to those published in ref. 12.

Table 2 Crystal data and structure refinement for **4**, **7** and **8**

Compound	**4**	**7**	**8**
Formula	$C_8H_{18}B_9N$	$C_6H_{14}B_{10}F_6O_6S_2$	$[C_{14}H_{24}B_9N_2][CF_3SO_3]$
M_r	225.52	468.39	466.71
Crystal colour, habit	Colorless prism	Colorless needle	Colorless plate
Crystal size/mm	0.45 × 0.35 × 0.25	0.35 × 0.30 × 0.30	0.30 × 0.30 × 0.10
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$Pna2_1$
Cell constants:			
a/Å	7.984(4)	6.821(1)	19.400(3)
b/Å	10.740(5)	26.485(5)	8.899(1)
c/Å	15.354(7)	10.634(2)	12.640(2)
β/°	93.345(9)	97.37(3)	90
V/Å^3	1314.3(10)	1905.2(7)	2182.3(5)
Z (Z')	4 (1)	4 (1)	4 (1)
D_c/g cm^{-3}	1.140	1.633	1.420
T/K	110	153	110
Scan mode	φ and ω	$\theta/2\theta$	φ and ω
$2\theta_{max}$/°	56	52	58
μ(Mo-Kα)/cm^{-1}	0.55	3.59	1.96
T_{max}, T_{min}	0.928, 0.290	—	0.983, 0.667
Reflections collected	12170	6818	16511
Independent reflections (R_{int})	3145 (0.0347)	3709 (0.0462)	5764 (0.0411)
Observed reflections ($I > 2\sigma(I)$)	2359	3290	4434
Absolute structure parameter	—	—	0.05(7)
Parameters	235	327	394
$R1$ (on F for obs. refls.)[a]	0.0560	0.0408	0.0486
wR_2 (on F^2 for all refls.)[b]	0.1325	0.1158	0.1139
Weighting scheme, a, b	0.0333, 1.2332	0.0733, 0.8047	0.0605, —
F(000)	472	936	960
GOOF	1.010	1.050	0.998
Largest diff. peak, hole/e Å^{-3}	0.355, −0.052	0.396, −0.428	0.684, −0.245

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum F_o$ for observed reflections. [b] $wR_2 = \{\sum[w(F^2_o - F^2_c)^2/\sum[w(F^2_o)^2]\}^{0.5}$ for all reflections.

[(*o*-Carboran-1-yl)methyl]triphenylphosphonium trifluoromethanesulfonate (10). A mixture of carborane **2** (0.4 g, 1.3 mmol) and PPh_3 (0.42 g, 1.6 mmol) in MeCN (7 mL) was refluxed under argon for 9 h. The solvent was evaporated to dryness and diethyl ether (15 mL) was added affording a white solid, which was filtered off, washed with diethyl ether (10 mL) and dried *in vacuo*. Yield 0.6 g (81%); mp 277–278 °C. ^{1}H NMR ([D$_6$]acetone, δ/ppm): δ 8.42–7.82 (m, 15 H, Ph), 5.25 (d, $^2J_{HP}$ = 14.8 Hz, 2 H, CH_2), 5.07 (s, 1 H, CH carborane), 3.0–1.3 (m, 10 H, BH). ^{11}B NMR ([D$_6$]acetone, δ/ppm): δ −2.28 (d, J_{BH} = 160 Hz, 1 B), −3.78 (d, J_{BH} = 150 Hz, 1 B), −7.92 (d, J_{BH} = 154 Hz, 2 B), −12.86 (d, J_{BH} = 140 Hz, 6 B). ^{31}P NMR ([D$_6$]acetone, δ/ppm): δ 22.8. Calc. for $C_{22}H_{28}B_{10}F_3O_3PS$ (568.61): C 46.47, H 4.96, B 19.01, F 10.02, P 5.45. Found: C 46.98, H 5.26, B 18.83, F 9.98, P 5.33%.

1-Cyanomethyl-*o*-carborane (11). Carborane **2** (1.53 g, 5 mmol) and MeCN (7 mL) were added to KCN (0.65 g, 10 mmol) and [$PdCl_2(PPh_3)_2$] (0.1 g, 0.14 mmol) and stirred at 60 °C under argon for 1 h. The mixture was poured into water (20 mL) and extracted with ethyl acetate. The organic layer was washed with water, dried over Na_2SO_4 and then the solvent was evaporated. The residue was subjected to chromatography on SiO_2 (15 × 1.5 cm column) with heptane–ethyl acetate as eluent affording 0.86 g (95%) of carborane **11**; mp 110–111 °C (heptane) (*cf.* mp 109–110 °C (heptane)[15]). Compound **11** was previously prepared and characterized by IR[15] and NMR (^{1}H and ^{13}C)[16] spectroscopy (in $CDCl_3$). ^{1}H NMR ([D$_6$]acetone, δ/ppm): δ 4.36 (s, 2 H, CH_2), 5.37 (s, 1 H, CH carborane), 3.7–1.74 (m, 10 H, BH). ^{11}B NMR ([D$_6$]acetone, δ/ppm):δ −1.56 (d, J_{BH} = 149 Hz, 1 B), −4.60 (d, J_{BH} = 150 Hz, 1 B), −8.30 (d, J_{BH} = 151 Hz, 2 B), −10.28 (d, J_{BH} = 180 Hz, 2 B), −11.16 (d, J_{BH} = 168 Hz, 2 B), −11.81 (d, J_{BH} = 168 Hz, 2 B).

X-Ray crystallographic study of 4, 7 and 8

Crystallographic data, data collection procedures and refinement parameters are listed in Table 2. Single crystals of compounds **4**, **7** and **8** suitable for X-ray studies were obtained by crystallization from CH_3CN (**4**), hexane (**7**) and aqueous ethanol (**8**).

Single-crystal X-ray diffraction experiments for **4** and **8** were carried out with a Bruker SMART 1000 CCD area detector,[20] using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure) at 110 K. The X-ray experiment for **7** was carried out with a rebuild Syntex $P2_1$ four-circle diffractometer, using graphite monochromated Mo-Kα radiation at 153 K.[21] The absorption correction for **4** and **8** was applied semi-empirically from equivalent reflections.[22]

The structures were solved by direct methods and refined by the full-matrix least-squares techniques against F^2. All hydrogen atoms of the carborane frames were located in the difference Fourier syntheses and refined in isotropic approximation (in **4**, **7** and **8**); the positions of the hydrogen atoms of the CH_2 groups and Py were calculated and included in the refinement by using the riding model approximation with the $U_{iso}(H) = 1.2U_{eq}(C)$ for the methine and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups, where $U_{eq}(C)$ is the equivalent isotropic temperature factor of the carbon atom bonded to the corresponding H atom.

All calculations were performed on an IBM PC/AT using the SHELXTL software.[23]

CCDC reference numbers 227517 (**4**), 227518 (**7**) and 227519 (**8**).

See http://www.rsc.org/suppdata/dt/b4/b417199c/ for crystallographic data in CIF or other electronic format.

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References

1 E. G. Rys, E. Hey-Hawkins, D. D. Sung, Z. A. Starikova, A. A. Korlyukov and V. N. Kalinin, *Research and Development in Neutron Capture Therapy*, Monduzzi Editore S.p.A., Bologna, Italy, 2002, p. 63.
2 J. F. Valliant, K. J. Guenther, A. S. King, P. Morel, P. Schaffer, O. O. Sogbein and K. A. Stephenson, *Coord. Chem. Rev.*, 2002, **232**, 173.
3 M. F. Hawthorne and A. Maderna, *Chem. Rev.*, 1999, **99**, 3421.
4 L. I. Zakharkin, V. A. Brattsev and Yu. A. Chapovskii, *Zh. Obshch. Khim.*, 1965, **35**, 2160.
5 A. V. Kazantsev, V. V. Butyaikin, I. E. Gaas, E. A. Otrashchekov and M. M. Aksartov, *Zh. Org. Khim.*, 2000, **36**, 1007.
6 A. A. Semioshkin, S. G. Inyushin, L. V. Ermanson, P. V. Petrovskii, P. Lemmen and V. I. Bregadze, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2041.
7 P. J. Stang, M. Hanack and L. R. Subramanian, *Synthesis*, 1982, 85.
8 Y. Wu, P. J. Carroll and W. Quintana, *Polyhedron*, 1998, **17**, 3391.
9 L. Barazhenok, V. G. Nenajdenko and E. S. Balenkova, *Tetrahedron*, 2000, **56**, 3007.
10 K. Ritter, *Synthesis*, 1993, 735.
11 L. I. Zakharkin, V. A. Brattsev and V. I. Stanko, *Zh. Obshch. Khim.*, 1966, **36**, 886.
12 M. A. Fox and K. Wade, *J. Organomet. Chem.*, 1999, **573**, 279.
13 L. I. Zakharkin and V. S. Kozlova, *Zh. Obshch. Khim.*, 1973, **43**, 1097.
14 J. G. Wilson, A. K. M. Anisuzzaman, F. Alam and A. H. Soloway, *Inorg. Chem.*, 1992, **31**, 1955.
15 L. I. Zakharkin, A. B. Grebennikov and A. I. L'vov, *Izv. Akad. Nauk, Ser. Khim.*, 1970, 106.
16 A. A. Semioshkin, S. G. Inyushin, V. A. Artemov, P. V. Petrovskii and V. I. Bregadze, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1825.
17 F. Teixidor, C. Vinas and R. W. Rudolph, *Inorg. Chem.*, 1986, **25**, 3339.
18 M. F. Hawthorne, D. C. Young, P. M. Carrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862.
19 J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge and M. M. Jones, *Inorg. Chem.*, 1970, **9**, 2374.
20 *SMART V5.051 and SAINT V5.00, Area Detector Control and Integration Software*, Bruker AXS Inc., Madison, WI-53719, 1998.
21 *P3 and XDISK, Release 4.1*, Siemens AXS, Madison, WI, 1989.
22 G. M. Sheldrick, *SADABS*, Bruker AXS Inc., Madison, WI-53719, 1997.
23 G. M. Sheldrick, *SHELXTL, v. 5.10. Structure Determination Software Suite*, Bruker AXS, Madison, WI, 1998.