ARTICLES PUBLICATS

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New Derivatives of [NHMe$_3$][7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_{10}$]

Jonathan Bould,[†] Anna Laromaine,[†,‡] Clara Viñas,[†] Francesc Teixidor,*[,†] Lawrence Barton,[§] Nigam P. Rath,[§] Rudolph E. K. Winter,[§] Raikko Kivekäs,[∥] and Reijo Sillanpää[⊥]

Institut de Ciencia de Materials de Barcelona, 08193 Bellaterra, Spain, Chemistry Department, University of Missouri, St. Louis, Missouri 63121, Department of Chemistry, P.O. Box 55, University of Helsinki, Helsinki FIN-00014, Finland, and Department of Chemistry, University of Jyväskylä, Jyväskylä FIN 40351, Finland

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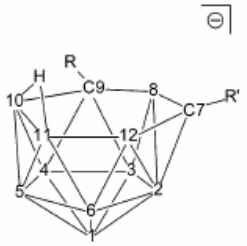
[NHMe$_3$][7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_{10}$] (**1**) reacts with [PdCl$_2$(PPh$_3$)$_2$] in refluxing ethanol solutions to afford four compounds which are the result of PPh$_3$ addition. Three of the products are structural isomers, viz. [5-PPh$_3$-7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_9$] (**2**), [6-PPh$_3$-7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_9$] (**3**), and [2-Me-3-{CHMe(PPh$_3$)}-*closo*-2-CB$_{10}$H$_9$] (**4**), and the fourth is [7-Me-8-OEt-9-{CHMe(PPh$_3$)}-*nido*-7-CB$_{10}$H$_{10}$] (**5**). The compounds were characterized by NMR spectrometry, high-resolution mass spectrometry, and single-crystal X-ray diffraction studies and are the first derivatives of the "unreactive" [7-R-μ-(9,10-HRC)-*nido*-7-CB$_{10}$H$_{10}$]$^-$ anion (R = Me) not involving degradation.

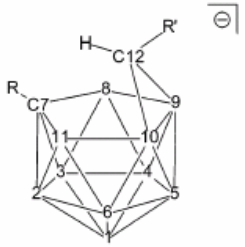
Introduction

It is well-known that the isomeric 1,2-*closo*-C$_2$B$_{10}$H$_{12}$, 1,7- and 1,12- carboranes, and some of their derivatives undergo a two-electron-reduction reaction with sodium[1] to form [C$_2$B$_{10}$H$_{12}$]$^{2-}$ carborane ions. Protonation of this dianion makes possible the formation of two monoanions of the formula [C$_2$B$_{10}$H$_{13}$]$^-$.[2] One of them is the kinetic compound [7,9-R$_2$-*nido*-C$_2$B$_{10}$H$_{11}$]$^-$ (**I**; R = R′ = H), also



I

known as the "reactive" form. Its dianionic [7,9-R$_2$-*nido*-7,9-C$_2$B$_{10}$H$_{10}$]$^{2-}$ form features an open six-membered face,[2c] and it has proven to be a versatile ligand for f-block and early-transition-metal elements.[3] The second isomer, which is the most stable, is the thermodynamic product [7-R-μ-(9,10-HR′C)-*nido*-7-CB$_{10}$H$_{11}$]$^-$, known as the "unreactive" form since it is inert in the usual reactions leading to metallacarboranes.[4,5] Recent studies verified this affirmation by theoretical calculations. It was found that, at the MP2/6-31G*/3-21G+ZPE level, the "unreactive" isomer is 6.7 kcal/mol more stable than the reactive one.[6] The kinetic isomer undergoes thermal rearrangement[2b,7] to the second isomer [7-R-μ-(9,10-HR′C)-*nido*-7-CB$_{10}$H$_{11}$]$^-$ (**II**; R = R′ = H). Recently, a



II

more convenient, direct, high-yield route[8] to alkylated derivatives of the thermodynamic isomer has been developed, thus prompting us to attempt to further investigate its chemistry.

† Institut de Ciència de Materials de Barcelona.
‡ Enrolled in the UAB Ph.D. program.
§ University of Missouri.
∥ University of Helsinki.
⊥ University of Jyväskylä.

(1) (a) Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1128. (b) Zakharkin, L.; Kalinin, V.; Podvisotskaya, L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *10*, 2310. (c) Zakharkin, L.; Kalinin, V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 164. (d) Stanko, V.; Gol'typin, Y. V.; Brattsev, V. *Zh. Obshch. Khim.* **1969**, *39*, 1175. (e) Dustin, D. F.; Dunks, G. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 1109.

(2) (a) Dunks, G. B.; Wiersema, R. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 899. (b) Dunks, G. B.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 3174. (c) Getman, T. D.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 158.

(3) (a) Dustin, D. F.; Dunks, G. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 1109. (b) Alcock, N. W.; Taylor, J. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1805. (c) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1976**, *15*, 2872. (d) Xie, Z.; Chui, K.; Yang, Q.; Mak, T. C. W. *Organometallics* **1999**, *18*, 3947. (e) Chui, K.; Yang, Q.; Mak, T. C. W.; Lam, W. H.; Liu, Z.; Xie, Z. *J. Am. Chem. Soc.* **2000**, *122*, 5758. (f) Khattar, R.; Manning, M. J.; Knobler, C. B.; Johnson, S. E.; Hawthorne, M. F. *Inorg. Chem.* **1992**, *31*, 268. (g) Zi, G.; Li, H. W.; Xie, Z. *Organometallics* **2002**, *21*, 3464. (h) Xie, Z.; Yan, Q.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 1761. (i) Chui, K.; Li, H.-W.; Xie, Z. *Organometallics* **2000**, *19*, 5447. (j) Zi, G.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2001**, 1110. (k) Wang, Y.; Wang, H.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 3311. (l) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 3464.

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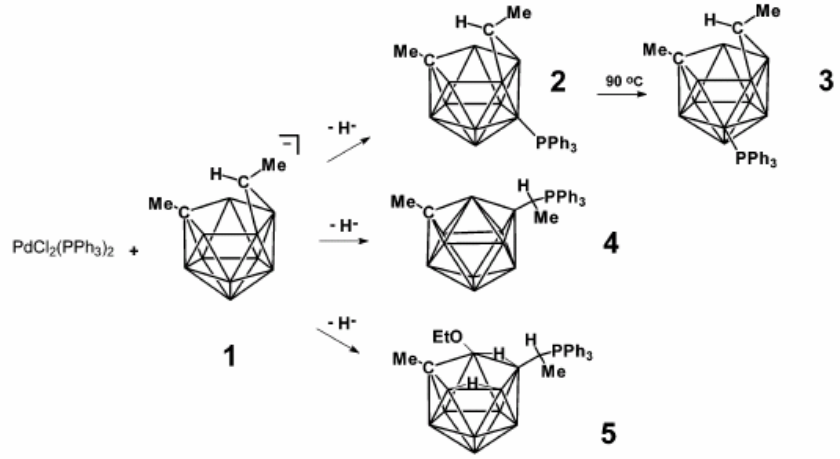
Scheme 1. Products from the Reaction of [NHMe$_3$][7-Me-μ-(9,10-HMeC)-*Nido*-7-CB$_{10}$H$_{10}$] (1), with [PdCl$_2$(PPh$_3$)$_2$] in a 1:1 Molar Ratio in Ethanol



Results and Discussion

Reflux of ethanol solutions of the anionic cluster species [NHMe$_3$][7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_{10}$] (**1**) and [PdCl$_2$(PPh$_3$)$_2$] in a 1:1 molar ratio followed by thin-layer chromatographic separation of the products affords low yields of two new zwitterionic non-metal-containing isomeric cluster species, [5-PPh$_3$-7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_9$] (compound **2**, 10%) and [6-PPh$_3$-7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_9$] (compound **3**, 16%), in which there has been an effective replacement of an exo-cluster hydrogen vertex by a PPh$_3$ unit. The reaction is shown in Scheme 1. The compounds were characterized by a combination of ^{11}B, ^{1}H, and ^{31}P NMR spectrometry, high-resolution mass spectrometry (HRMS), and single-crystal X-ray diffraction studies. The structures of compounds **2** and **3** are shown in Figures 1 and 2, respectively, and crystallographic data and selected distances and angles are given in Tables 1 and 2.

The ^{11}B spectrum of **2** shows a 2:1:1:2:2:2 relative intensity pattern appropriate for a molecule with C_s symmetry, and **3** shows 10 resonances of unit intensity resulting from the breaking of the pseudo-mirror-plane symmetry by the phosphonium group bonded to B(6). Both spectra contain a resonance of unit intensity coupled to phosphorus ($^1J(^{31}\text{P}-^{11}\text{B})$ = 140 Hz (**2**), 153 Hz (**3**)). A stick diagram illustrating the ^{11}B{^{1}H} NMR spectra of **2** and **3** and relating them to the previously assigned[7a] spectrum for [μ-(9,10-H$_2$C)-*nido*-7-CB$_{10}$H$_{11}$]$^-$ is given in Figure 3. The data reveal that PPh$_3$ has replaced a terminal hydrogen on the lower belt of boron atoms in the *nido*-11-vertex monocarbaundecaborane cluster. Substitution of terminal hydrogen atoms by Lewis base groups is a very common motif in borane and heteroborane chemistry,[9] where the electrons in the exo cluster B–L σ-bond arise from the Lewis base group. Thus, the exo cluster substituent brings an "extra" electron to the cluster, subrogating either a bridging hydrogen atom or a delocalized electronic charge in anionic clusters such as in compounds **2** and **3** reported here.

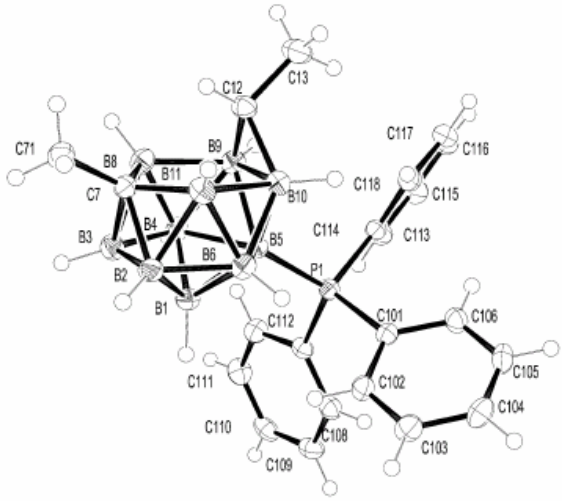


Figure 1. Molecular structure of [5-PPh$_3$-7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_{10}$] (**2**).

The detailed interatomic dimensions of **2** show little difference within experimental error from those of the unsubstituted anion **1**,[10] with the largest difference being that for the bridged B9–B10 edge, which is only 0.030 Å longer (from 1.847(2) Å in **2** to 1.879(3) Å in **1**) and which produces an attendant increase in the B9–C12–B10 angle from 68.3(1) to 69.78(14)°. The different positions of phosphine substitution make little difference in dimensions for compounds **2** and **3**. The asymmetric unit in **3** contains two independent molecules,

(4) Alcock, N. W.; Taylor, J. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1805.
(5) Hewes, J. D.; Knobler, C. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 206.
(6) McKee, M. L.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 1712.
(7) (a) Plesek, J.; Stibr, B.; Fontaine, X. L. R.; Kennedy, J. D.; Hermanek, S.; Jelinek, T. *Collect. Czech. Chem. Commun.* **1991**, *56*, 1618. (b) Plesek, J.; Jelinek, T.; Stibr, B.; Hermanek, S. *J. Chem. Soc., Chem. Commun.* **1988**, 348.
(8) Viñas, C.; Barberà, G.; Teixidor, F. *J. Organomet. Chem.* **2002**, *642*, 16.
(9) (a) Barton, L.; Srivastava, D. K. Metallaboranes. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds., Pergamon: Oxford, U.K., 1995; Vol. 1, Chapter 8, p 275. (b) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, *32*, 519. (c) **1986**, *34*, 211.
(10) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1973**, *12*(11), 2674.

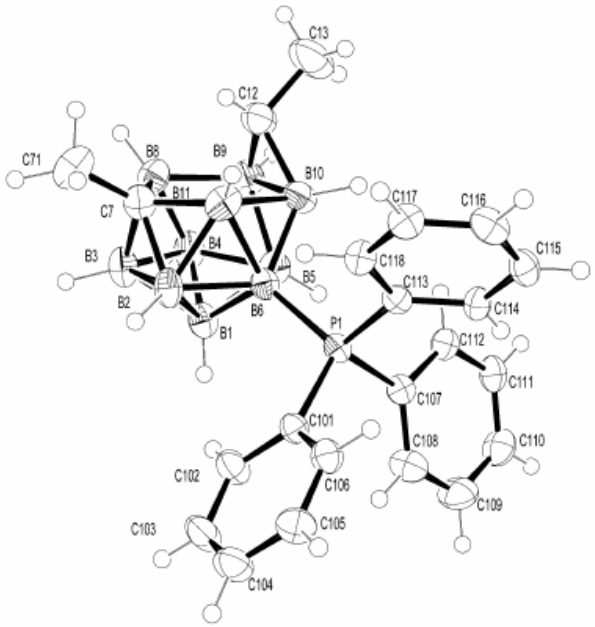


Figure 2. One of the two independent molecules in the unit cell of [6-PPh_3-7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_{10}$] (**3**), shown with 50% probability ellipsoids.

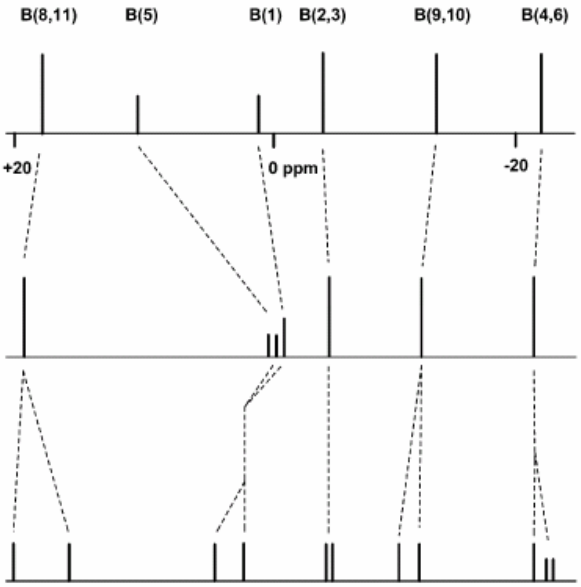


Figure 3. Stick diagrams of the $^{11}B\{^1H\}$ NMR spectra for (bottom) [6-PPh_3-7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_{10}$] (**3**), (middle) [5-PPh_3-7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_{10}$] (**2**), and (top) [μ-(9,10-H_2C)-*nido*-7-$CB_{10}H_{11}$]$^-$ (**1**).[3]

one of which featured an incompletely resolved disorder involving the phosphine group. However, the HRMS and NMR data fully support the structure shown in Figure 2.

The compounds are stable at room temperature, although in performing ^{11}B NMR measurements of **2** in $C_6D_5CD_3$ solution at 90 °C we noted that a slow **2** → **3** isomerization process occurs. This implies a vertex exchange mechanism. Vertex isomerization by a triangular face rotation has been invoked in [1,2-*closo*-$C_2B_{10}H_{12}$] clusters,[11] and this could also account for the

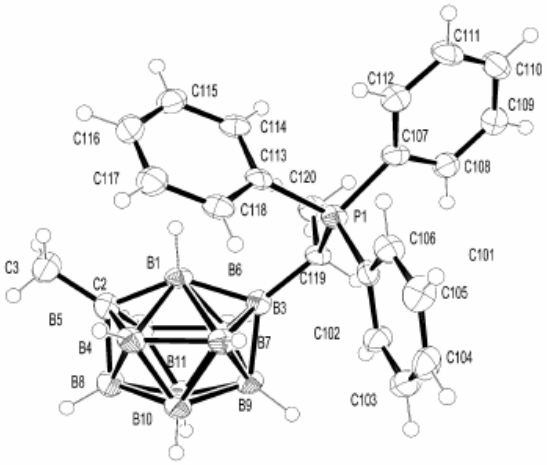


Figure 4. Molecular structure of [2-Me-3-{CHMe(PPh_3)}-*closo*-2-$CB_{10}H_9$] (**4**), with 50% probability ellipsoids.

observation here. A related thermal rearrangement of the Me_2S substituent in [7-(Me_2S)-*nido*-$B_{11}H_{13}$] from a position on the upper open face to the lower pentagonal belt and thence to the B1 position has been noted previously.[12]

These compounds represent the first derivatives of the "unreactive" [7-R-μ-(9,10-HRC)-*nido*-7-$CB_{10}H_{10}$]$^-$ anion (R = Me) which do not involve degradation of the cluster. The course of the reaction reported here, which adds phosphine to the cluster, is unclear. Phosphine migration from a metal center to a boron atom in metallacarborane and metallaborane species is well established.[13] For example, a related phosphine transfer has been previously reported in (phosphino)metallacarboranes with Rh,[14] Ni,[15] Pd,[16] and Pt.[17] In these examples a metal-bonded PPh_3 unit migrates and forms a B−PPh_3 bond[14,15,17] with the former B(10) in the free [-*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ ligand or a B−PPh_2 bond with the former B(11) in the free *nido*-*o*-carboranyl monophosphines[16a,c] and *nido*-*o*-carboranyl monothioethers.[16b] In an attempt to investigate whether the palladium species might have a catalytic behavior in the phosphine addition possibly through Pd metal released during the reaction the procedure was repeated using $^1/_2$ equiv of the palladium complex and excess triphenylphosphine. The result was a reduced yield of the compounds **2** and **3**. However, two further interesting minor products were

(11) Gimarc, B. M.; Warren, D. S.; Ott, J. J.; Brown, C. *Inorg. Chem.* **1991**, *30*(7), 1598.
(12) Keller, D. L.; Kester, J. G.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1993**, *32*, 5067.
(13) (a) Teixidor, F.; Casabo, J.; Romerosa, A. M.; Viñas, C.; Rius, J.; Miravitlles, C. *J. Am. Chem. Soc.* **1991**, *113*, 9895 and references therein. (b) Bould, J.; Brint, P.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2335. (c) Bould, J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1441. (d) Viñas, C.; Nuñez, R.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1999**, *18*, 4712. (e) Bould, J.; Rath, N. P.; Barton, L. *Angew. Chem.* **1995**, *34*, 1641.
(14) Baker, R. T.; Delaney, M. S.; King, R. E., III; Knobler, C. B.; Long, J. A.; Marder, T. B.; Paxson, T. E.; Teller, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2965.
(15) Miller, S. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1976**, 786.
(16) (a) Viñas, C.; Cirera, M. R.; Teixidor, F.; Kivekäs, R.; Sillanpää,R.; Llibre, J. *Inorg. Chem.* **1998**, *37*, 6746. (b) Teixidor, F.; Casabó, J.; Romerosa, A. M.; Viñas, C.; Rius, J.; Miravitlles, C. *J. Am. Chem. Soc.* **1991**, *113*, 9895.
(17) Barker, G. K.; Green, M.; Stone, F. G. A.; Welch, A. J.; Wolsey, W. C. *J. Chem. Soc., Chem. Commun.* **1980**, 627.

Table 1. Crystal and Structure Refinement Data

	2	3	4	5
empirical formula	$C_{22}H_{31}B_{10}P$	$C_{22}H_{31}B_{10}P$	$C_{22}H_{31}B_{10}P$	$C_{24.25}H_{38.50}B_{10}O_{1.50}P$
formula wt	434.54	434.54	434.54	493.12
temp/K	120(2)	120(2)	120(2)	120(2)
cryst syst	monoclinic	trigonal	monoclinic	monoclinic
space group	$P2_1/c$	$R\bar{3}$	$P2_1/n$	$P2_1/c$
a/Å	9.6187(8)	32.3006(3)	10.457(3)	13.5326(1)
b/Å	22.952(2)	32.3006(3)	14.955(4)	17.2277(2)
c/Å	11.9724(9)	14.9362(3)	15.893(4)	24.9167(3)
α, β, γ/deg	90, 111.677(5), 90	90, 90, 120	90, 91.82(2), 90	90, 91.4360(10), 90
V/Å^{-3}	2456.2(3)	13495.6(3)	2484.1(11)	5807.2(1)
Z	4	21	4	8
cryst size/mm	0.22 × 0.20 × 0.06	0.22 × 0.20 × 0.20	0.28 × 0.22 × 0.20	0.28 × 0.20 × 0.20
θ range for data collcn/deg	1.77−27.49	2.18−24.99	1.87−25.68	1.51−25.00
no. of rflns collected	21 776	62 698	24 003	73 224
F(000)	912	4788	912	2088
no. of indep rflns	5610 (R_{int} = 0.08)	5268 (R_{int} = 0.11)	4724 (R_{int} = 0.17)	10 210 (R_{int} = 0.17)
no. of data/restraints/params	5610/0/362	5268/21/325	4724/0/346	10 210/6/631
goodness of fit	1.005	1.075	0.998	1.010
final R indices ($I > 2\sigma(I)$)				
R1	0.046	0.067	0.079	0.105
wR2(F^2)	0.112	0.187	0.229	0.323
largest diff peak and hole/e Å^{-3}	0.37 and −0.25	0.56 and −0.52	0.59 and −0.54	0.98 and −0.90

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for [5-PPh_3-7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_9$] (2) and [6-PPh_3-7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_9$] (3)

	2	3		2	3
B−P1	1.950(2)	1.944(4)	B5−B9	1.809(3)	1.781(6)
B5−B1	1.786(3)	1.776(5)	B6−B10	1.741(3)	1.783(5)
B5−B10	1.808(3)	1.785(5)	B6−B11	1.798(3)	1.740(5)
B5−B6	1.768(3)	1.803(5)	B6−B2	1.794(3)	1.773(5)
C7−C71	1.526(3)	1.525(5)	B9−B10	1.879(3)	1.842(5)
C7−B8	1.634(3)	1.645(5)	B9−C12	1.644(3)	1.640(6)
C7−B11	1.623(3)	1.644(5)	B10−C12	1.641(3)	1.651(5)
B8−B9	1.872(3)	1.869(6)	C12−C13	1.527(3)	1.511(5)
B1−B6−P1		120.6(2)	B1−B5−P1	118.42(14)	
B9−C12−B10	69.78(14)	68.1(2)			

isolated and characterized by NMR spectroscopy, HRMS, and single-crystal X-ray diffraction studies as [2-Me-3-{CHMe(PPh_3)}-*closo*-2-$CB_{10}H_9$] (compound **4**, Scheme 1, 4%) and [7-Me-8-OEt-9-{CHMe(PPh_3)}-*nido*-7-$CB_{10}H_{10}$] (compound **5**, Scheme 1, <1%).

The structures of compounds **4** and **5** are shown in Figures 4 and 5, respectively, with selected distances and angles given in Tables 3 and 4. The $^{11}B\{^1H\}$ NMR spectrum of **4** shows a 1:1:3:3:2 pattern rather than the expected 1:1:1:1:2:2:2 pattern, indicating a coincidental overlap of four resonances. The low-field singlet in the ^{11}B NMR spectrum at +19.6 ppm indicates the presence of a substituent on boron. Indeed, the cluster hydrogen atoms overlapping peaks in the $^1H\{^{11}B\}$ NMR spectrum are all contained between +1.45 and +1.61 ppm. Features in the ^1H NMR spectrum due to the −CHMe(PPh_3) moiety are a doublet of doublets at +1.78 ppm for the Me group and two overlapping quartets at +3.58 ppm for the H atom, which collapse to a doublet and quartet, respectively, with ^{31}P decoupling ($^3J(^{31}P-^1H)$ = 20.4 Hz). The doublet and quartet are mutually coupled with $^3J(^1H-^1H)$ = 7.4 Hz.

A single-crystal X-ray diffraction study of compound **4** reveals a *closo*-monocarbaundecaborane cluster in which the phosphine substituent now resides on an organic side chain arising, presumably, from addition to the bridging {μ-HMeC} group in the starting carborane cluster and resulting in a zwitterionic alkylidene-triphenylphosphorane derivative. The group acts as a two-electron donor to the cluster, comparable to the PPh_3 substituent in compounds **2** and **3**, so that, together with the cluster carbon vertex, the cage achieves an overall $2n + 2$ skeletal electron pair count required for a closo 11-vertex cluster.[18] Only one other alkylidene-triphenylphosphorane-substituted borane cluster, CH_2-(PPh_3)B_3H_7, has been characterized previously, made directly from −CHR(PPh_3) (R = H, Me, Ph) and B_3H_7.thf.[19] A structural characterization has been car-

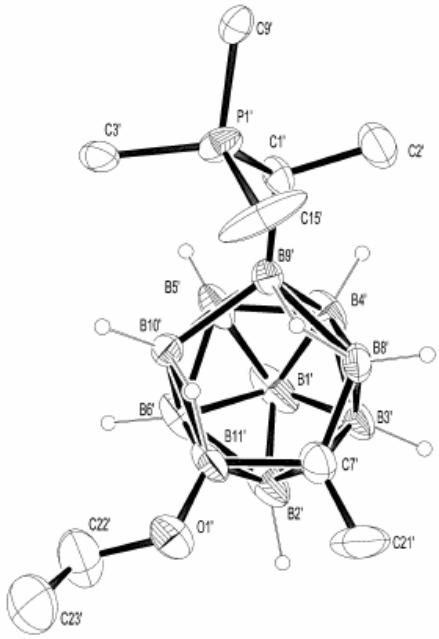


Figure 5. Molecular structure of one of the two independent molecules in the unit cell of [7-Me-8-OEt-9-{CHMe(PPh_3)}-*nido*-7-$CB_{10}H_{10}$] (**5**), shown with 50% probability ellipsoids and with phenyl rings, except for ipso carbon atoms, and noncage hydrogen atoms omitted to aid clarity.

(18) (a) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792. (b) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210. (c) Rudolph, R. W.; Pretzer, W. R. *Inorg. Chem.* **1972**, *11*, 1974. (d) Mingos, D. M. P. *Nature (Phys. Sci.)* **1972**, *236*, 99. (e) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67. (f) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (g) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for [2-Me-3-{CHMe(PPh3)}-*closo*-2-CB10H9] (4)

B1−C2	1.646(7)	B1−B3	1.768(7)
B1−B4	2.026(7)	B1−B5	2.005(7)
B1−B6	2.020(7)	B1−B7	2.074(7)
C(2)−C(3)	1.520(7)	C2−B4	1.575(7)
C2−B5	1.577(7)	C2−B8	1.673(7)
B3−C119	1.617(6)	C119−C120	1.547(6)
P1−C101	1.802(4)	P1−C113	1.798(4)
P1−C107	1.804(4)	P1−C119	1.806(4)
C120−C119−B3	112.4(4)	C120−C119−P1	111.2(3)
B3−C119−P1	113.8(3)	C113−P1−C119	109.8(2)
C101−P1−C119	110.99(19)	C107−P1−C119	112.2(2)
C3−C2−B1	124.0(4)	C119−B3−B9	135.5(4)
C3−C2−B8	126.2(4)		

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for [7-Me-8-OEt-9-{CHMe(PPh3)}-*nido*-7-CB10H10] (5)

B9′−C1′	1.607(9)	B9′−B10′	1.917(10)
C1′−P1′	1.810(6)	C1′−C2′	1.588(9)
B8′−B9′	1.917(10)	C7′−C21′	1.472(12)
B8′−C7′	1.661(11)	B11′−O1′	1.463(9)
C7′−B11′	1.665(10)	B10′−B11′	1.851(12)
C2′−C1′−P1′	107.7(4)	C2′−C1′−B9′	113.2(5)
P1−C1−B9	113.0(4)	C1′−B9′−B5′	121.6(6)
C1′−B9′−B4′	117.2(5)	C1′−B9′−B8′	125.1(5)
C21′−C7′−B2′	112.6(8)	C1′−B9′−B10′	130.0(5)
C21′−C7′−B3′	120.1(7)	C21′−C7′−B8′	124.1(7)
C21′−C7′−B11′	115.1(7)		

ried out for R = H.[20] The P−B distances are essentially equal at 1.632(8) Å in the triborane adduct and 1.607(9) Å in compound **4**. The geometry of **4** is comparable to that of the neutral *closo*-monocarbaundecaborane cluster with a Lewis base ligand [2-$(Me_3Si)_2$-6-Me_2S-2-$CB_{10}H_9$] (**6**), and related compounds,[21] and also to the *closo*-$[PhCB_{10}H_{10}]^-$ anion (**7**).[22] The most notable features for all these compounds are the distances for the apical six-connected B1 vertex to the lower belt B4−B7 vertexes. These range from 2.005(7) to 2.074(7) Å in **4**, and although they are somewhat long for interboron distances, they are comparable to those in **6** (1.747(3)−2.040(7) Å) and **7** (2.015(4)−2.057(4) Å) and are somewhat shorter than in $[B_{11}H_{11}]^{2-}$ itself, where they range from 1.959(7) to 2.159(7) Å.[23]

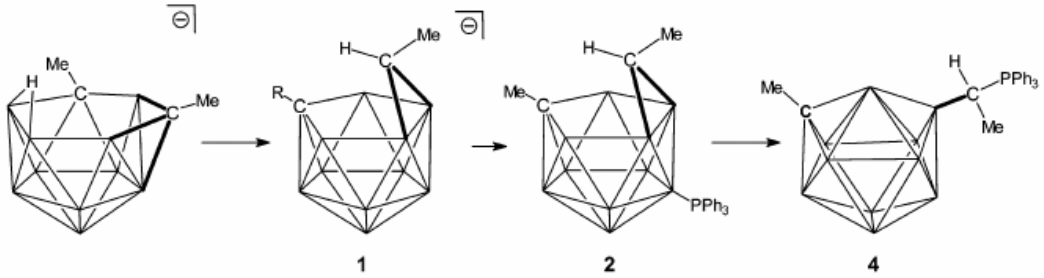
The syntheses of compounds **2** or **3** and **4** highlight the process of converting a nonclassical into a classical carbon atom. The sequence is shown in Scheme 2. Initially, in 1,2-R_2-*closo*-1,2-$C_2B_{10}H_{10}$ both carbon atoms are nonclassical (see Scheme 3) and contribute three atomic orbitals to the cluster molecular orbitals. The connectivity of these carbon atoms is 5. The species at the left in Scheme 2 corresponds to the "kinetic" isomer, [7,9-R_2-*nido*-7,9-$C_2B_{10}H_{11}]^-$. One of the two carbon atoms invests three atomic orbitals to generate a 3-fold connectivity. In the "thermodynamic" isomer [7-R-μ-(9,10-HRC)-*nido*-7-$CB_{10}H_{11}]^-$ (**1**), the endo carbon atom invests two atomic orbitals to produce a 2-fold connectivity. Finally, in **4**, the carbon atom invests one atomic orbital for a σ-bond. The exo cluster disposition of the −CHMe(PPh_3) group in **4** clearly proves the classical nature of this carbon. However, the endo nature of the bridging {μ-HMeC} group in **1** and **2** or **3** may balance the fact that the number of orbitals invested parallels the number of connectivities. The endo feature supports a nonclassical carbon, while the number of orbitals/number of connectivities suggests the contrary. We feel that the synthesis of **4** indicates that in **1**−**3** the bridging carbon in the {μ-HMeC} group has more nonclassical than classical character. The incoming PPh_3 requires an atomic orbital for the C−P coupling, which is available after disconnecting one C−B connectivity. Then, the original endo configuration of the former bridging {μ-HMeC} group is switched to an exo disposition. Our view is that if the bridging {μ-HMeC} group had not been an integral part of the cluster, relocation of the −CHMe(PPh_3) moiety to an exo cluster position would not have been necessary. A further argument that supports this view is that once the C−B connectivity is broken and in order to preserve the cluster integrity new B−B connectivities are generated that ultimately produce the closo species **4** (see Scheme 4).

Compound **5** is related to **4**, but with an additional two bridging hydrogen atoms, giving it a *nido* 11-vertex structure. ^{11}B NMR spectrometry shows a 1:1:2:1:1:2:1:1 pattern with two singlet resonances of unit intensity, corresponding to the presence of two substituents on boron. The $^1H\{^{11}B\}$ NMR spectrum showed two sets of the doublet of doublets, which are characteristic for the methyl group in the methyltriphenylphosphorane substituent, and the $^{31}P\{^1H\}$ spectrum showed two singlet resonances at +34.8 and +35.3 ppm, indicating the presence of two closely related species in solution. We were unable to chromatographically separate them, but slow evaporation of a CH_2Cl_2/hexane solution gave crystals of a single species suitable for a single-crystal X-ray study. The data reveal two unique molecules in the unit cell with −CHMe(PPh_3) and ethoxy substituents on two boron vertexes in a *nido*-monocarbaundecaborane cluster (Figure 4). The B−OEt and C−Me positions were disordered, as was one phenyl group on the triphenylphosphine moiety. The B11′−O1′ distance of 1.463(9) Å is similar to the C7′− C21′ distance, 1.472(12) Å, and is somewhat longer than a range of cage B−OR separations (1.371−1.409 Å),[24] although this is probably an artifact of the disorder. The bridging hydrogen atoms evident in the proton spectrum were also located in the X-ray structure determination. The molecular formulation shown is supported by the HRMS data, which exhibits a signal group pattern centered at *m*/*z* 478.3421 (478.3429 calculated) for $P^+ - H_2$ on $C_{24}H_{37}B_{10}PO$. The ethoxy substituent clearly comes from the ethanol solvent, and it may also supply the two extra hydrogen atoms required to achieve the observed nido cluster.

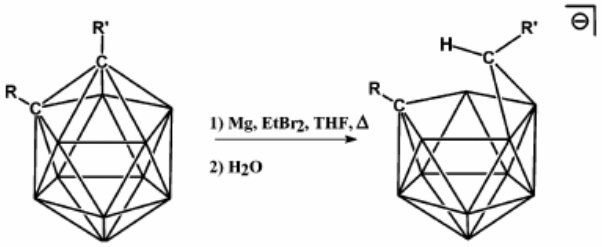
The EtO− substitution is not rare in boron chemistry clusters. Upon reaction of $[MCl_2(PPh_3)_2]$ (M = Pd, Pt) with borate anions in refluxing alcohols as solvent,

(19) Chung Choi, P.; Morris, J. H. *J. Chem. Soc., Dalton Trans.* **1984**, 2119.
(20) Andrews, S. J.; Welch, A. J. *Acta Crystallogr.* **1985**, *C41*, 1496.
(21) Ernest, R. L.; Quintana, W.; Rosen, R.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1987**, *6*, 80.
(22) Franken, A.; Kilner, C. A.; Thornton-Pett, M.; Kennedy, J. D. *J. Organomet. Chem.* **2002**, *657*, 180.
(23) Volkov, O.; Englebert, U.; Paetzold, P. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1193.
(24) (a) Hu, C. H.; Yong, W.; Dou, J. M.; Sun, J.; Hu, K. J.; Jin, R. S.; Zheng, P. J. *Chin. J. Chem.* **2002**, *20*, 536. (b) Nie, Y.; Hu, C, H.; Li, X.; Yong, W.; Dou, J. M.; Sun, J.; Jin, R. S.; Zheng, P. J. *Acta Crystallogr.* **2001**, *C57*, 897.

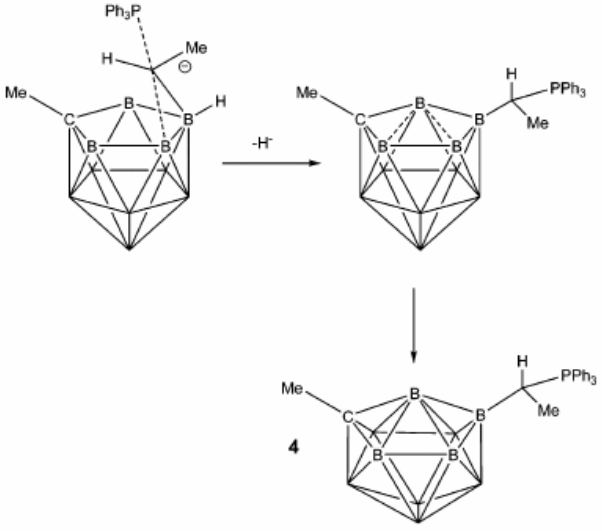
Scheme 2. Fate of a Nonclassical Carbon in the "Kinetic" Isomer [7,9-R_2-*nido*-7,9-$C_2B_{10}H_{11}$]− to a Classical One in [2-Me-3-{CHMe(PPh_3)}-*closo*-2-$CB_{10}H_9$] (4) through the "Thermodynamic" [7-R-μ-(9,10-HRC)-*nido*-7-$CB_{10}H_{10}$]− Isomer (1)



Scheme 3. Synthesis of the "Thermodynamic" Isomer [7-R-μ-(9,10-HRC)-*nido*-7-$CB_{10}H_{10}$]− (1), Produced Directly from the Reaction of 1,2-R_2-*closo*-1,2-$C_2B_{10}H_{10}$ with Magnesium Metal



Scheme 4. Suggested Pathway to Convert One Nonclassical Carbon Atom from [7-R-μ-(9,10-HRC)-*nido*-7-$CB_{10}H_{10}$]− (1) into a Classical One in [2-Me-3-{CHMe(PPh_3)}-*closo*-2-$CB_{10}H_9$] (4)



alkoxy group substitution to occupy terminal positions has been observed.[25]

The synthesis of compounds **2**−**5**, although obtained in low yield, opens a way to explore the derivative chemistry of the "thermodynamic" isomer, [7-R-μ-(9,10-HRC)-*nido*-7-$CB_{10}H_{11}$]$^-$ (**1**), considered up to now a nonreactive species. The diversity of generated compounds and the low yields are indicative of the difficulty of the [7-R-μ-(9,10-HRC)-*nido*-7-$CB_{10}H_{11}$]$^-$ (**1**) to react, but it fulfills the objective of this work, which potentially demonstrates that routes to monocarbaundecaboranes through the readily available [$NHMe_3$][7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_{10}$] (**1**) may be attainable.

Experimental Section

General Considerations. Experiments were carried out under a dry nitrogen atmosphere, with subsequent isolation and characterizations being carried out in air. Solvents were dried by conventional methods. [$NHMe_3$][7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_{10}$] and [$PdCl_2(PPh_3)_2$] were prepared by the literature methods.[8,26] ^1H and $^1H\{^{11}B\}$ NMR (300.13 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz), and ^{11}B NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were recorded from $CDCl_3$ solutions at 298 K. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3 \cdot OEt_2$, $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 (minus values upfield), and those for ^1H, $^1H\{^{11}B\}$, and $^{13}C\{^1H\}$ NMR spectra were referenced to $Si(CH_3)_4$. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in hertz. The mass spectra were measured in the FAB mode on a JEOL MStation JMS-70 spectrometer using 3-nitrobenzyl alcohol (3-NBA, or 3-NBA/CsI).[27] Thin-layer chromatography (TLC) plates were individually crafted from aqueous slurries of Aldrich standard grade TLC silica gel with a fluorescent indicator and dried at ambient temperature.

[5-PPh_3-7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_9$] (2) and [6-PPh_3-7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_9$] (3). [$NHMe_3$]-[7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_{10}$] (57 mg, 0.244 mmol) and [$PdCl_2(PPh_3)_2$] (175 mg, 0.25 mmol) were stirred at reflux overnight in ethanol. After it was cooled, the dark solution was filtered through a plug of silica gel and the filtrate was reduced in volume (rotary evaporator, ca. 40 °C) and subjected to preparative TLC (75/25 CH_2Cl_2/hexane). A colorless band observed under UV irradiation, A (R_f = 0.8), and B, a rusty brown band (R_f = 0.2), were obtained. Band B did not contain boron and was not further investigated. Band A was redeveloped (20/80 CH_2Cl_2/hexane), giving two further UV-active bands at R_f = 0.3 (C), 0.2 (D). Crystals suitable for single-crystal X-ray diffraction studies were grown for each compound by slow evaporation of layered hexane/$CDCl_3$ solutions of the compound. The bands were identified by NMR spectrometry, high-resolution mass spectrometry, and single-crystal X-ray diffraction analyses.

Band C: [5-PPh_3-7-Me-μ-(9,10-HMeC)-*nido*-7-$CB_{10}H_9$] (compound **2**, 10.3 mg, 24 μmol, 10%). ^1H NMR: δ 7.75−7.52 (m,

(25) (a) Hu, C. H.; Yong, W.; Dou, J. M.; Sun, J.; Hu, K. J.; Jin, R. S.; Zheng, P. J. *Chin. J. Chem.* **2002**, *20*, 536−538. (b) Nie, Y.; Hu, C, H.; Li, X.; Yong, W.; Dou, J. M.; Sun, J.; Jin, R. S.; Zheng, P. J. *Acta Crystallogr.* **2001**, *C57*, 897−899.

(26) Blackburn, J. R.; Nordberg, R.; Stevie, F.; Albridge, R. G.; Jones, M. M. *Inorg. Chem.* **1970**, *9*, 2374.

(27) Siuzdak, G.; Wendeborn, S. V.; Nicolaou, K. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *112(1)*, 79.

15H, H_{aryl}), 3.64 (quartet, $^3J(^1H-^1H) = 6.3$, 1H, C12−*H*), 3.69−1.33 (br m, 9H, B−*H*), 1.81 (s, 3H, C7−*Me*), 1.42 (d, $^3J(^1H-^1H) = 6.3$, 3H, C12-*Me*). $^1H\{^{11}B\}$ NMR: δ 7.75−7.52 (m, 15H, H_{aryl}), 3.64 (quartet, $^3J(^1H-^1H) = 6.3$, 1H, C12−H), 3.69 (br s, 2H, B8−*H* and B11−*H*), 2.92 (br s, 1H, B1−*H*), 1.96 (br s, 2H, B2−*H* and B3−*H*), 1.49 (br s, 2H, B9−*H* and B10−*H*), 1.33 (br s, 2H, B4−*H* and B6−*H*), 1.81 (s, 3H, C7−*Me*), 1.42 (d, $^3J(^1H-^1H) = 6.3$, 3H, C12−*Me*). $^{11}B\{^1H\}$ NMR: δ +19.3 (s, 2B, B8 and B11), 0.0 (d, $^1J(^{11}B-^{31}P) = 140$, 1B, B5), −0.6 (s, 1B, B1), −5.3 (s, 2B, B2 and B3), −12.8 (s, 2B, B9 and B10), −21.6 (s, 2B, B4 and B6). $^{31}P\{^1H\}$ NMR: δ +5.7 (quartet, $^1J(^{31}P-^{11}B) = 140$). Mass spectrometry shows two envelopes centered at *m*/*z* 433.3121 and 419.2982, within 7.6 and 12 ppm of the calculated peak profile for $(P^+ + H) - H_2$ and $(P^+ + H) - CH_4$ in $C_{22}H_{31}B_{10}P$.

Band D: [6-PPh$_3$-7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_9$] (compound **3**, 16.6 mg, 40.2 μmol, 16%). ^1H NMR: δ 7.75−7.52 (m, 15H, H_{aryl}), 4.06 (quartet, $^3J(^1H-^1H) = 6.0$, 1H, C12−*H*), 1.74 (s, 3H, C7−*Me*), 1.48 (d, $^3J(^1H-^1H) = 6.0$, 3H, C12−*Me*). $^{11}B\{^1H\}$ NMR: δ +21.0 (s, 1B, B8 or B11), +14.7 (s, 1B, B11 or B8), +3.9 (s, 1B, B1 or B5), −1.6 (s, 1B, B5 or B1), −5.5 (s, 1B, B2 or B3), −6.6 (s, 1B, B3 or B2), −12.4 (s, 1B, B9 or B10), −15.2 (s, 1B, B10 or B9), −20.4 (s, 1B, B4), −23.2 (d, $^1J(^{31}P-^{11}B) = 153$, 1B, B6). $^{31}P\{^1H\}$ NMR: δ +6.2 (quartet, $^1J(^{31}P-^{11}B) = 153$). Mass spectrometry showed two envelopes centered at *m*/*z* 433.3057 (433.3099 calcd) and 419.2936 (419.2942 calcd) within 9.6 and 1.4 ppm, respectively, of that calculated for $(P^+ + H) - H_2$ and $(P^+ + H) - CH_4$ in $C_{22}H_{31}B_{10}P$.

[2-Me-3-{CHMe(PPh$_3$)}-*closo*-2-CB$_{10}$H$_9$] (4) and [7-Me-8-OEt-9-{CHMe(PPh$_3$)}-*nido*-7-CB$_{10}$H$_{10}$] (5). In a similar experiment [NHMe$_3$][7-Me-μ-(9,10-HMeC)-*nido*-7-CB$_{10}$H$_{10}$] (72 mg, 0.31 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (111 mg, 0.16 mmol) with added PPh$_3$ (161 mg, 0.61 mmol) were refluxed in ethanol for 24 h, and after cooling the solution was filtered, giving a sandy colored, non-boron-containing solid (yield 61 mg). The filtrate was reduced in volume and subjected to preparative TLC as described above (80/20 CH_2Cl_2/hexane), giving colorless bands observed under UV illumination at R_f = 0.8, 0.7, and 0.2. The first band contained a mixture of compounds **2** and **3** (5 mg). The second band was characterized as [2-Me-3-{CHMe(PPh$_3$)}-*closo*-2-CB$_{10}$H$_9$] (compound **4**, 5.0 mg, 12 μmol, 4%). ^1H NMR: δ 7.75−7.52 (m, 15H, H_{aryl}), 3.58 (overlapping doublet of quartets, $^3J(^1H-^1H) = 7.4$, $^3J(^{31}P-^1H) = 20.4$, 1H, C(119)−*H*), 1.78 (doublet of doublets, $^3J(^1H-^1H) = 7.3$, $^3J(^{31}P-^1H) = 20.4$, 3H, C119−*Me*), 1.61−1.45 (br m, 9H, B−*H*), 1.28 (s, 3H, C2−*Me*). $^1H\{^{11}B\}$ NMR: δ 7.75−7.52 (m, 15H, H_{aryl}), 3.58 (overlapping doublet of quartets, $^3J(^1H-^1H) = 7.4$, $^3J(^{31}P-^1H) = 20.4$, 1H, C(119)−*H*), 1.78 (doublet of doublets, $^3J(^1H-^1H) = 7.3$, $^3J(^{31}P-^1H) = 20.4$, 3H, C119−*Me*), 1.61 (br s, 3H, B−H), 1.51 (br s, 3H, B−H), 1.45 (br s, 3H, B−H), 1.28 (s, 3H, C2−*Me*). $^{11}B\{^1H\}$ NMR: δ +19.6 (s, 1B), −6.4 (s, 1B), −12.1 (s, 3B), −14.3 (s, 3B), −20.2 (s, 2B). $^{31}P\{^1H\}$ NMR: δ +32.2 (s). Mass spectrometry ((NBA/CsI)) shows an peak envelope centered at *m*/*z* 567.2216 within −2.8 ppm of that calculated for the peak profile of P^+ in $C_{22}H_{31}PB_{10}Cs$ (567.2232). Colorless cubic single crystals were obtained by slow evaporation of a CH_2Cl_2/hexane solution of the compound.

The third band (ca. 1 mg) contained two very closely related species. The mixture was crystallized by slow evaporation of a CH_2Cl_2/hexane solution. The compound was characterized by a single-crystal X-ray diffraction study, together with NMR and HRMS, as [7-Me-8-OEt-9-{CHMe(PPh$_3$)}-*nido*-7-CB$_{10}$H$_{10}$] (compound **5**). $^{11}B\{^1H\}$ NMR: δ +7.9 (s, 1B, B9′), −6.3 (s, 1B), −8.6 (s, 2B), −11.6 (s, 1B), −16.5 (s, 1B, B11′), −26.9 (s, 2B), −32.6 (s, 1B), −35.1 (s, 1B). $^{31}P\{^1H\}$ NMR: δ +34.8, +35.3 in ca. 2:1 ratio, respectively. $^1H\{^{11}B\}$ NMR: overlapping peaks for both species A and species B in a ca. 2:1 ratio at δ 7.80−8.00 (m, 15H, H_{aryl}), 3.5 (1H, C9−*H*), two sets of doublets of doublets for isomers A and B at δ +1.62 ($^3J(^1H-^1H) = 7.3$, $^3J(^{31}P-^1H) = 20.5$, CHPPh$_3$−CH$_3$), 1.49 ($^3J(^1H-^1H) = 7.6$, $^3J(^{31}P-^1H) = 20.5$, CHPPh$_3$−CH$_3$), 1.38 (s, 3H, C7′−CH$_3$); B−*H* atoms show overlapping peaks for the two species at δ +2.38, +2.27, +1.91, +1.73, +1.22, +0.88, +0.75, −0.38, −0.30 (μ-H(9′-10′)), −2.34 (μ-H(10′-11′)), −3.42, −3.70. Mass spectrometry shows a peak envelope centered at *m*/*z* 478.3421 within −1.6 ppm of that calculated for the peak profile of P^+-H_2 in $C_{24}H_{37}B_{10}PO$ (478.3412).

X-ray Crystallography. Crystals of appropriate dimensions were mounted on glass fibers in a random orientation. Preliminary examination and data collection was performed using a Brüker SMART charge coupled device (CCD) detector system single-crystal X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) equipped with a sealed-tube X-ray source at 120 K. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.4° in ϖ) scans. A typical data set consisted of 3636 frames with a frame width of 0.3° in ϖ and typical counting time of 15−30 s/frame at a crystal to detector distance of 4.900 cm. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages[28] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of *xyz* centroids. Collected data were corrected for systematic errors using SADABS[29] based on the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are listed in Table 1.

Structure solution and refinement for compounds **2**, **4**, and **5** were carried out using the SHELXTL-PLUS software package.[30] The structures were solved by direct methods and refined successfully in the monoclinic space groups $P2_1/c$, $P2_1/n$, and $P2_1/c$, respectively. Full-matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The cage hydrogen atoms for all three compounds were located from difference Fourier syntheses and refined freely for compounds **2** and **4**. The cage H's for compound **5** were located but not refined. All other hydrogen atoms were treated using the appropriate riding model (AFFIX m3).

Refinement for compound **3** was carried out using SHELX-97.[28] The asymmetric unit of compound **3** contains one ordered molecule and one-sixth of a disordered molecule. There are two neighboring equivalent positions for the disordered molecule, although only one can be present in either position. The phosphorus atom and the boron atom connected to the phosphorus atom of the disordered molecule lie on a 3-fold axis, and the rest of the non-hydrogen atoms are in the vicinity of the 3-fold axis. Each phenyl group of the disordered molecule assumes two orientations. Owing to the disorder and low occupancy of the disordered molecule, the Me and μ-HMeC groups could not be accurately located or the cage carbon atom reliably identified. Therefore, all non-hydrogen atoms of the disordered cage were treated as boron atoms in the final calculations. The H atoms of the disordered cage were not located. EADP constraints and DFIX restraints were utilized in order to keep bond parameters reasonable for the disordered cage. All non-hydrogen atoms of the ordered molecule and the phosphorus atom of the disordered molecule were refined anisotropically, but the atoms of the disordered cage were refined with isotropic thermal displacement parameters. Hydrogen atoms were placed at calculated distances from their host atoms and treated as riding atoms using the SHELX97 default parameters.[31] Refinements of the structure in the lower symmetry space groups also resulted in a partially disordered structure.

(28) Brüker Analytical X-ray, Madison, WI, 2002.
(29) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.
(30) Sheldrick, G. M. Brüker Analytical X-ray Division, Madison, WI, 2002.

The asymmetric unit of compound **5** contains two unique molecules, and both exhibit disorder. A phenyl group was disordered in one of the two molecules and shows large thermal motion. Rigid-body refinement (AFFIX 66) and thermal ellipsoid constraints (EADP) were used to model this disorder. In the second molecule, the C−Me and B−Et positions are disordered. These two positions were modeled with partial occupancy of all the involved atoms, and positional and thermal parameter restraints (EXYZ and EADP) were used to model the disorder.

Structure refinement parameters are listed in Table 1. Drawings of the molecules were made with ORTEP[32] with nonhydrogen atoms represented by 50% probability ellipsoids.

(31) Sheldrick, G. M. SHELX97; University of Göttingen, Göttingen, Germany, 1997.

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Supporting Information Available: Tables giving complete X-ray data for compounds **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

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1,2-Bis(methylsulfanyl)-1,2-dicarba-*closo*-dodecaborane(12)

Anna Laromaine,[a] Clara Viñas,[a] Reijo Sillanpää[b] and Raikko Kivekäs[c]*

[a]Institut de Ciència de Materials de Barcelona, CSCI, Campus UAB, 08193 Bellaterra, Spain, [b]Department of Chemistry, University of Jyväskylä, FIN-40351 Jyväskylä, Finland, and [c]Department of Chemistry, PO Box 55, FIN-00014 University of Helsinki, Finland
Correspondence e-mail: raikkok@saunalahti.fi

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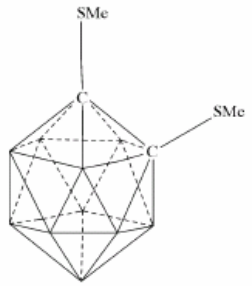
In the title compound, 1,2-$(SCH_3)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ or $C_4H_{16}B_{10}S_2$, the methylsulfanyl groups are bonded to the C atoms of the 1,2-dicarba-*closo*-dodecaborane cage. The $C_{cage}-C_{cage}$ distance is 1.8033 (18) Å and the $S-C_{cage}-C_{cage}-S$ torsion angle is 1.07 (13)°. The $C_{cage}-C_{cage}$ distance is compared with those in other 1,2-dicarba-*closo*-dodecaborane derivatives.

Comment

The contribution of substituents at the cluster C atoms on the lengthening of the $C_{cage}-C_{cage}$ or C1—C2 bond in 1,2-*closo*-$C_2B_{10}H_{12}$ or *o*-carborane derivatives is well known (Kivekäs, Sillanpää *et al.*, 1995; Sillanpää *et al.*, 1996). Different C1—C2 distances in icosahedral *o*-carborane derivatives can be achieved by modifying the substituents at the C atoms of the cluster compound. This is important both from the theoretical point of view and also in order to understand the isomerization process that takes place from *ortho*-, *meta*- and *para*-carborane isomers.

The C1—C2 distance is strongly dependent on the number of substituents connected to the cluster C atoms and the atomic species of those substituents. Accordingly, shortest distances of 1.629 (6) and 1.630 (6) Å have been reported for two crystallographically independent molecules of the unsubstituted parent compound 1,2-*closo*-$C_2B_{10}H_{12}$, carrying H atoms at both cluster C atoms (Davidson *et al.*, 1996). Dealing with one atomic species, it is observed that a substituent at only one of the cluster C atoms does not increase the distance significantly, or affects the distance only slightly, but increased lengthening is observed if both cluster C atoms are substituted. Table 1 lists the C1—C2 bond lengths for a wide range of comparable compounds and the following observations have been noted. Firstly, the lengthening caused by aliphatic C substituents at both cluster C atoms is smaller than that of aromatic C. Secondly, in Si-substituted compounds, the C1—C2 distance is approximately comparable with that in the compound bearing two aliphatic C atoms at the cluster C atoms. Thirdly, the contribution of two P-substituents is comparable with that of two aryl groups. Finally, the longest C1—C2 distances (*ca* 1.80–1.86 Å) have been reported for 1,2-S_2-disubstituted *o*-carborane derivatives (Llop *et al.*, 2002; Teixidor, Viñas *et al.*, 1990; Teixidor, Romerosa *et al.*, 1990). As far as we know, no crystallographic data are available for 1,2-N_2- and 1,2-O_2-disubstituted *o*-carborane compounds. However, a C1—C2 distance as long as 2.001 (3) Å has been reported for the $[1\text{-O-2-}C_6H_5\text{-1,2-}closo\text{-}C_2B_{10}H_{10}]^-$ anion, containing a C═O bond (Brown *et al.*, 1987).



(I)

We have suggested an empirically derived equation (Kivekäs, Sillanpää *et al.*, 1995; Kivekäs, Teixidor *et al.*, 1995) to calculate the C1—C2 distance, as well as carrying out computational analyses to understand the nature of the bond (Llop *et al.*, 2002; Paavola, 2002). As this kind of lengthening is exceptional and unique in chemistry, we have continued our research on this topic and now report the crystal structure of the title compound, (I), the preparation of which has been reported previously by Llop *et al.* (2001).

In compound (I), the SCH_3 groups are oriented in approximately the same direction from the cluster (Fig. 1). This is also indicated by the torsion angles of 101.13 (11) and −92.41 (11)° for C1—C2—S2—C14 and C2—C1—S1—C13, respectively. The molecule has approximately C_s symmetry,

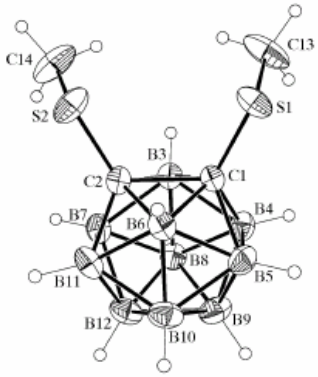


Figure 1
A view of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

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with the pseudo-mirror plane passing through the mid-point of the C1—C2 bond and through atoms B3, B6, B8 and B10. The intramolecular S1···S2 distance of 3.4359 (6) Å is only 0.16 Å shorter than the sum of the corresponding van der Waals radii (Bondi, 1964), thus indicating only minor interaction between the atoms. The free electron pairs of the S atoms are oriented away from each other to avoid steric repulsion. The S1—C1—B6 and S2—C2—B6 angles of 112.05 (9) and 112.45 (9)°, respectively, are narrower than the mean S—C_{cage}—X (X is C_{cage} or B) angles of *ca* 119.5°, thus indicating that the S atoms are displaced slightly from their ideal radial orientation towards atom B6.

The main interest of (I) is in its C1—C2 bond. The bond length of 1.8033 (18) Å is in line with the previously observed distances in 1,2-disubstituted *o*-carborane derivatives. The bond is clearly longer than the relevant bond in the C-, Si- and P-1,2-disubstituted compounds and is comparable with the distances in the 1,2-S_2-disubstituted compounds. Thus, the C1—C2 distance in (I) is equal to the distance of 1.799 (3) Å in 1,2-$(SC_6H_5)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (Llop *et al.*, 2002) and is equal to or slightly shorter than the distances of 1.816 (6), 1.826 (5) and 1.858 (5) Å in 1,2-μ-$SCH_2CH_2OCH_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$ (Teixidor, Romerosa *et al.*, 1990) and 1,2-μ-$SCH_2(CH_2OCH_2)_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$ (Teixidor, Viñas *et al.*, 1990). The C1—C2 distance in (I) is also equal to the distance of 1.792 (5) Å observed in the [2-CH_3-1-S-1,2-*closo*-$C_2B_{10}H_{10}]^-$ anion (Kivekäs *et al.*, 1999), thus indicating that the contribution of methyl and sulfide groups is comparable with that of two SCH_3 groups. The C1—C2 distance found in (I) is a further confirmation that the S atoms in 1,2-disubstituted *o*-carborane derivatives lengthen the C1—C2 distance considerably.

In the [2-CH_3-1-S-*closo*-$C_2B_{10}H_{10}]^-$ anion, there is a short intramolecular distance of 2.68 Å between a methyl H atom and the sulfide group, indicating a hydrogen bond between the atoms (Kivekäs *et al.*, 1999). In (I), containing neutral SCH_3 substituents at the cluster C atoms, the shortest S···H(CH_3) distance between different SCH_3 substituents is intermolecular and as long as 3.24 Å, *ca* 0.2 Å longer than the sum of the corresponding van der Waals radii (Bondi, 1964). The shortest intermolecular (S2···H12) contact is 2.95 Å. These distances indicate that there are only weak van der Waals packing forces between the molecules.

Experimental

Compound (I) was synthesized from 1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$ and CH_3I, and crystallized from petroleum ether (b.p. 313–333 K; Llop *et al.*, 2001).

Crystal data

$C_4H_{16}B_{10}S_2$
M_r = 236.39
Monoclinic, $P2_1/n$
a = 7.16670 (10) Å
b = 15.1733 (2) Å
c = 11.8894 (2) Å
β = 92.9760 (10)°
V = 1291.14 (3) Å^3
Z = 4
D_x = 1.216 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2472 reflections
θ = 2.9–25.7°
μ = 0.37 mm^{-1}
T = 173 (2) K
Prism, colourless
0.22 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
4565 measured reflections
2397 independent reflections
2208 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 25.7°
$h = -8 \rightarrow 8$
$k = -18 \rightarrow 16$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.086
S = 1.07
2397 reflections
147 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.5289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
C1—C2 distances (Å) for selected C_{cage}-substituted 1,2-dicarba-*closo*-dodecaborane(12) derivatives (compounds containing metal ions or strained rings are not included).

Compound	C1—C2	Reference
(1,2-*closo*-$C_2B_{10}H_{12}$·hmpa)$_2$	1.629 (6) and 1.630 (6)	*a*
1-COOH-*closo*-$C_2B_{10}H_{11}$	1.631 (2)	*b*
1,2-$(COOH)_2$-*closo*-$C_2B_{10}H_{10}$·0.5C_2H_6O	1.651 (2)–1.660 (2)	*c*
1-P(C_6H_5)$_2$-1,2-*closo*-$C_2B_{10}H_{11}$	1.666 (9)	*d*
1-COOH-2-CH_3-*closo*-$C_2B_{10}H_{10}$	1.6694 (17)	*e*
1-CH_2CH_2SH-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$	1.670 (3)	*f*
1-COOH-2-C_6H_5-*closo*-$C_2B_{10}H_{10}$	1.678 (3) and 1.691 (3)	*e*
1,1′-Si(CH_3)$_2$-2,2′-Si(CH_3)$_2$-(1,2-*closo*-$C_2B_{10}H_{10}$)$_2$	1.688 (5)	*g*
1-C_6H_5-2-CO(C_6H_5)-*closo*-$C_2B_{10}H_{10}$	1.695 (3)	*e*
1-P(C_6H_5)$_2$-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$	1.702 (6)	*h*
1-COOH-2-C_6H_5-*closo*-$C_2B_{10}H_{10}$·2H_2O	1.705 (2)	*e*
1,2-[P(2-C_3H_7)$_2$]$_2$-1,2-*closo*-$C_2B_{10}H_{10}$	1.719 (3)	*i*
1,2-[P(C_6H_5)$_2$]$_2$-1,2-*closo*-$C_2B_{10}H_{10}$	1.722 (4)	*j*
1,2-(C_6H_5)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$	1.720 (4) and 1.733 (4)	*k*
1-P(2-C_3H_7)$_2$-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$	1.731 (9)	*j*
1-P(C_6H_5)$_2$-2-S(2-C_3H_7)-1,2-*closo*-$C_2B_{10}H_{10}$	1.747 (5)	*l*
1-P(C_6H_5)$_2$-2-C_6H_5-1,2-*closo*-$C_2B_{10}H_{10}$	1.755 (6)	*m*
1-P(2-C_3H_7)$_2$-2-C_6H_5-1,2-*closo*-$C_2B_{10}H_{10}$	1.769 (4)	*n*
[$PCH_3(C_6H_5)_3$][1-CH_3-2-S-1,2-*closo*-$C_2B_{10}H_{10}$]	1.792 (5)	*o*
1,2-(SC_6H_5)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$	1.799 (3)	*p*
1,2-(SCH_3)$_2$-*closo*-1,2-$C_2B_{10}H_{10}$	1.8033 (18)	*q*
1,2-μ-$SCH_2CH_2OCH_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$	1.816 (6)	*r*
1,2-μ-$SCH_2(CH_2OCH_2)_2CH_2S$-1,2-*closo*-$C_2B_{10}H_{10}$	1.826 (5) and 1.858 (5)	*s*

References: (*a*) Davidson *et al.* (1996) (hmpa is hexamethylphosphoramide); (*b*) Welch *et al.* (2001); (*c*) Venkatasubramanian *et al.* (2003); (*d*) Kivekäs, Teixidor *et al.* (1995); (*e*) Venkatasubramanian *et al.* (2004); (*f*) Kivekäs *et al.* (1998); (*g*) Kivekäs, Romerosa & Viñas (1994); (*h*) Kivekäs, Sillanpää *et al.* (1994); (*i*) Kivekäs, Sillanpää *et al.* (1995); (*j*) Paavola (2002); (*k*) Lewis & Welch (1993); (*l*) Teixidor *et al.* (1997); (*m*) McWhannell *et al.* (1996); (*n*) Sillanpää *et al.* (1996); (*o*) Kivekäs *et al.* (1999); (*p*) Llop *et al.* (2002); (*q*) this work; (*r*) Teixidor, Romerosa *et al.* (1990); (*s*) Teixidor, Viñas *et al.* (1990).

Methyl groups were refined as rotating groups, with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C). The other H atoms were refined using a riding model, with B—H = 1.12 Å and U_{iso}(H) = 1.2U_{eq}(B), starting from idealized positions.

Table 2
Selected geometric parameters (Å, °).

S1—C1	1.7610 (13)	C1—B6	1.7233 (19)
S1—C13	1.7876 (18)	C1—C2	1.8033 (18)
S2—C2	1.7630 (14)	C2—B6	1.7121 (19)
S2—C14	1.7929 (18)	C2—B3	1.7255 (19)
C1—B3	1.7208 (19)		
C1—S1—C13	104.27 (7)	S1—C1—C2	117.90 (8)
C2—S2—C14	104.25 (8)	B7—C2—S2	126.21 (9)
B4—C1—S1	126.22 (9)	B11—C2—S2	120.03 (10)
B5—C1—S1	119.05 (9)	B6—C2—S2	112.45 (9)
B3—C1—S1	122.47 (9)	B3—C2—S2	121.43 (9)
B6—C1—S1	112.05 (9)	S2—C2—C1	117.29 (9)
S1—C1—C2—S2	1.07 (13)	C2—C1—S1—C13	−92.40 (12)
C1—C2—S2—C14	101.12 (11)		

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1059). Services for accessing these data are described at the back of the journal.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Brown, D. A., Clegg, W., Colquhoun, H. M., Daniels, J. A., Stephenson, I. R. & Wade, K. (1987). *J. Chem. Soc. Chem. Commun.* pp. 889–891.
Davidson, M. G., Hibbert, T. G., Howard, J. A. K., Mackinnon, A. & Wade, K. (1996). *Chem. Commun.* pp. 2285–2286.
Kivekäs, R., Benakki, R., Viñas, C. & Sillanpää, R. (1999). *Acta Cryst.* C**55**, 1581–1583.
Kivekäs, R., Pedrajas, J., Teixidor, F. & Sillanpää, R. (1998). *Acta Cryst.* C**54**, 1716–1718.
Kivekäs, R., Romerosa, A. & Viñas, C. (1994). *Acta Cryst.* C**50**, 638–640.
Kivekäs, R., Sillanpää, R., Teixidor, F., Viñas, C. & Nuñez, R. (1994). *Acta Cryst.* C**50**, 2027–2030.
Kivekäs, R., Sillanpää, R., Teixidor, F., Viñas, C., Nuñez, R. & Abad, M. (1995). *Acta Cryst.* C**51**, 1864–1868.
Kivekäs, R., Teixidor, F., Viñas, C. & Nuñez, R. (1995). *Acta Cryst.* C**51**, 1868–1870.
Lewis, Z. G. & Welch, A. (1993). *Acta Cryst.* C**49**, 705–710.
Llop, J., Viñas, C., Oliva, J. M., Teixidor, F., Flores, M. A., Kivekäs, R. & Sillanpää, R. (2002). *J. Organomet. Chem.* **657**, 232–238.
Llop, J., Viñas, C., Teixidor, F., Kivekäs, R. & Sillanpää, R. (2001). *Organometallics*, **19**, 4024–4030.
McWhannell, M. A., Rosair, G. M., Welch, A. J., Teixidor, F. & Viñas, C. (1996). *Acta Cryst.* C**52**, 3135–3138.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Paavola, S. (2002). PhD thesis (URL: http://ethesis.helsinki.fi/julkaisut/mat/kemia/vk/paavola/), University of Helsinki, Finland.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Sillanpää, R., Kivekäs, R., Teixidor, F., Viñas, C. & Nuñez, R. (1996). *Acta Cryst.* C**52**, 2223–2225.
Teixidor, F., Romerosa, A., Rius, J., Miravitlles, C., Casabó, J., Viñas, C. & Sanchez, E. (1990). *J. Chem. Soc. Dalton Trans.* pp. 525–529.
Teixidor, F., Viñas, C., Benakki, R., Kivekäs, R. & Sillanpää, R. (1997). *Inorg. Chem.* **36**, 1719–1723.
Teixidor, F., Viñas, C., Rius, J., Miravitlles, C. & Casabó, J. (1990). *Inorg. Chem.* **29**, 149–152.
Venkatasubramanian, U., Donohoe, D. J., Ellis, D., Giles, B. T., Macgregor, S. A., Robertson, S., Rosair, G. M., Welch, A. J., Batsanov, A. S., Boyd, L. A., Copley, R. C. B., Fox, M. A., Howard, J. A. K. & Wade, K. (2004). *Polyhedron*, **23**, 629–636.
Venkatasubramanian, U., Ellis, D., Rosair, G. M. & Welch, A. J. (2003). *Acta Cryst.* C**59**, o559–o561.
Welch, A. J., Venkatasubramanian, U., Rosair, G. A., Ellis, D. & Donohoe, D. J. (2001). *Acta Cryst.* C**57**, 1295–1296.

ANNEX- ARTICLES PUBLICATS

(Posteriors Comissió de Doctorat 20 de Juliol de 2004)

FULL PAPER

Dalton
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Sulfur, tin and gold derivatives of 1-(2′-pyridyl)-*ortho*-carborane, 1-R-2-X-1,2-$C_2B_{10}H_{10}$ (R = 2′-pyridyl, X = SH, $SnMe_3$ or $AuPPh_3$)

Andrei S. Batsanov,[a] Mark A. Fox,*[a] Thomas G. Hibbert,[a] Judith A. K. Howard,[a] Raikko Kivekäs,[b] Anna Laromaine†,[c] Reijo Sillanpää,[d] Clara Viñas*[c] and Kenneth Wade[a]

[a] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: m.a.fox@durham.ac.uk*

[b] *Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014, Finland*

[c] *Institut de Ciència de Materials de Barcelona (CSIC), Campus de la U.A.B., E-08193 Bellaterra, Spain. E-mail: clara@icmab.es; Fax: + 34 93 5805729; Tel: + 34 93 5805729*

[d] *Department of Chemistry, University of Jyväskylä, FIN-40351, Finland*

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Reaction of the lithium salt of 1-(2′-pyridyl)-*ortho*-carborane, Li[1-R-1,2-$C_2B_{10}H_{10}$] (R = 2′-NC_5H_4), with sulfur, followed by hydrolysis, gave the mercapto-*o*-carborane, 1-R-2-SH-1,2-$C_2B_{10}H_{10}$ which forms chiral crystals containing helical chains of molecules linked by intermolecular S–H···N hydrogen bonds. The cage C(1)–C(2) and *exo* C(2)–S bond lengths (1.730(3) and 1.775(2) Å, respectively) are indicative of *exo* S=C π bonding. The tin derivative 1-R-2-$SnMe_3$-1,2-$C_2B_{10}H_{10}$, prepared from Li[1-R-1,2-$C_2B_{10}H_{10}$] and Me_3SnCl, crystallises with no significant intermolecular interactions. The pyridyl group lies in the C(1)–C(2)–Sn plane, oriented to minimise the N···Sn distance (2.861(3) Å). The tin environment is distorted trigonal bipyramidal with axial N and Me. The gold derivative 1-R-2-$AuPPh_3$-1,2-$C_2B_{10}H_{10}$, prepared from Li[1-R-1,2-$C_2B_{10}H_{10}$] and $AuClPPh_3$, reveals no N···Au interaction in its crystal structure.

Derivatives of *ortho*-carborane of formula 1-R-1,2-$C_2B_{10}H_{11}$, bearing a nitrogen-containing substituent R on one cage carbon atom, have attracted much recent attention as potential medicinal agents for use in boron neutron capture therapy (BNCT)[1,2] and as potentially-chelating carboranyl ligand precursors.[3–8] For example many metal complexes 1-R-2-ML_n-1,2-$C_2B_{10}H_{10}$ (with an *exo*-cluster C–M bond) or 1-R-2-X-3-ML_n-1,2-$C_2B_9H_9$ (where ML_n replaces one boron vertex) have been prepared from dialkylaminomethyl-*ortho*-carborane (**1**, R = Me or Et)[4–6] (Fig. 1) or from 1-(2′-picolyl)-*ortho*-carborane (**2**).[7] When a metal atom is linked to amino or picolyl nitrogen atoms in these derivatised carboranes, five-membered C_3NM rings are formed if a *closo*-C_2B_{10} cage is retained; four-membered C_2NM rings are found in MC_2B_9 systems in which the ML_n unit occupies a cage site.

We have previously reported the syntheses of 1-(2′-pyridyl)-*ortho*-carborane **3** which resembles **1** in the proximity of its nitrogen atom to the cage.[9,10] Compound **3** has two notable properties. Firstly, it contains a strong intramolecular hydrogen bond between the pyridyl nitrogen atom and the acidic hydrogen atom bonded to the cage carbon (C2), significantly stronger than the comparable intramolecular hydrogen bonds in compounds **1** and **2**.[9] Secondly, substitution on the cage carbon (C2) of compound **3**, to form 1-(2′-pyridyl)-2-aryl-*ortho*-carboranes, with aryl bromides or iodides in the presence of a copper catalyst is facile.[10] By contrast, attempted reaction of 1-phenyl-*ortho*-carborane with aryl bromides or iodides in presence of a copper catalyst did not afford 1,2-diaryl-*ortho*-carboranes. The formation of 1-(2′pyridyl)-2-aryl-*ortho*-carboranes from **3** was believed to proceed through a copper intermediate **4** (M = Cu) involving an intramolecular Cu…N interaction. A copper derivative 1-R-2-Cu-1,2-$C_2B_{10}H_{10}$ synthesised from the lithio derivative of **1** (R = Et) with copper(I) chloride was found to be air-sensitive and believed to contain a Cu···N interaction.[4] With **1** (R = Me) instead of **1** (R = Et), a stable compound 2,2′-(1-R-1,2-$C_2B_{10}H_{10})_2$Cu was obtained with two Cu···N interactions. Copper carboranes are apparently more stable when two or more cage C–Cu bonds are present.[11,12] The only crystal structures of *ortho*-carboranes with cage C–Cu single bonds are found in salts of $[\{(C_2B_{10}H_{10})_2\}_2Cu]^-$ and $[\{(C_2B_{10}H_{10})_2\}_2Cu]^{2-}$ where the copper atom is bonded to four cage carbons with C–Cu bond lengths between 2.01 and 2.07 Å.[12]

Here, we report the synthesis, spectroscopic and structural characterisation of three new derivatives 1-(2′-pyridyl)-*ortho*-carborane **3**. One of these is the 2-mercapto derivative (**5**), which we believe to be the first derivative of *ortho*-carborane containing a mercapto group –SH to be structurally characterised. It was expected (rightly, in the event) to be of interest in connection with its hydrogen bonding, and can also be seen as a potential precursor for chelated metal complexes containing 6-membered C_3NMS rings (*cf* the related thiol of **1** (R = Me) which has been previously studied[8]). The second derivative we describe here is compound **6**, the first *ortho*-carborane with a trimethylstannyl (as opposed to an organotin halide[6]) substituent to be structurally characterised. It was seen as a possible model for the copper intermediate **4** (M = Cu) though it was appreciated that the very weak Lewis acidity and relative bulk of the $SnMe_3$ residue might

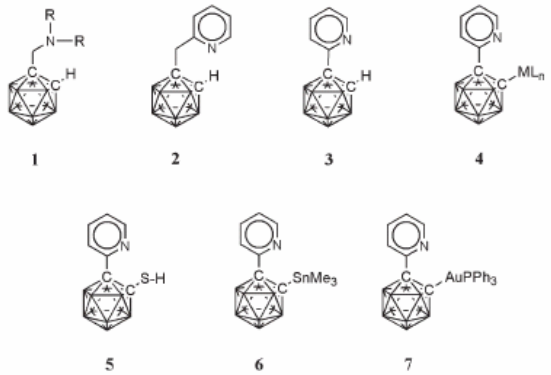

Fig. 1 Compounds **1–7** discussed in this study. Each naked cluster vertex represents BH.

† Enrolled in the UAB Ph. D. Program.

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discourage chelation and force the pyridyl ring plane out of the C–C(1)–C(2) plane. The third derivative is the gold compound **7**, also structurally characterised. We assess the effect of the pyridyl group on the cage geometry by comparing with several known gold carborane complexes of formula 1-R-2-AuL-1,2-$C_2B_{10}H_{10}$ (L = PPh_3, $AsPh_3$). Compound **7** is also a possible model for the copper intermediate **4** (M = Cu) though it is appreciated that gold is a weaker acceptor than copper towards pyridyl nitrogen.

Experimental

All manipulations were carried out under dry, oxygen-free N_2. Commercial grade acetonitrile, pentane, *n*-butyllithium in hexanes and resublimed sulfur were used without further purification. Dry Et_2O and THF were obtained by reflux and distillation over Na wire. Demineralised water was used in the aqueous stages of syntheses. Compound **3** was prepared by the literature methods.[7,9]

Infrared spectra were recorded as KBr discs using a Perkin Elmer 1720X FTIR spectrometer. Elemental analyses were performed using Exeter Analytical CE-440 apparatus. ^1H, ^{11}B, ^{31}P, ^{13}C, ^{119}Sn NMR spectra were recorded as room temperature solutions on Varian Unity 300 MHz spectrometer equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B-NMR spectra were referenced to external $BF_3{\cdot}OEt_2$, those for ^1H-, $^1H\{^{11}B\}$- and $^{13}C\{^1H\}$- NMR spectra were referenced to $SiMe_4$, and for ^{119}Sn-NMR spectrum was referenced to $SnMe_4$. ^1H-NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm). ^{13}C-NMR spectra were referenced to the solvent resonance ($CDCl_3$, 77.0 ppm; $(CD_3)_2CO$, 30.0; C_6D_6, 128.0). ^{31}P-NMR spectrum was referenced to external 85% H_3PO_4. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz.

Preparation of 1-(2′-pyridyl)-2-mercapto-ortho-carborane (5)

To a solution of **3** (117 mg, 0.53 mmol) in dry Et_2O (20 cm^3) at 0 °C was added 1.6 *M* n-BuLi in hexanes (0.35 cm^3, 0.56 mmol). After stirring for *ca.* 20 minutes resublimed sulfur (51 mg, 1.59 mmol, 200% excess) was added and the reaction mixture was stirred at room temperature for 24 h. Water (20 cm^3) was then added and stirring continued for 1 h. Unreacted sulfur was then removed by filtration and the Et_2O solution was sequentially extracted with 1 *M* HCl solution (3 × 40 cm^3) and water (3 × 40 cm^3). The combined aqueous fractions were extracted with Et_2O (40 cm^3) and the recombined Et_2O fractions were then dried over $MgSO_4$. Filtration, followed by removal of the Et_2O *in vacuo* gave **5** as a white powder, recrystallised from acetone. Yield: 114 mg, 85%. $C_7H_{15}B_{10}NS$ requires N, 5.5; C, 33.2; H, 6.0; S, 12.7; found: N, 5.3; C, 33.4; H, 6.2; S, 12.4. IR: ν[cm^{-1}] 2935 (C_{aryl}–H), 2644 (S–H); 2596, 2584, 2572 (B–H); 1585 (C=N); 1463, 1433 (C–N); 885 (S–H); 740, 725 (C_{aryl}–H). $^1H\{^{11}B\}$-NMR ($CDCl_3$): 8.68 (d, 1H, $^3J_{HH}$ = 4.4, H6′), 7.80 (m, 2H, H3′, H4′), 7.43 (dd, 1H, $^3J_{HH}$ = 4.4, $^4J_{HH}$ = 1.4, H5′), 3.77 (s, SH, 1H), 2.95 (br s, BH, 2H), 2.61 (br s, BH, 2H), 2.52 (br s, BH, 3H), 2.29 (br s, BH, 1H), 2.21 (br s, BH, 2H). ^{11}B-NMR ($CDCl_3$): −2.0 (d, $^1J_{BH}$ = 164, 1B), −4.3 (d, $^1J_{BH}$ = 134, 1B), −7.8 (d, $^1J_{BH}$ = 177, 2B), −9.5 (d, $^1J_{BH}$ = 187, 4B), −10.0 (d, $^1J_{BH}$ = 142, 2B). $^{13}C\{^1H\}$-NMR (d_6-acetone): 149.5 (C2′), 148.6 (C6′), 137.7 (C4′), 126.1 (C3′), 125.5 (C5′), 85.8 (C1), 77.6 (C2).

Preparation of 1-(2′-pyridyl)-2-(trimethylstannyl)-ortho-carborane (6)

To a solution of **1** (221 mg, 1.00 mmol) in dry THF (30 cm^3) at 0 °C was added 2.42 M n-BuLi in hexanes (0.42 cm^3, 1.02 mmol). After stirring at 0 °C for 30 minutes Me_3SnCl (200 mg, 1.00 mmol) was added and the reaction mixture was stirred for a further hour, and allowed to warm to room temperature. The nascent LiCl was removed by filtration and the THF removed *in vacuo* giving a tacky yellow solid. This solid was triturated with pentane (2 × 20 cm^3) and recrystallised from Et_2O. Yield: 285 mg, 74%. M.p. 195–6 °C. $C_{10}H_{23}B_{10}NSn$ requires: C 31.4, H 6.1, N 3.7. Found: C 31.4, H 6.0, N 3.0. IR: ν[cm^{-1}] 2986w, 2916w, 2876w (pyridyl/CH_3 str.) 2597vs, 2558sh (BH) 1636m, 1591m, 1471m, 1432vs (pyridyl skel.) 1079m, 1061m, 1003m, 825w, 765s,br (BH wag). $^1H\{^{11}B\}$-NMR ($CDCl_3$): 8.15 (d, 1H, $^3J_{HH}$ = 5, H6′), 7.65 (d, 1H, $^3J_{HH}$ = 8, H4′), 7.51 (d, 1H, $^3J_{HH}$ = 8, H3′), 7.25 (dd, 1H, $^3J_{HH}$ = 8, $^3J_{HH}$ = 5, H5′), 2.43 (br s, 2H, BH), 2.31 (br s, 4H, BH), 2.11 (br s, 2H, BH), 1.94 (br s, 2H, BH), 0.20 (br s + d, 9H, J_{SnH} = 54, $SnCH_3$). $^{11}B\{^1H\}$-NMR ($CDCl_3$): −1.3 (d, $^1J_{BH}$ = 145, 1B), −1.7 (d, $^1J_{BH}$ = 155, 1B), −5.9 (d, $^1J_{BH}$ = 149, 2B), −8.9 (d, 4B), −10.1 (d, $^1J_{BH}$ = 156, 2B); $^{13}C\{^1H\}$-NMR: (C_6D_6): 151.8 (C2′), 145.9 (C6′), 137.5 (C4′), 123.9 (C5′), 122.5 (C3′), 77.3 (C1), 67.5 (C2), −3.2 (CH_3); ^{119}Sn-NMR ($CDCl_3$): 21.9.

Preparation of 1-(2′-pyridyl)-2-(AuPPh₃)-ortho-carborane (7)

To a stirring solution of [1-(2′-pyridyl)-1,2-$C_2B_{10}H_{11}$] (15.5 mg, 0.07 mmol) in 4 ml of dry diethyl ether at 0 °C, was added dropwise, 0.044 ml of a 1.6 M of n-BuLi (0.07 mmol). After addition the reaction mixture was stirred at 0 °C for 30 minutes then at ambient temperature for 30 minutes, then 35 mg of $AuClPPh_3$ (0.07 mmol) was added. After stirring for 30 minutes, the solid was filtered off and recrystallized from chloroform and hexane, to obtain an orange solid in 85% yield (40 mg, 0.059 mmol). $C_{25}H_{29}B_{10}NPAu$ requires C, 44.2, H, 4.3, N, 2.1. Found: C, 44.0; H, 4.3, N, 2.1. $H\{^{11}B\}$-NMR ($CDCl_3$): 8.06–7.10 (m, 19H, PPh_3, C_5H_4N), 2.83 (br s, 2H, B–H), 2.37 (br s, 8H, B–H). ^{11}B-NMR ($CDCl_3$): −3.5 (d, $^1J_{BH}$ = 119, 2B), −9.3 (m, 8B). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ = 147.8 (s, C2′), 136.3 (s, C6′), 134.1 (d, ^2J(C, P) = 12, C_{PPh3}), 131.8 (d, ^3J(C, P) = 29, C_{PPh3}), 130.0 (s, C4′), 129.1 (d, ^4J(C, P) = 8, C_{PPh3}), 123.5 (s, C5′), 123.3 (s, C3′). ^{31}P-NMR ($CDCl_3$): 36.4 (s, PPh_3).

X-ray crystallography

Single crystals of **5** and **7** (colourless) were grown from acetone, those of **6** (pale yellow) from Et_2O, at room temperature. X-ray experiments for **5**–**7** were carried out at low temperatures, using Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostats. Compound **5** was studied also at room temperature; this structure (**5a**) is practically identical with the (more precise) low-temperature one (**5**), which is referred to in the discussion. Diffraction data were collected on an Enraf Nonius Kappa diffractometer (for **5** and **7**) or Bruker SMART 3-circle diffractometer (for **5a** and **6**) equipped with CCD area detectors. Graphite-monochromated Mo–*Kα* radiation ($\bar{\lambda}$ = 0.71073 Å) was used.

Reflection intensities were corrected for absorption by numerical integration (based on crystal face-indexing) for **6** and by the empirical method for **7**. All structures were solved by direct methods; carbon and boron atoms of the carborane cage could be reliably distinguished by the bond distances and electron density concentration. All non-hydrogen atoms were refined with anisotropic displacement parameters and H atoms 'riding' in idealised positions (except the H atom bonded to S in **5** and **5a**, which was refined in isotropic approximation), by full-matrix least squares against F^2 of all reflections, using SHELXL programs.[13] The absolute configuration of **5** was determined by refinement of Flack *x* parameter[14] converging at 0.02(8). The crystal data and experimental details are listed in Table 1. CCDC deposition nos. 245430 (**5**), 239447 (**5a**), 239448 (**6**), 245431 (**7**).

Computational section

The *ab initio* computations were carried out with the Gaussian 98 package.[15] The two minima of **5** discussed here were optimised at the HF/6–31G* level with no symmetry constraints. Frequency calculations were computed on these optimised geometries at the HF/6–31G* level and revealed no imagi-

Table 1 Crystal data

Compound	5	6	7
Formula	$C_7H_{15}B_{10}NS$	$C_{10}H_{23}B_{10}NSn$	$C_{25}H_{29}B_{10}NPAu$
M	253.36	384.08	679.53
Temp., K	173	150	173
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$ #4	$P2_1/c$ #14	$P2_1/c$ #14
a, Å	8.3207(2)	10.009(1)	12.6732(3)
b, Å	8.1789(2)	13.544(1)	15.8053(6)
c, Å	10.5083(2)	13.516(1)	14.3786(5)
β, °	109.596(1)	107.28(1)	103.159(2)
U, Å^3	673.71(3)	1749.6(3)	2804.46(16)
Z	2	4	4
D_{calc} (g/cm^3)	1.249	1.458	1.609
μ, mm^{-1}	0.21	1.45	5.32
Reflections measured	2547	8408	8500
Unique reflections	2547	3149	4915
R_{int}	-	0.043	0.027
$R[F^2 \geq 2\sigma(F^2)]$	0.036	0.031	0.023
w$R(F^2)$, all data	0.087	0.074	0.049

nary frequencies. Optimisation of these geometries were then carried out at the MP2/6–31G* level. Selected parameters for minimum (total energy at −974.79590 au) of similar geometry to experimental: C(1)–C(2) 1.692 Å, N–C(12)–C(1)–C(2) −70.7°, H(2)–S–C(2)–C(1) 81.2°, N…H 3.056 Å, for less stable minimum (−974.79491 au) C(1)–C(2) 1.697 Å, N–C(12)–C(1)–C(2) 77.2°, H(2)–S–C(2)–C(1) 106.6°. The shorter C(1)–C(2) bond lengths in these optimised geometries compared to experimental are partly due to the different orientations of the SH and pyridyl groups.[26,28]

Results and discussion

Synthetic and spectroscopic aspects

1-(2′-pyridyl)-2-mercapto-*ortho*-carborane (**5**) was prepared from compound **3**: the second cage carbon atom of the parent pyridyl carborane was lithiated using butyllithium, sulfur was inserted into the carbon–lithium bond by reaction with elemental sulfur, and the thiol liberated by working up the product with aqueous acid. The IR spectrum of **5** as a KBr disc has an absorption at 2642 cm^{-1}, consistent with the presence of a hydrogen bonded S–H moiety.[16]

Compound **6**, 1-(2′-pyridyl)-2-(trimethylstannyl)-*ortho*-carborane, was also prepared from compound **3** *via* the lithio derivative. With trimethyltin chloride, this lithio derivative afforded **6** and lithium chloride. The tin atom in compound **6** has a tetrahedral arrangement in solution, indicated by the ^{119}Sn chemical shift of 21.9 and the $^2J(^{119}Sn–C^1H_3)$ coupling constant of 54 Hz in chloroform.[6,17] A related compound, 1-phenyl-2-(trimethylstannyl)-*ortho*-carborane (*i.e.* with a phenyl group in place of the pyridyl group in **6**), has a $^2J(^{119}Sn–C^1H_3)$ coupling constant of 58 Hz in chloroform.[18] A low temperature (−60 °C in CD_2Cl_2 solution) ^{1}H NMR study of **6** was carried out to explore whether the Sn···N interaction might be strong enough to lock the trimethyltin residue in a particular orientation at lower temperatures, so rendering the tin-attached methyl groups inequivalent. However, these methyl groups remained equivalent, consistent with free rotation of the $SnMe_3$ group about the *exo*-cluster C–Sn bond, implying that any Sn…N interactions are very weak, as expected in view of the low Lewis acidity of the $SnMe_3$ residue.

Compound **7**, 1-(2′-pyridyl)-2-(triphenylphosphine)gold-*ortho*-carborane, was also prepared from the lithio derivative of compound **3**. With $AuClPPh_3$, this lithio derivative afforded **7** and lithium chloride. Comparison of the NMR data for **7** with those reported for 1-phenyl-2-(triphenylphosphine)gold-*ortho*-carborane[19] indicates little Au…N interaction is present in solutions of **7**. The ^{31}P chemical shifts are 36.4 ppm and 38.6 ppm respectively.

Structural aspects

Compound **5** crystallises in a chiral space group $P2_1$, hence it deserves checking for non-linear optical (NLO) properties, for which a non-centrosymmetric structure is a prerequisite.[20] Previous studies of carborane derivatives for NLO purposes have been reported.[21] The crystal structure of **5** shows no intramolecular S–H···N interactions; the torsion angle C(2)–C(1)–C(12)–N is 96.4(2)°. Instead, the molecules (Fig. 2) are linked by S–H···N hydrogen bonds into helices, spiralling around a 2_1 screw axis (Fig. 3).

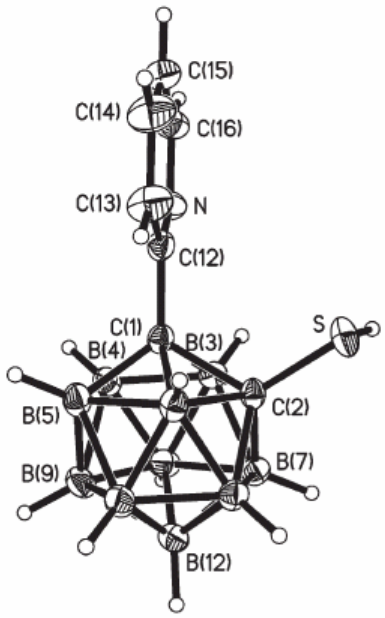

Fig. 2 Molecular structure of 1-(2′-pyridyl)-2-mercapto-*ortho*-carborane **5**. Selected bond distances (Å) and torsion angles (°): C(1)–C(2) 1.730(3), C(1)–C(12) 1.507(3), C(2)–S 1.775(2); N–C(12)–C(1)–C(2) 96.4(2), H(2)–S–C(2)–C(1) −99(2).

Within the helices, the hydrogen-bonded S···N distance of 3.445(2) Å and the S–H···N angle of 152(2)° lie within the ranges of 3.2–3.6 Å and 140–180° typical of S–H···N systems. It is interesting that the S–H···N hydrogen bonding in **5** is exclusively *inter*molecular, in marked contrast to the exclusively *intra*molecular C–H···N hydrogen bonding in the parent 1-(2′-pyridyl)-*ortho*-carborane **3**. In crystalline **3**, the pyridine ring is locked in an orientation coplanar with the C(1)–C(2)–H plane

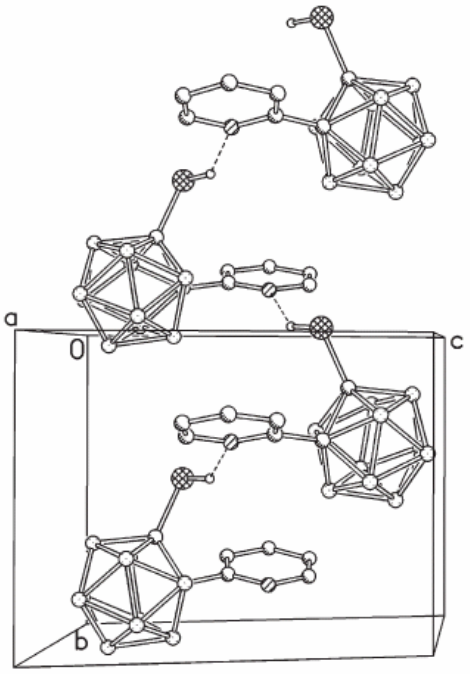

Fig. 3 Intermolecular hydrogen bonds in the crystal of **5**. Hydrogen bond distances (Å) and angles (°), S–H 1.27(3), H···N 2.17(3), S···N 3.445(2), S–H···N 152(2).

by intramolecular C(2)–H···N hydrogen bonding, involving the protic hydrogen on C(2). A similar orientation of the pyridine ring in **5** might have permitted S–H···N hydrogen bonding within a 6-membered $C_3SH\cdots N$ ring in place of the 5-membered $C_3H\cdots N$ ring in **3**. However, there is no *intra*molecular S–H···N hydrogen bonding in the crystals of **5**, in which the pyridyl and thiol substituents are orientated in planes roughly perpendicular to the C(12)–C(1)–C(2)–S plane, orientations incompatible with intramolecular S–H···N interactions.

Further discussions of hydrogen bonding interactions in organonitrogen derivatives of *ortho*-carborane, including the *inter*- and *intra*-molecular N…H–C interactions in **2** (which contains dimeric 1-(2′-picolyl)-1,2-$C_2B_{10}H_{11}$ units in the crystal) and also in an isomer of **5** (again with dimeric 1-(2′-pyridyl)-2-SH-1,2-$C_2B_{10}H_{10}$ units in the crystal) are to be found elsewhere.[9,22,23] Calculations on **5** optimised at the MP2/6–31G* level of theory have revealed two minima, one minimum comparable to that found experimentally and a slightly less stable minimum (*ca* 0.7 kcalmol^{-1}). The latter minimum has the hydrogen atom at sulfur pointing away from the pyridyl nitrogen. The experimental and computed geometries of **5** suggest intramolecular H-bonding is not favourable in **5** due to the lack of flexibility along the S–C–C–C–N link compared to the C–C–C–C–N link in **2**.

The π orbital overlap between phenyl group and tangential cluster orbitals has been invoked to explain the cage C–C lengthening in aryl-*ortho*-carborane derivatives.[24,25] This was further explored by *ab initio* RHF/6–31G* and MP2/6–31G* calculational studies on 1-phenyl-*ortho*-carborane and other aryl-carboranes in order to probe the orientational preferences of aryl groups attached to the carbon atoms of *ortho*-carborane.[26,27] These calculations have indicated that, although the overall energy of an aryl-carborane may vary only slightly with the aryl group orientation, the latter does have a perceptible influence on the C(1)–C(2) bond distance, which is greatest when the aryl group is aligned perpendicular to the aryl C–C(1)–C(2) plane. This is because this orientation optimises transfer of electronic charge from the filled π orbitals of the aryl group into a cage LUMO that is σ-antibonding with respect to the cage bond C(1)–C(2). Similar calculations on hydroxyl, amino or thiolato derivatives of *ortho*-carborane show that such derivatives also experience C(1)–C(2) bond elongation as the substituent orientation changes from coplanar to perpendicular, so increasing the capacity for dative π-bonding from what would otherwise be a lone pair p orbital on the *exo*-atom.[28] The sulfur 'lone-pair' orbital of the SH group has a similar influence on the C(1)–C(2) bond to the π orbitals of the phenyl group. Molecular orbital computations on the crystal structure of 1,2-$(SPh)_2$-1,2-$C_2B_{10}H_{10}$ indicate the transfer of electron density from the lone pairs at the sulfur atoms to the cage as mainly responsible for its long C(1)–C(2) bond length (1.798(3) Å) perhaps reinforced by the lone-pair repulsion between the two neighbouring sulfur atoms.[29,30]

These *exo*-dative π-bonding effects are believed to be responsible for the length of the cage C(1)–C(2) bond in compound **5**, which at 1.730(3) Å is *ca* 0.1 Å longer than its counterpart in pyridyl-*ortho*-carborane **3**. Even longer cage C(1)–C(2) bonds have been found in anionic thiolate compounds [1-R-2-S-1,2-$C_2B_{10}H_{10}]^-$ (R = Ph[31] or Me[32]) in which the absence of the proton on sulfur allows even stronger S–C(2) *exo* dative π-bonding than in **5**. Relevant data are listed in Table 2, which shows how the cage C(1)–C(2) bond lengthens as the *exo* C(2)–S bond shortens. The data in Table 2 also show that the cage bond-lengthening effect of a pyridyl or phenyl group or a thiolate residue at C(1) is far less than that of a pyridyl or phenyl group at C(1) and a thiolate residue at C(2).[9,33–35] It has to be pointed out that, unlike in the disubstituted carboranes, the groups at C(1) of the monosubstituted derivatives are not orientated to maximise *exo*-dative π-bonding.

The crystal structure of compound **6** (see Fig. 4) differs markedly from that of **5** in that there are no significant *inter*molecular interactions. The pyridyl ring orientation is that which minimises the N···Sn distance: the C(2)–C(1)–C(12)–N torsion angle is zero within experimental error, and the tin atom lies within 0.10 Å from the pyridyl ring plane. The Sn···N distance, 2.861(3) Å, though shorter than the sum of the van der Waals radii of Sn and N (3.75 Å), is understandably longer than the sum of their covalent radii (2.15 Å), as expected in view of the low Lewis acidity of species Me_3SnR.[36] The coordination at tin is distorted from 4-coordinate tetrahedral towards 5-coordi-

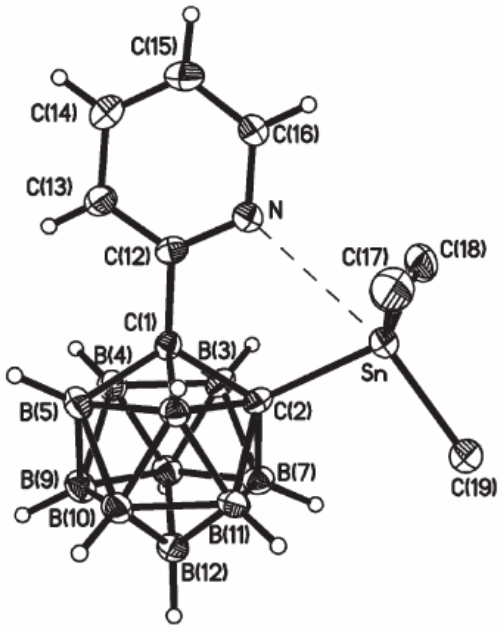

Fig. 4 Molecular structure of 1-(2′-pyridyl)-2-trimethylstannyl-*ortho*-carborane **6**. Selected bond distances (Å) and torsion angles (°): C(1)–C(2) 1.668(5), C(1)–C(12) 1.512(5), C(2)–Sn 2.207(4), N–C(12)–C(1)–C(2) −0.4(4). Methyl hydrogens are omitted for clarity.

Table 2 Bond distances (Å) in *ortho* carborane derivatives 1-R-2-X-1,2-$C_2B_{10}H_{10}$

R	X	d(C(1)–C(2))	d(C(1)–R)	d(C(2)–X)	Reference
H	H	1.620(3)			33
2′-pyridyl	H	1.632(3)	1.513(3)		9
H	S–(2′-pyridyl)	1.643(3)		1.778(2)	22
Ph	H	1.649(2)	1.511(2)		34
2′-pyridyl	2′-pyridyl	1.689(3)	1.505(4)	1.506(3)	35
2′-pyridyl	SH	1.730(3)	1.507(3)	1.775(2)	This work
Me	S^-	1.792(5)	1.510(5)	1.735(4)	32
Ph	S^-	1.836(5)	1.495(5)	1.729(4)	31

nate trigonal bipyramidal (TBP) in which the axial positions are occupied by the nitrogen atom and a methyl carbon atom, C(19), the N–Sn–C(19) angle being 168.1(1)°. The two geometries can be distinguished by the difference between the average equatorial and average apical angles, zero for a tetrahedron, 30° for an ideal TBP.[37] In **6** this difference (for C–C–C angles only), is 8.8(2)°, *i.e.* closer to tetrahedron than TBP. The most pronounced distortion is the widening to 118.0(2)° of the C(17)–Sn–C(18) angle, into which the pyridyl group is 'wedged'.

Conversely, **6** may be compared with an extensively studied series of systems R_3SnNX with a hypervalent interaction along the N···Sn···X axis,[38,39] (the path for nucleophilic substitution of X) with Sn···N distances ranging from 2.37 to 2.65 Å.[39] These additional intramolecular interactions can have important chemical effects, such as enhanced reactivity of Sn–C bonds[40] or stabilisation toward hydrolytic decomposition[41] and may afford unique synthetic routes to particular organotin compounds.[42] Most such studies have involved systems in which X is a relatively electronegative ligand, *e.g.* a halogen. Tetraorganotin compounds are very weak Lewis acids and only one case of additional N···SnR_4 coordination seem to have been studied structurally, a pyrazine–trimethyltin derivative with a long Sn···N distance of 3.101(5) Å and only very slight elongation of the Sn–CH_3 bond trans to the latter (2.171 Å) compared to the two *cis* (pseudo-equatorial) bonds, averaging 2.134 Å.[41] In **6** the Sn···N distance is shorter; however, the pseudo-apical Sn–C(19) bond (2.153(4) Å) is not significantly longer than the pseudo-equatorial bonds Sn–C(17), 2.134(4) Å and Sn–C(18), 2.141(4) Å. The pyridine group tilts slightly toward the tin atom, apparently due to the Sn···N attraction, but the tilt is small with the B(12)–C(1)–C(12) angle in **6** being 176.6(3)°.

Of more relevance to **6**, perhaps, is the crystal structure of a dimeric carborane assembly consisting of two 1-Me_2NCH_2-2-$SnMe_2$-1,2-$C_2B_{10}H_{10}$ moieties linked by a Sn–Sn bond.[6] This was made from **1**, BuLi and Me_2SnBr_2 followed by reduction with sodium metal. In this structure the Sn···N distances are long, averaging 3.640(8) Å, and the coordination environment of the tin atom is effectively tetrahedral.

The gold carborane **7** crystallises in a form where no *inter*molecular interactions are detected. Both the Au···N distance of 3.192(3) Å and the orientation of the pyridyl group imply weak attraction between the two atoms (Fig. 5). As there are five crystal structures in the literature[19,43–45] of the formula 1-R-2-AuL-1,2-$C_2B_{10}H_{10}$ (L = PPh_3, $AsPh_3$), selected data are listed in Table 3 for comparison with **7**. On close inspection of the table, it appears that the more electron-withdrawing the R group is, the longer the Au–C(2) bond becomes. A second trend is the more bulky the R group is, the cage C(1)–C(2) bond length increases. These trends thus may reflect electronic and steric effects respectively.

The C(1)–C(2) bond distance of 1.668(5) Å in **6** is about 0.04 Å longer than in **3** but 0.06 Å shorter than in **5**. The shortening of the bond compared to **5** can be attributed in part to the parallel orientation between the pyridyl ring and the C(1)–C(2) bond[26] but more importantly to the absence of *exo* C(2)–S π bonding in **6**. However, the lengthening of the cage C–C bond in **6** compared to that in **3** is probably due to steric effects between the two bulky substituents as found elsewhere.[46] The C(1)–C(2) bond distance

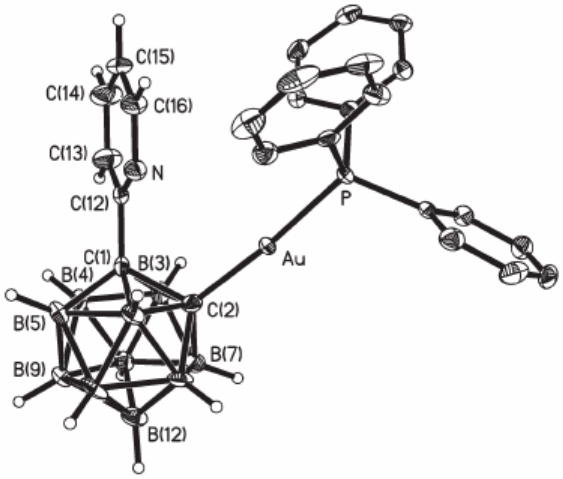

Fig. 5 Molecular structure of 1-(2′-pyridyl)-2-$AuPPh_3$-*ortho*-carborane **7**. Selected bond distances (Å) and torsion angles (°); C(1)–C(2) 1.684(5), C(1)–C(12) 1.518(5), C(2)–Au 2.069(3), Au–P 2.272(1), N–C(12)–C(1)–C(2) −64.3(4). Phenyl hydrogens are omitted for clarity.

of 1.684(5) Å in **7** is only 0.01 Å longer than in **6** (possibly due to the different orientation of the pyridyl group). The similarities in the [1-(2′-pyridyl)-1,2-$C_2B_{10}H_{10}$] moiety for **6** and **7** suggest this carborane geometry is present in the copper intermediate **4** (M=Cu). Stronger metal···nitrogen intramolecular interaction in **4** (M=Cu) is likely as copper is a better ligand acceptor than trimethyltin and gold moieties.

Conclusions and further work

Here we have described the syntheses and structural characterisation of three compounds made from 1-(2′-pyridyl)-*ortho*-carborane **3**. The pyridyl group in these carboranes appears to facilitate growth of suitable crystals for X-ray crystallography.

• For 1-(2′-pyridyl)-2-mercapto-*ortho*-carborane **5**, the pyridyl nitrogen is involved in intermolecular hydrogen bonding—of a type which may be a suitable candidate for NLO materials—and gives the first structurally determined example of an *ortho*-carborane with a thiol substituent.

• For 1-(2′-pyridyl)-2-(trimethylstannyl)-*ortho*-carborane **6**, the pyridyl nitrogen interacts weakly with the tin atom. This is the first structurally determined example of an *ortho*-carborane with a $SnMe_3$ substituent.

Compounds **3** and **5** are potential chelating ligands in transition metal complexes. Thus, 1-(2′-pyridyl)-*ortho*-carborane **3** can chelate a metal atom through an *exo*-cluster bond C–M and a (pyridyl)N→M bond whereas the thiol **5** can chelate a metal atom through a S–M bond and a N→M bond. In fact, we have recently found that the thiol **5** gives complexes of the type 1-(C_5H_4N)-2-SML_n-1,2-$C_2B_{10}H_{10}$ with the metal atom chelated by the S and N atoms of **5**.[47] We are also looking at the possibility of preparing 1-(2′-pyridyl)-2-X-3-ML_n-1,2-$C_2B_9H_9$ (where ML_n replaces a BH unit on one vertex) containing a (pyridyl)N→M bond from 1-(2′-pyridyl)-*ortho*-carborane **3**.

Table 3 Bond distances (Å) in *ortho* carborane derivatives 1-R-2-AuL-1,2-$C_2B_{10}H_{10}$

R	L	d(C(2)–Au)	d(C(1)–C(2))	Reference
H	PPh_3	2.039(8)	-[a]	43
$MeOCH_2$	$AsPh_3$	2.039(8)	1.667(11)	19
$AuPPh_3$	PPh_3	2.044(15)[b]	1.71(2)	44
$SiMe_2{}^tBu$	PPh_3	2.050(4)	1.706(6)	45
2′-pyridyl	PPh_3	2.069(3)	1.684(5)	This work
$CB_{10}H_{10}CAuPPh_3$	PPh_3	2.11(3)[b]	-[c]	44

[a] Cage disorder present in crystal. [b] Averaged. [c] Values of 1.595 and 1.655 for the two C(1)–C(2) bonds suggest poor quality data. The parent bis(carborane) has a C(1)–C(2) bond length of 1.625 Å.[28]

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References

1 See for examples, A. Maderna, R. Huertas, M. F. Hawthorne, R. Luguya and M. G. H. Vicente, *Chem. Commun.*, 2002, 1784; A. H. Soloway, W. Tjarks, B. A. Barnum, F. G. Rong, R. F. Barth, I. M. Codogni and J. G. Wilson, *Chem. Rev.*, 1998, **98**, 1515; A. Cappelli, G. P. Mohr, A. Gallelli, G. Giuliani, M. Anzini, S. Vomero, M. Fresta, P. Porcu, E. Maciocco, A. Concas, G. Biggio and A. Donati, *J. Med. Chem.*, 2003, **46**, 3568; C. H. Lee, H. G. Lim, J. D. Lee, Y. J. Lee, J. Ko, H. Nakamura and S. O. Kang, *Appl. Organometal. Chem.*, 2003, **17**, 539; G. Rana, K. Vyakaranam, S. C. Ledger, S. L. Delaney, J. A. Maguire and N. S. Hosmane, *Appl. Organometal. Chem.*, 2003, **17**, 361; P. Basak and T. L. Lowary, *Can. J. Chem.*, 2002, **80**, 943; J. F. Valliant and P. Schaffer, *J. Inorg. Biochem.*, 2001, **85**, 43; C. Frixa, M. F. Mahon, A. S. Thompson and M. D. Threadgill, *Org. Biomol. Chem.*, 2003, 306; M. G. H. Vicente, A. Wickramasinghe, D. J. Nurco, H. J. H. Wang, M. M. Nawrocky, M. S. Makar and M. Miura, *Bioorg. Med. Chem.*, 2003, **11**, 3101.

2 L. I. Zakharkin, G. G. Zhigareva, V. A. Ol'shevskaya and L. E. Vinogradova, *Russ. J. Gen. Chem.*, 1997, **67**, 770.

3 Y. Zhu, K. Vyakaranam, J. A. Maguire, W. Quintana, F. Teixidor, C. Viñas and N. S. Hosmane, *Inorg. Chem. Commun.*, 2001, **4**, 486; Y. J. Lee, J. D. Lee, J. Ko, S. H. Kim and S. O. Kang, *Chem. Commun.*, 2003, 1364.

4 L. I. Zakharkin and I. S. Savel'eva, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, 1294.

5 J. D. Lee, C. K. Baek, J. Ko, K. Park, S. Cho, S. K. Min and S. O. Kang, *Organometallics*, 1999, **18**, 2189; J. S. Park, D. H. Kim, J. Ko, S. H. Kim, S. Cho, C. H. Lee and S. O. Kang, *Organometallics*, 2001, **20**, 4632; D. H. Kim, J. H. Won, S. J. Kim, J. Ko, S. H. Kim, S. Cho and S. O. Kang, *Organometallics*, 2001, **20**, 4298; J. S. Park, D. H. Kim, S. J. Kim, J. Ko, S. H. Kim, S. Cho, C. H. Lee and S. O. Kang, *Organometallics*, 2001, **20**, 4483.

6 J. D. Lee, S. J. Kim, D. Yoo, J. Ko, S. Cho and S. O. Kang, *Organometallics*, 2000, **19**, 1695.

7 A. R. Oki, O. Sokolova, R. Barnett and G. Pardhiva, *Synth. React. Inorg. Met. -Org. Chem.*, 1998, **28**, 757.

8 J. Y. Bae, Y. J. Lee, S. J. Kim, J. Ko, S. Cho and S. O. Kang, *Organometallics*, 2000, **19**, 1514; S. W. Chung, J. Ko, P. Park, S. Cho and S. O. Kang, *Coll. Czech. Chem. Commun.*, 1999, **64**, 883.

9 E. S. Alekseyeva, A. S. Batsanov, L. A. Boyd, M. A. Fox, T. G. Hibbert, J. A. K. Howard, J. A. H. MacBride, A. Mackinnon and K. Wade, *Dalton Trans.*, 2003, 475.

10 R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride and K. Wade, *J. Organomet. Chem.*, 1993, **462**, 19.

11 L. I. Zakharkin and N. F. Shemyakin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, 2572.

12 D. E. Harwell, J. McMillan, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1997, **36**, 5951.

13 G. M. Sheldrick, *SHELX97*. University of Göttingen, Germany, 1997.

14 H. D. Flack, *Acta Crystallogr.*, 1983, A**39**, 876.

15 *Gaussian 98*, Revision A.9, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

16 W. Kemp, *Qualitative Organic Analysis: Spectrochemical Techniques*, 2nd Edn,. McGraw-Hill, Maidenhead, UK, 1986.

17 B. Wrackmeyer, *Ann. Rep. NMR Spectroscopy*, 1985, **16**, 73; J. Otera, *J. Organomet. Chem.*, 1981, **221**, 57; V. S. Petrosyan, N. S. Yashina and O. A. Reutov, *Adv. Organomet. Chem.*, 1976, **14**, 63; T. N. Mitchell, *J. Organomet. Chem.*, 1973, **59**, 189.

18 L. A. Fedorov, V. N. Kalinin, K. G. Gasanov and L. I. Zakharkin, *J. Gen. Chem. USSR.*, 1975, 581.

19 B. D. Reid and A. J. Welch, *J. Organomet. Chem.*, 1992, **438**, 371.

20 D. W. Bruce, D. O'Hare, *Inorganic Materials*, 2nd Edn., John Wiley and Sons, Chichester, UK, 1996.

21 B. Grüner, Z. Janoušek, B. T. King, J. N. Woodford, C. H. Wang, V. Všetečka and J. Michl, *J. Am. Chem. Soc.*, 1999, **121**, 3122; M. Lamrani, R. Hamasaki, M. Mitsuishi, T. Miyashita and Y. Yamamoto, *Chem. Commun.*, 2000, 1595; D. M. Murphy, D. M. P. Mingos and J. M. Forward, *J. Mater. Chem.*, 1993, **3**, 67; D. M. Murphy, D. M. P. Mingos, J. L. Haggitt, H. R. Powell, S. A. Westcott, T. B. Marder, N. J. Taylor and D. R. Kanis, *J. Mater. Chem.*, 1993, **3**, 139; J. Taylor, J. Caruso, A. Newlon, U. Englich, K. Ruhlandt-Senge and James T. Spencer, *Inorg. Chem.*, 2001, **40**, 3381.

22 O. Crespo, M. C. Gimeno and A. Laguna, *Polyhedron*, 1999, **18**, 1279.

23 M. A. Fox and A. K. Hughes, *Coord. Chem. Rev.*, 2004, **248**, 457.

24 W. Clegg, R. Coult, M. A. Fox, W. R. Gill, J. A. H. MacBride and K. Wade, *Polyhedron*, 1993, **12**, 2711.

25 R. Kivekäs, R. Sillanpää, F. Teixidor, C. Viñas and R. Nuñez, *Acta Cryst. C*, 1994, **50**, 2027.

26 E. S. Alekseyeva, M. A. Fox, J. A. K. Howard, J. A. H. MacBride and K. Wade, *Appl. Organometal. Chem.*, 2003, **17**, 499.

27 P. T. Brain, J. Cowie, D. J. Donohue, D. Hnyk, D. W. H. Rankin, D. Reed, B. D. Reid, H. E. Robertson and A. J. Welch, *Inorg. Chem.*, 1996, **35**, 1701.

28 L. A. Boyd, W. Clegg, R. C. B. Copley, M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, R. J. Peace and K. Wade, *Dalton Trans.*, in press.

29 J. Llop, C. Viñas, J. M. Oliva, F. Teixidor, M. A. Flores, R. Kivekäs and R. Sillanpää, *J. Organomet. Chem.*, 2002, **657**, 232.

30 J. M. Oliva and C. Viñas, *J. Mol. Struct.*, 2000, **556**, 33.

31 R. Coult, M. A. Fox, W. R. Gill, K. Wade and W. Clegg, *Polyhedron*, 1992, **11**, 2717.

32 R. Kivekäs, R. Benakki, C. Viñas and R. Sillanpää, *Acta Crystallogr.*, 1999, C**55**, 1581.

33 M. J. Hardie and C. L. Raston, *Cryst. Eng. Comm.*, 2001, 39.

34 R. L. Thomas, G. M. Rosair and A. J. Welch, *Acta Crystallogr. Sect. C*, 1996, **52**, 1024.

35 W. Clegg, M. A. Fox, J. A. H. MacBride and K. Wade, *unpublished studies*.

36 J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., HarperCollins, New York, 1993.

37 M. Dräger, *J. Organomet. Chem.*, 1983, **251**, 209.

38 D. Britton and J. D. Dunitz, *J. Am. Chem. Soc.*, 1981, **103**, 2871; U. Kolb, M. Dräger, M. Dargatz and K. Jurkschat, *Organometallics*, 1995, **14**, 2827; H.-B. Bürgi, V. Shklover, in: *Structure Correlations*, H.-B. Bürgi and J. D. Dunitz, eds. VCH, Weinheim, 1994, vol. 1, p. 307.

39 C. Pettinari, M. Pellei, M. Miliani, A. Cingolani, A. Cassetta, L. Barba, A. Pifferi and E. Rivarola, *J. Organomet. Chem.*, 1998, **553**, 345.

40 J. T. B. H. Jastrzebski and G. Van Koten, *Adv. Organomet. Chem.*, 1993, **35**, 241.
41 M. Veith, M. Zimmer, V. Huch, F. Denat, H. Gaspard-Iloughmane and J. Dubac, *Organometallics*, 1993, **12**, 1012.
42 M. Murakami, T. Yoshida, S. Kawanami and Y. Ito, *J. Am. Chem. Soc.*, 1995, **117**, 6408.
43 T. V. Baukova, L. G. Kuz'mina, N. V. Dvortsova, M. A. Porai-Koshits, D. N. Kravtsov and E. G. Perevalova, *Organomet. Chem. USSR.*, 1989, **2**, 1098.
44 D. E. Harwell, M. D. Mortimer, C. B. Knobler, F. A. L. Anet and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1996, **118**, 2679.
45 O. Crespo, M. Concepcion Gimeno, A. Laguna and A. M. Pena, *Polyhedron*, 1998, **17**, 4163.
46 Z. G. Lewis and A. J. Welch, *Acta Cryst. Sect. C*, 1993, **49**, 705; T. D. McGrath and A. J. Welch, *Acta Cryst. C*, 1995, **51**, 646; T. D. McGrath and A. J. Welch, *Acta Cryst. C*, 1995, **51**, 651; T. D. McGrath and A. J. Welch, *Acta Cryst. C*, 1995, **51**, 654; R. L. Thomas and A. J. Welch, *Polyhedron*, 1999, **18**, 1961; U. Venkatasubramanian, D. J. Donohue, D. Ellis, B. T. Giles, S. A. Macgregor, S. Robertson, G. M. Rosair, A. J. Welch, A. S. Batsanov, L. A. Boyd, R. C. B. Copley, M. A. Fox, J. A. K. Howard and K. Wade, *Polyhedron*, 2004, **23**, 629; T. D. McGrath and A. J. Welch, *Acta Cryst. C*, 1995, **51**, 649.
47 A. Laromaine and C. Viñas, *unpublished studies*.

ANNEX- ARTICLES ACCEPTATS PENDENTS DE PUBLICACIÓ

(Posteriors Comissió de Doctorat 20 de Juliol de 2004)

Carbon extrusion in 1,2-dicarba-*closo*-dodecaboranes. A route for the regioselective B substitution in ten-vertex *closo*-monocarbaborane anionic compounds**

Anna Laromaine, Francesc Teixidor, Clara Viñas*

Institut de Ciència de Materials de Barcelona (CSIC)

Campus UAB

08193 Bellaterra, Spain

Fax. (+34) 93 580 57 29

E-mail: clara@icmab.es

While dicarba-*closo*-dodecaboranes are the most investigated of polyhedral boron-containing clusters[1,2] *closo*-monocarbaboranes are much less examined[1] probably because of the absence of suitable protocols of synthesis. Currently, monocarbaboranes [1-*closo*-$CB_9H_{10}]^-$ and [1-*closo*-$CB_{11}H_{12}]^-$ and their derivatives attract much attention.[3,4] This has stimulated the search for new methods of synthesis; [1-*closo*-$CB_9H_{10}]^-$ was originally obtained from $B_{10}H_{14}$ and CN^- but nowadays is more conveniently produced by a de-hydrogenation step from [6-(NMe_3)-*nido*-6-CB_9H_{11}].[5] The method of Brellochs,[6] based on the reaction of RCHO with the *arachno* $B_{10}H_{14}$, is gaining importance for the synthesis of phenyl derivatives of [1-*closo*-$CB_9H_{10}]^-$.[4,7] Ultimately all these methods are based on a single carbon insertion into a $B_{10}H_{14}$ cluster followed by a deboronation step. In theory, an alternative way to the [1-*closo*-$CB_9H_{10}]^-$ cluster would be a carbon extrusion pursued by boron elimination of the highly stable and widely studied 1,2-dicarba-*closo*-dodecaboranes. This is the objective of this work.

Taking the well known benzyl cation-tropylium ion rearrangement as a model, Figure 1a,[8] Jemmis et al,[9] have examined the rearrangement by theoretical means of the dicarbaboranyl methyl cation to generate tricarbaborane cations. We considered that a monocarbaborane could be produced from a dicarbaborane by a similar one cluster carbon extrusion. The close suggested analogy system in boron chemistry to the benzyl cation-tropylium equilibrium is represented in Figure 1b.

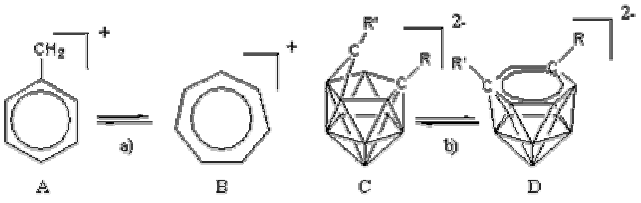


Figure 1. a) Rearrangement benzyl cation-tropylium. b) Rearrangement of the 12 vertex dicarba-nido-dodecaborate(-2).

Although there is no experimental proof for the latter, this is supported by the fact that isomer E, in Figure 2, which is structurally similar to C in Fig 1, is produced on treatment of D with water. A second isomer, F, (less stable than E by 6.7 Kcal mol^{-1}) is also produced.[10] Indeed F was considered to be the only reactive isomer,[11,12] and pioneering work for carbon extrusion from F had been reported,[11c,13] in which a mixture of non-*closo* compounds, the nature of which varied with the nucleophile, was obtained. To our understanding, the reactive nature of F, and its lax C_2B_4 open face facilitated the range of products. It was anticipated that the more rigid structure of E would be more likely to undergo a regioselective reaction.C.

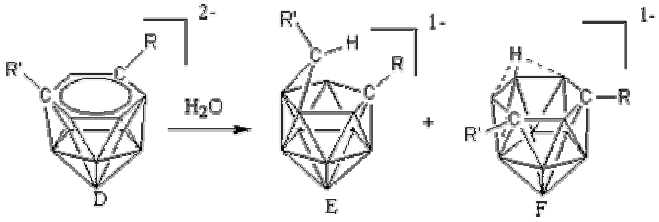


Figure 2. Protonation of $[C_2B_{10}RR'H_{10}]^{2-}$ produces both [7-R-μ-(9,10-HR'C)-7-*nido*-$CB_{10}H_{11}]^-$ and [7-R-9-R'-7,9-*nido*-$C_2B_{10}H_{11}]^-$ isomers.

Two drawbacks were apparent: the synthesis of the E isomer had been in low yield, around 20%[11b] and the E isomer had been considered unreactive [11, 12] Recently a convenient route to E with Mg as a reducing agent has been described giving yields close to 95 % for R=H, Me, Ph.[14]

Concerning the low reactivity of E, we have recently proved that it can be forced to react with $[PdCl_2(PPh_3)_2]$ to generate a mixture of compounds.[15] These were mostly obtained in low yield and some of them were generated via carbon extrusion but no [1-*closo*-$CB_9H_{10}]^-$ derivatives were found among the reaction products.

In order to generate the latter, a regioselective cluster deboronation on E was of utmost importance, and suitable nucleophiles were needed. We tested several nucleophiles to do this task and $K[NC_4H_4]$ and $K[NC_4Me_2H_2]$ proved to be the most suitable ones.[16a]

In a typical experiment, carried out in a dinitrogen atmosphere, 0.12 mmol of $[NMe_4][\mu\text{-}(9,10\text{-}H_2C)\text{-}7\text{-}nido\text{-}CB_{10}H_{11}]$ (E in Fig 2, with R=H) in 20 mL of THF was added to 0.48 mmol of freshly prepared $K[NC_4H_4]$. The mixture was refluxed for 72h.

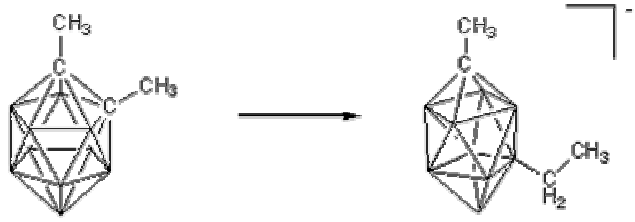


Figure 3. Carbon extrusion for regioselective synthesis of [1-CH_3-6-CH_2CH_3-1-*closo*-CB_9H_9]$^-$ from 1,2-$(CH_3)_2$-1,2-*closo*-$C_2B_{10}H_{10}$ species.

Monitoring of the reaction was done by $^{11}B\{^1H\}$ NMR examining the appearance of a resonance near +30 ppm. Following workup of the products, [NMe_4][6-Me-1-*closo*-CB_9H_9] was obtained in 55% yield. This was characterized by ^{11}B, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, $^1H\{^{11}B\}$ NMR and MALDI-TOF analysis. A pattern 1(d):1(s):2(d):2(d):2(d):1(d) at 30.3, -16.2, -17.1, -18.2, -22.2, -26.5 ppm, respectively, in agreement with a 6 substituted bicapped square antiprism was observed in the $^{11}B\{^1H\}$ NMR spectrum. Comparison with resonances for [1-*closo*-CB_9H_{10}]$^-$, application of ^{11}B NMR rules[17] for *closo* species and the NMR position of the singlet at -16.2 ppm indicated that a regioselective alkyl substitution at the 6 position in [1-*closo*-CB_9H_{10}]$^-$ had been discovered from the readily available 1,2-*closo*-$C_2B_{10}H_{12}$ neutral compounds. In only two steps [1-R-6-CH_2R'-1-*closo*-CB_9H_8]$^-$ derivatives could be generated. [6-Me-1-*closo*-CB_9H_9]$^-$ is the first example of a monoalkyl substitution on B in [1-*closo*-CB_9H_{10}]$^-$ derivatives.

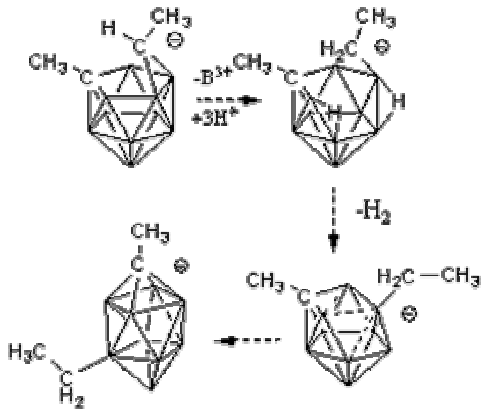
Compound	[1-R-6-CH_2R'-1-*closo*-CB_9H_8]$^-$		
	R	R'	Yield (%)
[NMe_4][**1**]	H	H	55
[NBu_4][**2**]	H	Me	30
[NBu_4][**3**]	Me	Me	47
[NBu_4][**4**]	H	Ph	45

Table 1. Non-optimized yields for the synthesis of [1-R-6-CH_2R'-1-*closo*-CB_9H_8]$^-$

In order to demonstrate the versatility of this reaction, it was also applied to 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$, 1,2-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$, and 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$. In all cases anions corresponding to [1-R-6-CH_2R'-1-*closo*-CB_9H_8]$^-$ were obtained. Non-optimized yields are shown in Table 1.

In Figure 3 the transformation from the neutral dicarbaborane to the anionic monocarbaborane cluster is exemplified for [1-Me-6-Et-1-*closo*-CB_9H_8]$^-$. Considering that carbon extrusion takes place, the alkyl group at 6 position necessarily will have one more carbon than in the precursor dicarbaborane. As an example if [6-Pr-1-*closo*-CB_9H_9]$^-$ was sought, 1-Et-1,2-$C_2B_{10}H_{11}$ would be required as starting compound.

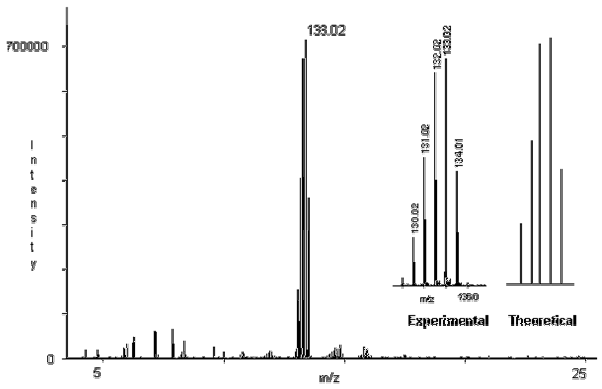
A plausible pathway for this reaction is shown in Figure 4, for the synthesis of [**3**]$^-$. A B^{3+} unit is formally removed from [7-Me-μ-(9,10-HMeC)-7-*nido*-$CB_{10}H_{11}$]$^-$ by using [NC_4H_4]$^-$. At this stage the non-classical bridging carbon of μ-(9,10-HMeC) is converted to a classical one. The boron removed is B(9) or B(10) generating a six member open face. Dehydrogenation leads to the *closo* monocarbaborane anion. The deboronation step is very relevant in this synthetic process. In work preceding this research,[15] a neutral nucleophile (PPh_3) attacked the bridging μ-(9,10-HMeC)- to generate the moiety –CH(Me)PPh_3. The result was a nucleophilic addition. The negative [NC_4H_4]$^-$ removes B(9) or B(10) to produce a *closo* {CB_9} anionic cluster and $(H_4C_4N)_3$B-THF.[16b] As the deboronation succeeded with an anionic nucleophile, tests were also done with CN^- and F^- on [7-Me-μ-(9,10-HMeC)-7-*nido*-$CB_{10}H_{11}$]$^-$. For CN^-, [1-Me-6-Et-1-*closo*-CB_9H_8]$^-$ was formed in yields <3% and with F^- the starting material was fully recovered. The effect of an enhanced nucleophilicity was monitored by ^{11}B NMR using [$NC_4Me_2H_2$]$^-$. Interestingly



the same conversion (55%) as for [NC_4H_4]$^-$ was obtained in 24h (72 h for [NC_4H_4]$^-$).

Figure 4. Suggested pathway for deboronation and C extrusion in the [7-Me-μ-(9,10-HMeC)-7-*nido*-$CB_{10}H_{11}$]$^-$.

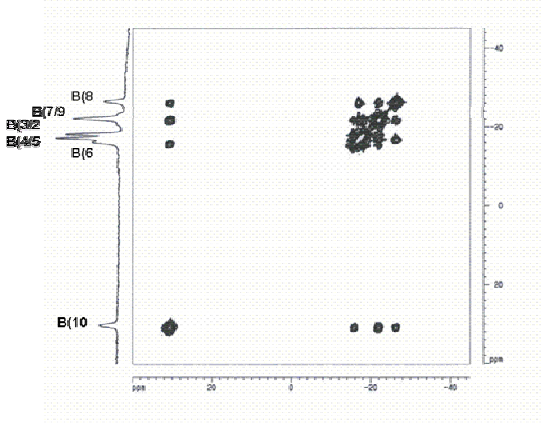
The inadequacy of isomer F for this reaction was proved by attempting to produce [**1**]$^-$ from this isomer using the same conditions and K[$NC_4Me_2H_2$] as a nucleophile. In this case a yield of only 2 % of [**1**]$^-$, was produced, along with 21 % of [NMe_4] [7,8-*nido*-$C_2B_9H_{11}$] and 58 % of 1,2-*closo*-$C_2B_{10}H_{12}$. Even the low yield of [**1**]$^-$ cannot be claimed to originate from F because the latter slowly isomerizes in the applied reaction conditions to yield E, which in turn may generate the [6-Me-



1-*closo*-CB_9H_9]$^-$ cluster.

MALDI-TOF-MS for the species [NMe_4][**1**] with a comparison of the theoretical and experimental distribution for the molecular peak.

With these results it has been proved that [1-H-6-CH_2R'-1-*closo*-CB_9H_8]$^-$ (R'= H, Me, Ph) or [1-Me-6-CH_2Me-1-*closo*-CB_9H_8]$^-$ derivatives can be produced in a regioselective way from the available 1-H-2-R'-1,2-*closo*-$C_2B_{10}H_{10}$ (R'= H, Me, Ph) or 1,2-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$. Work is now underway for the case of unsymmetrical alkyl/aryl substitution on both C cluster atoms in the dicarbaboranes, to discern which group will occupy the 6th position in the resulting [1-*closo*-CB_9H_{10}]$^-$ derivatives, and which functional groups are compatible with such rearrangement



$^{11}B\{^1H\}$-$^{11}B\{^1H\}$ 2D COSY NMR spectrum of compound $[NMe_4][$**1**$]$ with the assignments deduced from the off-diagonal resonances.

Experimental Section

General Details. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)]. The ^1H, $^1H\{^{11}B\}$ NMR (300.13 MHz), ^{11}B NMR (96.29 MHz) and $^{13}C\{^1H\}$ NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. All NMR spectra were recorded from acetone-d_6 solutions at 25ºC. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$, and those for ^1H, $^1H\{^{11}B\}$ and $^{13}C\{^1H\}$ NMR spectra were referenced to $Si(CH_3)_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz.

All reactions were performed under an atmosphere of dinitrogen employing standard Schlenk techniques. THF was distilled from sodium benzophenone prior to use. Compounds 1,2-*closo*-$C_2B_{10}H_{10}$, 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ and 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ were supplied by Katchem Ltd. (Prague) and used as received. 1,2-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$[18] was synthesized according to the literature. Pyrrole and 2,5-dimethylpyrrole from Aldrich were freshly distilled before use. Potassium was refluxed in THF prior to use.

Preparation of $[NMe_4][\mu$-(9,10-HCR)-7-R'-*nido*-$CB_{10}H_{11}]$. General Procedure. The starting *nido* species were synthesized according to the general procedure described in the literature for $[NMe_4][\mu$-(9,10-H_2C)-7-*nido*-$CB_{10}H_{11}]$[19]. For the following preparations only the reagents are indicated.

Synthesis of [6-R-1-R'-*closo*-CB_9H_8]. General Procedure.

The reaction, under nitrogen, of $[NMe_4][\mu$-(9,10-HCR)-7-R'-*nido*-$CB_{10}H_{11}]$ in dry THF and potassium pyrrolyl in a ratio 1:4 respectively. After 72 hours of refluxing, the solvent was evaporated. Products, after addition of water, were precipitated with $[NMe_4]$Cl or $[NBu_4]$Cl. These were filtered off, washed with water and diethyl ether and dried under vacuum.For the following preparations only the reagents are indicated.

No starting anion D remained. All closo-$\{CB_9\}$generated anions, were white solids, and were studied by ^1H- and ^{11}B NMR spectroscopy. Their mass spectra were studied by MALDI-TOF analysis confirming in all cases the structures proposed. Structural confirmation was obtained by comparing the ^{11}B NMR of these anions with reported [6-R-1-$CB_9H_9]^-$ data. All the spectra are in deuterated acetone.

Synthesis of [NMe_4][6-Me-1-*closo*-CB_9H_9].

Procedure a: 200 mg, 0.91 mmol $[NMe_4][\mu$-(9,10-H_2C)-7-*nido*-$CB_{10}H_{11}]$, 389 mg, 3.64 mmol $K[NC_4H_4]$ obtained 103 mg, 0.5 mmol $[NMe_4]$[6-Me-1-*closo*-CB_9H_9] after 72 hours.

Procedure b: 30 mg, 0.14 mmol $[NMe_4][\mu$-(9,10-H_2C)-7-*nido*-$CB_{10}H_{11}]$, 21 mg, 0.54 mmol $K[NC_4Me_2H_2]$ obtained 48 mg, 0.22 mmol $[NMe_4]$[6-Me-1-*closo*-CB_9H_9] after 24 hours.

Anal. Calcd. for $C_6H_{24}B_9N$. 0.2 CH_3COCH_3: C: 36.89, H: 11.39, N: 6.32 %. Found: C: 36.60, H: 11.18, N: 6.23 %. IR ν (cm^{-1}): 2928, 2857 (C-H_{alkyl}), 2537, 2498 (B-H), 1482 (∂ Me). ^1H NMR δ: 5.24 (br s, 1H, C_c-H), 3.44 (s, 12H, $N(Me)_4$), -0.21 (br s, 3H, B_c- Me). $^1H\{^{11}B\}$ NMR δ: 5.24 (s, 1H, C_c-H), 4.48 (s, B-H), 3.44 (s, 12H, $N(Me)_4$), 1.47 (s, B-H), 0.88 (s, B-H), 0.44 (s, B-H), - 0.21 (s, 3H, B_c- Me). $^{13}C\{^1H\}$ NMR: δ: 55.16 (s, $N(Me)_4$), 51.12 (s, Me).^{11}B NMR : δ: 30.3 (d, ^1J(B, H)= 142, 1B), -16.2 (s,1B), -17.1 (d, ^1J(B, H)= 150, 2B), -18.2 (d, ^1J(B, H)= 154, 2B), -22.2 (d, ^1J(B, H)= 136, 2B), -26.5 (d, ^1J(B, H)= 140, 1B). MALDI-TOF (m/z): 133.2 (100) $[M]^-$.

Reaction of $[NMe_4][\mu$-(9,10-HCMe)-7-*nido*-$CB_{10}H_{11}]$ with CN^-: 30 mg, 0.17 mmol $[NMe_4][$7-Me-μ-(9,10-HCMe)-7-*nido*-$CB_{10}H_{11}]$, 38 mg, 0.58 mmol KCN. No reaction was observed after 72 hours at room temperature, and no reaction was observed after 72 extra hours at reflux.

Reaction of $[NMe_4][\mu$-(9,10-HCMe)-7-*nido*-$CB_{10}H_{11}]$ with F^-: 50 mg, 0.23 mmol $[NMe_4][\mu$-(9,10-H_2C)-7-*nido*-$CB_{10}H_{11}]$, 245 mg, 0.92 mmol $[NBu_4]$F at reflux for 24 hours. No reaction was observed.

Synthesis of [NBu_4][6-CH_2Me-1-*closo*-CB_9H_9].

150 mg, 0.64 mmol $[NMe_4][\mu$-(9,10-HCMe)-7-*nido*-$CB_{10}H_{11}]$, 274 mg, 2.56 mmol $K[NC_4H_4]$ obtained 75 mg, 0.19 mmol $[NBu_4]$[6-CH_2Me-1-*closo*-CB_9H_9].

IR ν (cm^{-1}): 2966, 2934, 2890, 2877 (C-H_{alkyl}), 2529 (B-H), 1470 (∂ Me).^1H NMR: δ 5.25 (br s, 1H, C_c-H), 3.19 (t, ^3J(H,H)= 8.2, 8H, $N(Bu)_4$), 1.6 (m, 8H, $N(Bu)_4$), 1.46 (q, ^3J(H,H)= 7.2, 8H, $N(Bu)_4$), 1.05 (t, ^3J(H,H)= 7.2, 12H, $N(Bu)_4$), - 0.21 (br s, 3H, B_c-Me). $^1H\{^{11}B\}$ NMR: δ: 5.25 (s, 1H, C_c-H), 3.19 (t, ^3J(H,H)= 8.2, 8H, $N(Bu)_4$), 1.6 (m, 8H, $N(Bu)_4$), 1.47 (s, B-H), 1.46 (q, ^{3}J(H,H)= 7.2, 8H, $N(Bu)_4$), 1.05 (t, ^3J(H,H)= 7.2, 12H, $N(Bu)_4$), 0.44 (s, B-H), - 0.21 (s, 3H, B_c- Me). $^{13}C\{^1H\}$ NMR: δ: 58.5 (s, $N(Bu)_4$), 23.49 (s, $N(Bu)_4$), 19.47 (s, $N(Bu)_4$), 15.04 (s, Me) 12.92 (s, $N(Bu)_4$) ^{11}B NMR: δ: 30.02 (d, ^1J(B, H)= 148, 1B), -15.39 (s, 1B), -16.39 (d, ^1J(B, H)= 168, 2B), -17.44 (d, ^1J(B, H)= 142, 2B), -21.41 (d, ^1J(B, H)= 134, 2B), -25.78 (d, ^1J(B, H)= 143, 1B). MALDI-TOF (m/z): 160.3 (100) $[M]^-$.

Synthesis of [NBu_4][1-Me-6-CH_2Me-1-*closo*-CB_9H_8].

85 mg, 0.35 mmol $[NMe_4]$[7-Me-μ-(9,10-HCMe)-7-*nido*-$CB_{10}H_{11}]$, 148 mg, 1.38 mmol $K[NC_4H_4]$ obtained 66 mg, 0.16 mmol $[NBu_4]$[1-Me-6- CH_2Me-*closo*-CB_9H_9].

IR: ν (cm^{-1}): 2964, 2939, 2877 (C-H_{alkyl}), 2541 (B-H).^1H NMR: δ: 5.20 (br s, 3H, C_c-Me), 3.19 (t, ^3J(H,H)= 8.3, 8H, $N(Bu)_4$), 1.6 (m, 8H, $N(Bu)_4$), 1.45 (q, ^3J(H,H)= 7.3, 8H, $N(Bu)_4$), 1.06 (t, ^3J(H,H)= 7.2, 12H, $N(Bu)_4$), 0.58 (br s, 2H, B_c-CH_2Me), -0.14 (br s, 3H, B_c-CH_2Me). $^1H\{^{11}B\}$ NMR: δ: 5.20 (s, 3H, C_c-Me), 3.19 (t, ^3J(H,H)= 8.3, 8H, $N(Bu)_4$), 1.6 (m, 8H, $N(Bu)_4$), 1.45 (q, ^3J(H,H)= 7.3, 8H, $N(Bu)_4$), 1.06 (t, ^3J(H,H)= 7.2, 12H, $N(Bu)_4$), 0.58 (s, 2H, B_c-CH_2Me), -0.01 (s, B-H), - 0.14 (s, 3H, B_c-CH_2Me). $^{13}C\{^1H\}$ NMR: δ: 58.5 (s, $N(Bu)_4$), 23.49 (s, $N(Bu)_4$), 19.47 (s, $N(Bu)_4$), 15.04 (s, Me) 12.92 (s, $N(Bu)_4$. ^{11}B NMR: δ: 27.66 (d, ^1J(B, H)= 142, 1B), -15.45 (s,1B), -17.74 (d, 2B), -18.10 (d, ^1J(B, H)= 142, 2B,), -21.92 (d, ^1J(B, H)= 121, 2B), -26.40 (d, ^1J(B, H)= 129, 1B). MALDI-TOF (m/z): 161.4 (100) $[M]^-$.

Synthesis of [NBu_4][6-CH_2Ph-1-*closo*-CB_9H_9].

100 mg, 0.34 mmol $[NMe_4][\mu$-(9,10-HCPh)-7-*nido*-$CB_{10}H_{11}]$, 145 mg, 1.36 mmol $K[NC_4H_4]$ obtained 69 mg, 0.15 mmol $[NBu_4]$[6-CH_2Ph-1-*closo*-CB_9H_9].

We obtain a mixture of 50% [6-CH_2Ph-1-*closo*-$CB_9H_8]^-$ (4a) and 50 % [7-Ph-7,8-*nido*-$C_2B_9H_{11}]^-$ (4b).

IR: ν (cm^{-1}): 2064, 2939, 2877 (C-H_{aryl}), 2541 (B-H). ^{1}H NMR: δ: 7.98-6.98 (m, 10H, Ph), 5.56 (br s, 1H, C_c-H), 3.21 (t, ^3J(H,H)= 8.2, 8H, $N(Bu)_4$), 1.6 (m, 8H, $N(Bu)_4$), 1.46 (q, ^3J(H,H)= 7.2, 8H, $N(Bu)_4$), 1.05 (t, ^3J(H,H)= 7.2, 12H, $N(Bu)_4$), -0.14 (br s, 2H, CH_2). $^1H\{^{11}B\}$ NMR δ: 7.98-6.98 (m, 10H, Ph), 5.56 (s, 1H, C_c-H), 3.21 (t, ^3J(H,H)= 8.2, 8H, $N(Bu)_4$), 2.19, 1.88, 1.71 (s, B-H), 1.6 (m, 8H, $N(Bu)_4$), 1.46 (q, ^3J(H,H)= 7.2, 8H, $N(Bu)_4$), 1.05 (t, ^3J(H,H)= 7.2, 12H, $N(Bu)_4$), 0.75, 0.64, 0.54, 0.27 (s, B-H), -0.14 (s, 2H, CH_2), -2.40 (s, 1H, H_{bridge}). $^{13}C\{^1H\}$ NMR: δ: 130.33, 127.23, 127.05, 126.57, 125.16, 124.05 (Ph), 58.5 (s, $N(Bu)_4$), 23.49 (s, $N(Bu)_4$), 19.47 (s, $N(Bu)_4$), 12.92 (s, $N(Bu)_4$). ^{11}B NMR: δ: 32.46 (d, ^1J(B, H)= 157, 1B, 4a), -6.47 (d, ^1J(B, H)= 141, 1B, 4b), -7.95 (d, ^1J(B, H)= 130, 1B, 4b), -11.16 (d, ^1J(B, H)= 159, 3B, 4a), -12.17 (d, ^1J(B, H)= 102, 2B, 4a, 1B, 4b), -14.06 (d, ^1J(B, H)= 161, 1B, 4b), -15.76 (d, ^1J(B, H)= 131, 1B, 4b), -17.26 (d, ^1J(B, H)= 146, 1B, 4b), -18.79 (d, ^1J(B, H)= 148, 2B, 4a), -20.53 (d, ^1J(B, H)= 142, 1B, 4b), -23.07 (d, ^1J(B, H)=129, 1B, 4a), -30.39 (d, ^1J(B, H)= 139, 1B, 4b), -33.48 (d, ^1J(B, H)=150, 1B, 4b). MALDI-TOF (m/z): 209.5 (100) $[M]^-$.

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REFERENCES

[1] B. Stíbr, Chem. Rev. 1992, 92, 225.
[2] V. I. Bregadze, Chem. Rev. 1992, 92, 209.
[3] a) Z. Xie, T. Jelinek, R. Bau, C. Reed, J. Am. Chem. Soc. 1994, 116, 1907; b) C. Reed, Acc. Chem. Res. 1998, 31, 133; c) S. Strauss, Chem. Rev. 1993, 93, 927; d) B.T. King, Z. Janousek, B. Grüner, M. Trammell, B.C. Noll, J. Michl, J. Am. Chem. Soc. 1996, 118, 3313.
[4] P. Kaszynski, Collect. Czech. Chem. Commun. 1999, 64, 895 and references therein.
[5] a) K. Nestor, B. Stíbr, J. D. Kennedy, M. Thornton-Pett, T. Jelinek, Collect. Czech. Chem. Commun. 1992, 57, 1262; b) T. Jelinek, B. Stíbr, J. Plesek, M. Thornton-Pett, J. D. Kennedy, J. Chem. Soc., Dalton Trans. 1997, 4231.
[6] B. Brellochs, In Contemporary Boron Chemistry (Eds: M. G. Davidson, A. K. Hughes, T. B. Marder, K. Wade), Royal Society of Chemistry, Cambridge, UK, 2000, pp. 212.
[7] a) J. Plesek, T. Jelinek, B. Stíbr, S. Hemánek, J. Chem. Soc., Chem. Commun. 1988, 348; b) T. Jelinek, B. Stíbr, J. Plesek, J. D. Kennedy, M. Thornton-Pett, J. Chem. Soc., Dalton Trans. 1995, 431.
[8] a) A. Nicolaides, L. Radom, J. Am. Chem. Soc. 1994, 116, 9769; b) S. K. Shin, Chem. Phys. Lett. 1997, 280, 260; c) C. Lifshitz, Acc. Chem. Res. 1994, 27, 138; d) C.-H. Shin, K-C. Park, S.-J. Kim, B. Kim, Bull. Korean. Chem. Soc. 2002, 23, 337.
[9] E. D. Jemmis, E. G. Jayasree, Inorg. Chem. 2003, 43, 7725.
[10] M. L. McKee, M. Bühl, P. v. R. Schleyer, Inorg. Chem. 1993, 32, 1712.
[11] a) G. B. Dunks, R. J. Wiersema, M. F. Hawthorne, J. Chem. Soc., Chem. Commun. 1972, 899; b) G. B. Dunks, R. J. Wiersema, M. F. Hawthorne, J. Am. Chem. Soc. 1973, 95, 3174; c) J. Plesek,, T. Jelinek, B. Stíbr, S. Hermánek, J. Chem. Soc., Chem. Commun. 1988, 348.
[12] a) D. Grafstein, J. Dvorak, Inorg. Chem. 1963, 2, 1128; b) L. Zakharkin, V. Kalinin, L. Podvisotskaya, Izv. Akad. Nauk SSSR, Ser. Khim. 1967, 10, 2310; c) Y. Stanko, V. Goltypin, V. Brattsev, Zh. Obshch. Khim. 1969, 39, 1175.
[13] J. Plesek, B. Stíbr, X. L. R. Fontaine, T. Jelinek, M. Thornton-Pett, S. Hermánek, J. D. Kennedy, Inorg. Chem. 1994; 13; 2994.
[14] C. Viñas, G. Barberà, F. Teixidor, J. Organometal. Chem. 2002, 642, 16.
[15] J. Bould, A. Laromaine, C. Viñas, F. Teixidor, L. Barton, N. P. Rath, R. E. K. Winter, R. Kivekäs, R. Sillanpää, Organometallics 2004, 23, 3335.
[16] a) M. Lamrani, S. Gómez, C. Viñas, F. Teixidor, R. Sillanpää, R. Kivekäs, New J. Chem, 1996, 20, 909; b) F. Teixidor, S. Gómez, M. Lamrani, C. Viñas, R. Sillanpää, R. Kivekäs, Organometallics 1997, 16, 1278.
[17] F. Teixidor, C. Viñas, R.W. Rudolph, Inorg. Chem., 1986, 19, 3339.
[18]. T.L. Heying, J.W. Jr. Ager, S.L. Clark, D.J. Mangold, H.L. Goldstein, M. Hillman, R.J. Polak, T. Szymanski, *Inorg. Chem.* 1963, **2**, 1089.
[19] C. Viñas, G. Barberà, F. Teixidor, *J. Organomet. Chem.* 2002, **642**, 16.

[18] T.L. Heying, J.W. Jr. Ager, S.L. Clark, D.J. Mangold, H.L. Goldstein, M. Hillman, R.J. Polak, T. Szymanski, *Inorg. Chem.* 1963, **2**, 1089.
[19] C. Viñas, G. Barberà, F. Teixidor, *J. Organomet. Chem.* 2002, **642**, 16.