SOME HALOGENATION REACTIONS OF *nido*-7,8,9,11-$P_2C_2B_7H_9$

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday for his pioneering work in the area of boron-cluster chemistry.

Halogenations of the diphosphadicarbaborane *nido*-7,8,9,11-$P_2C_2B_7H_9$ using the $AlCl_3/CCl_4$, and $I_2/AlCl_3/C_6H_6$ halogenation systems resulted in the formation of a mixture of mono- and disubstituted derivatives 10-X-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (for X = Cl and I, yields 6 and 21%, respectively) and 5,10-X_2-*nido*-7,8,9,11-$P_2C_2B_7H_7$ (for X = Cl and I, yields 57 and 46%, respectively). These results show that the halogenation under electrophilic conditions takes place at positions most distant from the P atoms, but at sites adjacent to the CH units. In contrast, the bromination with *N*-bromosuccinimide in CH_2Cl_2 is probably of radical character, proceeding in positions adjacent to the P centres to give 3-Br-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (yield 41%) and 2,3-Br_2-*nido*-7,8,9,11-$P_2C_2B_7H_7$ (yield 5%). The mixtures of the halo derivatives were separated by column chromatography on silica gel. Individual compounds were characterized by mass spectrometry and multinuclear (^{11}B, ^{1}H, and ^{31}P) spectroscopy combined with two-dimensional [^{11}B-^{11}B]-COSY NMR techniques. Various NMR effects of halogen substitutions are discussed.

Keywords: Boron; Boranes; Diphosphadicarbaboranes; NMR spectroscopy; Phosphaboranes; Phosphacarboranes; Halogenations; Carboranes.

The chemistry of phosphacarboranes, which can be obtained *via* PCl_3 or $RPCl_2$ (R = alkyl or aryl) insertion reactions into open-structured (*nido* or *arachno*) carboranes in the presence of deprotonation agents[1], attracts recently a lot of interest. Todd *et al.* were the first to prepare in this manner all three isomers (1,2, 1,7, and 1,12) of *closo*-$PCB_{10}H_{11}$ [2]. These compounds are the phosphacarborane analogues of the well-known twelve-vertex dicarbaboranes $C_2B_{10}H_{12}$, because of the isolobal relation between CH and P cluster units. Recent work in this phosphacarborane field included a high-yield synthesis of the eleven-vertex *P*-substituted phosphadicarbaboranes, 7-R-*nido*-7,8,9-$PC_2B_8H_{10}$ (R = alkyl or aryl) based on the reaction between

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nido-5,6-$C_2B_8H_{12}$ and $RPCl_2$ in the presence of PS (PS = proton sponge = 1,8-bis-(dimethylamino)naphthalene)[3]. The same reaction with PCl_3, however, generated the unsubstituted phosphadicarbaborane *nido*-7,8,9-$PC_2B_8H_{11}$ [4]. Another paper from our laboratory deals with the incorporation of PCl_3 or $RPCl_2$ into the [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ dianion to generate the phosphadicarbaboranes *nido*-7,8,11-$PC_2B_8H_{11}$ or 7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$, respectively[5]. Reactions with some borane and carborane substrates also result in multiple insertion of P-cluster units, as exemplified by the formation of *closo*-1,2-$P_2B_8H_{10}$ [6], the isomeric *nido*-$P_2C_2B_7H_9$ [7] compounds, and the derivatives of *nido*-$P_3CB_7H_8$ [8]. These compounds were isolated from reactions of PCl_3 with $B_{10}H_{14}$ and the two (4,6- and 4,5-) *arachno*-$C_2B_7H_{13}$ isomers. Except for the bromination[2b] of the 1,2- and 1,7-isomers of *closo*-$PCB_{10}H_{11}$, no direct halogenations in the field of phosphacarboranes have been reported so far. We report in this work some halogenation reactions of a very stable phosphadicarbaborane *nido*-7,8,9,11-$P_2C_2B_7H_9$ [7], the primary reason for this study being the determination of the extent and site of halogen substitution. The numbering system for the eleven-vertex *nido* compounds discussed in this work is in Scheme 1.

EXPERIMENTAL

All reactions were carried out using standard vacuum or inert-atmosphere techniques as described by Shriver[9], although some operations, such as column LC, were performed in air. The starting phosphacarborane **1** was prepared according to the literature[7]. The Fluka hexane, benzene, and dichloromethane were dried over CaH_2 and freshly distilled before use. Other chemicals were reagent or analytical grade and were used as purchased. Column chromatography was carried out on silica gel (Aldrich, 130–270 mesh) as the stationary phase. The purity of individual chromatographic fractions was checked by analytical TLC on Silufol (silica gel on aluminum foil; detection by iodine vapor, followed by 2% aqueous $AgNO_3$ spray). Melting points were measured in sealed capillaries under nitrogen and are uncorrected. Low-resolution mass spectra were obtained using a Finnigan MAT Magnum ion trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basel, Switzerland (70 eV, EI ionisation). ^{1}H, ^{11}B, and ^{31}P NMR spectroscopies were performed at 11.75 T on a Varian XL-500 instrument in $CDCl_3$ and the chemical shifts are given as follows: $\delta(^1H)$ (multiplicity, $^2J_{PH}$ in Hz, assignment), $\delta(^{11}B)$ (multiplicity, $^1J_{BH}$ in Hz, assignment), and $\delta(^{31}P)$ (multiplicity, $^1J_{PP}$ in Hz, assignment). The [^{11}B-^{11}B]-COSY[10] and ^{1}H-{^{11}B(selective)}[11] NMR experiments were essentially as described in other related papers from our laboratories[12]. Chemical shifts are given in ppm to high-frequency (low field) of Ξ = 32.083971 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm), Ξ = 40.4805 MHz (H_3PO_4) for ^{31}P (quoted ±0.5 ppm), and Ξ = 100 MHz ($SiMe_4$) for ^{1}H (quoted ±0.05 ppm), Ξ being defined as in ref.[13]. Solvent resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B\text{-}^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz.

10-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (**2**) and 5,10-Cl_2-*nido*-7,8,9,11-$P_2C_2B_7H_7$ (**3**)

A solution of *nido*-7,8,9,11-$P_2C_2B_7H_9$ (**1**) (400 mg, 2.3 mmol) in CCl_4 (20 ml) was treated with anhydrous $AlCl_3$ (660 mg, 5.0 mmol) and the mixture was left stirring at ambient temperature for 24 h. The mixture was then carefully decomposed with water (20 ml) and CH_2Cl_2 (20 ml) under cooling to 0 °C. The organic layer was separated, evaporated, and the residual solid was separated by column (2.5 × 30 cm) chromatography on silica gel. Elution with hexane and then with a CH_2Cl_2–hexane mixture resulted in the separation of two main fractions of R_F (hexane) 0.13 and 0.05. These were evaporated to dryness and identified by ^{11}B NMR spectroscopy as **2** (30 mg, 6%) and **3** (320 mg, 57%), respectively. Analytical samples of **2** and **3** were obtained by slow evaporation of hexane solutions as white crystalline compounds. For **2**: R_F (hexane) 0.13; m.p. 208 °C. MS, *m/z* (%): 208 (17.0) $[M]^+$, 205 (100). For $C_2H_8B_7ClP_2$ (205.2) calculated: 36.91% B; found: 35.21% B. $^1H\{^{11}B\}$ NMR: 2.84 (br s, –, H2,4); 2.79 (s, –, H5,6); 2.46 (br s, –, H9,11); 2.12 (s, –, H1); 2.12 (t, 11.5, H3). ^{11}B NMR: 7.6 (s, –, B10); –1.0 (d, 161, B5,6); –7.0 (br d, 169, B2,4); –21.2 (br d, 173, B3); –33.9 (d, 162, B1); all [^{11}B-^{11}B]-COSY crosspeaks observed. $^{31}P\{^1H\}$ NMR: –51.6 (s, –, P7,8). For **3**: R_F (hexane) 0.05; m.p. 190 °C. MS, *m/z* (%): 244 (4.3) $[M]^+$, 239 (100). For $C_2H_7B_7Cl_2P_2$ (239.7) calculated: 31.60% B; found: 29.84% B. $^1H\{^{11}B\}$ NMR: 3.01 (d, 16.5, H4); 2.82 (s, –, H6); 2.79 (d, 17.0, H2); 2.59 (d, 28.5, H9); 2.45 (d, 30.0, H11); 2.19 (s, –, H1); 2.04 (t, 18.0, H3). ^{11}B NMR: 6.7 (s, –, B10); 4.0 (s, –, B5); –2.1 (br d, 169, B6); –7.5 (br d, ≈160, B4); –8.4 (br d, ≈160, B2); –22.1 (br d, 170, B3); –34.4 (d, 158, B1); all [^{11}B-^{11}B]-COSY crosspeaks observed. $^{31}P\{^1H\}$ NMR: –48.7 (as d, 227, P8); –111.5 (as d, 246, P7).

3-Br-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (**4**) and 2,3-Br_2-*nido*-7,8,9,11-$P_2C_2B_7H_7$ (**5**)

A solution of **1** (400 mg, 2.3 mmol) in CH_2Cl_2 (20 ml) was treated at 0 °C with several portions of *N*-bromosuccinimide (1 500 mg, 8.4 mmol) under stirring and cooling until the initial exothermic reaction had ceased. The mixture was then left stirring at ambient temperature for 24 h. The mixture was then evaporated with silica gel and the residual solid was transferred onto a column (2.5 × 30 cm) packed with silica gel. Elution with hexane and then with a CH_2Cl_2–hexane mixture resulted in the separation of two main fractions of R_F (hexane) 0.12 and 0.06 which were evaporated to dryness and identified by ^{11}B NMR spectroscopy as **4** (240 mg, 41%) and **5** (40 mg, 5%), respectively. Analytical samples of **4** and **5** were obtained by slow evaporation of hexane solutions as white crystalline solids. For **4**: R_F (hexane) 0.12; m.p. 175 °C. MS, *m/z* (%): 252 (44) $[M]^+$, 250 (100). For $C_2H_8B_7BrP_2$ (249.7) calculated: 30.34% B; found: 28.93% B. $^1H\{^{11}B\}$ NMR: 3.09 (s, –, H10); 3.05 (br s, –, H2,4); 2.60 (s, –, H5,6); 2.55 (br s, –, H9,11); 2.26 (s, –, H1). ^{11}B NMR: –1.6 (d, ≈150, B5,6); –2.5 (br d, ≈154, B2,4); –3.8 (d, 154, B10); –9.9 (br s, –, B3); –31.7 (d, 158, B1); all [^{11}B-^{11}B]-COSY crosspeaks observed. $^{31}P\{^1H\}$ NMR: –26.3 (s, –, P7,8). For **5**: R_F (hexane) 0.06; m.p. 150 °C. MS, *m/z* (%): 332 (3) $[M]^+$, 329 (100). For $C_2H_7B_7Br_2P_2$ (328.6) calculated: 23.05% B; found: 22.10% B. $^1H\{^{11}B\}$ NMR: 3.42 (d, 15.0, H4); 3.21 (s, –, H10); 3.03 (s, –, H6); 2.82 (d, 34.0, H11); 2.74 (d, 48.5, H9); 2.68 (s, –, H5); 2.28 (s, –, H1). ^{11}B NMR: –0.3 (br s, –, B2); –1.6 (d, ≈158, B5,6); –2.5 (d, 157, B4); –2.9 (d, 154, B10); –9.6 (br s, –, B3); –30.3 (d, 158, B1); all [^{11}B-^{11}B]-COSY crosspeaks observed. $^{31}P\{^1H\}$ NMR: –18.4 (as d, 235, P7); –25.4 (as d, 262, P8).

10-I-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (**6**) and 5,10-I_2-*nido*-7,8,9,11-$P_2C_2B_7H_7$ (**7**)

A solution of **1** (400 mg, 2.3 mmol) in benzene (20 ml) was treated with $AlCl_3$ (135 mg, 5.0 mmol) and then with I_2 (1270 mg, 5.0 mmol) and the mixture was left stirring at ambient temperature for 24 h. The mixture was then decomposed carefully with water (20 ml) and CH_2Cl_2 (20 ml) under cooling to 0 °C. The organic layer was separated, evaporated, and the residual solid was separated by column (2.5 × 30 cm) chromatography as in the preceding experiments. Fractions of R_F (hexane) 0.10 and 0.05 were evaporated to dryness and identified by ^{11}B NMR spectroscopy as **6** (148 mg, 22%) and **7** (451 mg, 46%), respectively. Analytical samples of **6** and **7** were obtained by slow evaporation of hexane solutions as white crystalline solids. For **6**: R_F (hexane) 0.10; m.p. 155 °C. MS, *m/z* (%): 298 (59) $[M]^+$, 297 (100). For $C_2H_8B_7IP_2$ (296.7) calculated: 25.53% B; found: 25.05% B. $^1H\{^{11}B\}$ NMR: 2.99 (br s, –, H2,4); 2.93 (s, –, H5,6); 2.59 (br s, –, H9,11); 2.56 (t, 19.5, H3); 2.12 (s, –, H1). ^{11}B NMR: 0.0 (d, 161, B5,6); –4.3 (br d, 169, B2,4); –13.1 (s, –, B10); –18.4 (br d, 165, B3); –33.3 (d, 162, B1); all [^{11}B-^{11}B]-COSY crosspeaks observed. $^{31}P\{^1H\}$ NMR: –38.5 (s, –, P7,8). For **7**: R_F (hexane) 0.05; m.p. 117 °C. MS, *m/z* (%): 424 (59) $[M]^+$, 423 (100). For $C_2H_7B_7I_2P_2$ (422.6) calculated: 17.92% B; found: 16.84% B. $^1H\{^{11}B\}$ NMR: 3.56 (d, 16.0, H4); 3.27 (s, –, H6); 3.06 (d, 15.5, H2); 2.87 (d, 29.5, H9); 2.60 (t, 14.0, H3); 2.57 (d, 27.5, H11); 2.35 (s, –, H1). ^{11}B NMR: 0.05 (d, 158, B6); –4.4 (br d, 177, B2,4); –11.45 (s, –, B10); –16.1 (s, –, B5); –17.9 (br d, 173, B3); –32.3 (d, 165, B1); all [^{11}B-^{11}B]-COSY crosspeaks observed except for B1-B6, B2-B6, B6-B10. $^{31}P\{^1H\}$ NMR: –34.5 (as d, 217, P8); –74.7 (as d, 256, P7).

RESULTS AND DISCUSSION

Synthesis

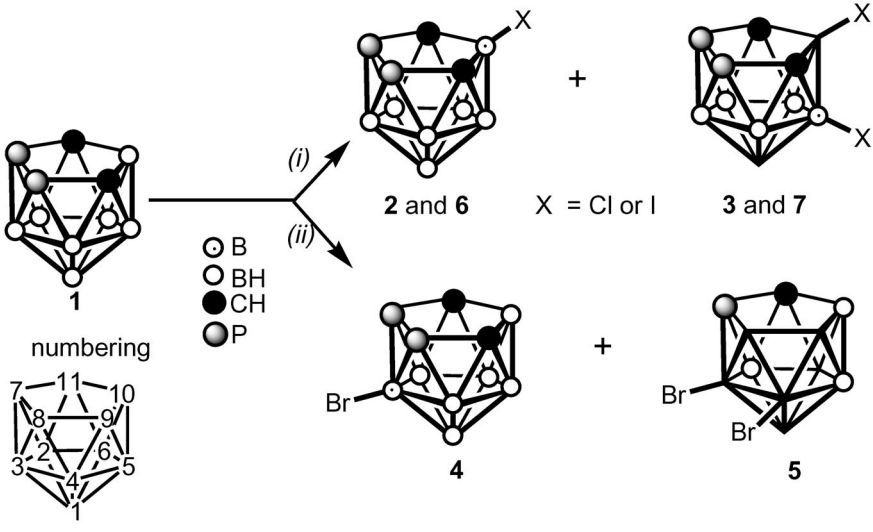
Chlorination of the air-stable diphosphadicarbaborane[7] *nido*-7,8,9,11-$P_2C_2B_7H_9$ (**1**) using the $CCl_4/AlCl_3$ system at ambient temperature (see ref.[14], for example) resulted in the isolation of the mono- and dichloro derivatives, 10-Cl-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (**2**) and 5,10-Cl_2-*nido*-7,8,9,11-$P_2C_2B_7H_7$ (**3**) in yields 6 and 5%, respectively (path (*i*) of Scheme 1). Surprisingly, no bromination of **1** could be achieved using $Br_2/AlBr_3$ or $BrCH_2CH_2Br/AlBr_3/CS_2$, $CHBr_3/AlBr_3$, and $CBr_4/AlBr_3$ systems[14]. Application of these bromination methods led to the decomposition of the starting compound **1** and no reasonable products could be isolated. Smooth bromination, however, was achieved *via* reaction of **1** with *N*-bromosuccinimide in CH_2Cl_2 at room temperature (path (*ii*) of Scheme 1), in which the derivatives 3-Br-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (**4**) and 2,3-Br_2-*nido*-7,8,9,11-$P_2C_2B_7H_7$ (**5**) were isolated by chromatography in yields 41 and 5%, respectively. Without any problems proceeded also the room-temperature reaction between **1** and elemental iodine in benzene using the $AlCl_3$ catalyst. The reaction led to compounds 10-I-*nido*-7,8,9,11-$P_2C_2B_7H_8$ (**6**) and

5,10-I_2-*nido*-7,8,9,11-$P_2C_2B_7H_7$ (**7**) (path (*i*) of Scheme 1), which were isolated again by chromatography in yields 21 and 46%, respectively.

All the mono- and dihalogenated derivatives of **1** were crystallized by slow evaporation of their hexane solutions and obtained as white, air-stable compounds. The halogenation reactions of **1** are outlined in Scheme 1. It can be concluded that chlorination and iodination of the diphosphadicarbaborane *nido*-7,8,9,11-$P_2C_2B_7H_9$ (**1**) under electrophilic conditions take place regiospecifically at the cage BH(5,10) vertices *most distant* from the cage P-atoms (γ and δ) but, in contrast to most carboranes[1b,1c,15], in positions adjoining the CH units. In contrast to these reactions, bromination with *N*-bromosuccinimide is probably of radical character and proceeds exclusively in positions B(2,3) which are *adjacent* to the P-centre.

NMR Spectroscopy

The structure of the cage of **1** was established by the X-ray diffraction analysis on its 3-Cl derivative[7] and the structures of the halo derivatives isolated in this work can be suggested unambiguously on the basis of NMR spectroscopy. The ^{11}B NMR spectra of all diphosphadicarbaborane com-



SCHEME 1

(*i*) $AlCl_3/CCl_4$, room temperature, 24 h (for X = Cl); $AlCl_3/I_2$, benzene, room temperature, 24 h (for X = I). (*ii*) *N*-bromosuccimimide, CH_2Cl_2, room temperature, 24 h

pounds discussed in this work can be easily assigned using two-dimensional [^{11}B-^{11}B]-COSY spectroscopy[10] combined with ^{1}H{^{11}B(selective)}[11] measurements. Moreover, all ^{1}H{^{11}B} resonances of individual BH and CH vertices adjacent to the cluster P-vertex are split into doublets or triplets (B(3) position neighbouring two P-vertices) due to ^{2}J(^{1}H-^{31}P) coupling, which helps in easy assigning all cluster resonances. Mass spectra of all compounds show typical molecular cut-offs, the intensities in the parent envelope being very close to theoretical isotope distributions.

The C_s-symmetry structures of the monohalogenated compounds **2** and **6**, bearing the halogen substituent on the single open-face boron vertex B(10), are in agreement with all NMR data. The ^{11}B NMR spectra consist of one B(10) singlet, two intensity-1 doublets due to atoms B(1) and B(3) in the symmetry plane, and two intensity-2 doublets belonging to B(2,4) and B(5,6) resonances. As expected[16], the 10-substitution is associated with remarkable shielding changes $\Delta\rho$ at the substituted B(10) α-site ($\Delta\rho(^{11}B) = \delta(^{11}B)_p - \delta(^{11}B)_s$, where subscripts p and s relate to the parent[16] and substituted compound). The values increase from Cl (–8.1) to I (+12.6) ($\Delta\rho(^{11}B)_\alpha$ values in parentheses). The ^{1}H NMR spectra contain a broad CH(9,11) singlet due to the ^{2}J(^{1}H-^{31}P) coupling and the vicinal (β) shielding changes at the CH(9,11) sites increase from I (–0.38) to Cl (–0.25) ($\Delta\rho(^{1}H)_\beta$ values in parentheses). Remarkably sensitive to the B(10) substitution are the ^{31}P NMR spectra in which the γ-shielding changes at the P(7,8) sites decrease from Cl (+8.2) to I (–4.9) ($\Delta\rho(^{31}P)_\gamma$ values in parentheses). Antipodal (δ) ^{11}B shieldings by the 10-X substituent at the B(3) site are not so high, decreasing from Cl (+3.7) to I (+0.9) ($\Delta\rho(^{11}B)_\delta$ values in parentheses).

The ^{11}B NMR spectra of the C_s-symmetry **4** consist of one B(3) singlet, two intensity-1 doublets due to atoms B(1) and B(10) in the symmetry plane, and two intensity-2 doublets belonging to B(2,4) and B(5,6) resonances. The 3-Br substitution is associated with moderate deshielding $\Delta\rho(^{11}B)_\alpha = -7.6$ at the substituted B(3) site and a small antipodal shielding of the B(10) site at $\Delta\rho(^{11}B)_\delta = +3.3$. The ^{1}H NMR spectra of **4** contain a broad CH(9,11) singlet with a Br deshielding of $\Delta\rho(^{1}H)_\gamma = -0.34$. Quite high is the β-deshielding effect decreasing[7] from Cl (–18.2) to Br (–17.1) ($\Delta\rho(^{31}P)_\beta$ in parentheses) in the ^{31}P NMR spectrum.

The ^{11}B NMR spectra of the C_1-symmetry dihalogenated compounds **3**, **5**, and **7** consist of two, B(5) and B(10) or B(2) and B(3), singlets and five intensity-1 doublets. Due to the approximate additivity of the shielding changes[16], the spectra cumulate the properties of the monosubstituted counterparts with added changes brought about by the second substitution. The double halogen substitution is associated with remarkable ^{11}B shielding

changes at the substituted α-sites increasing, as usually, in the series Cl < Br < I. Due to the asymmetry, the ^{1}H NMR spectra contain two CH(9) and CH(11) doublet resonances and the combined β and γ-shielding changes at the CH sites generally increase in the series Cl < Br < I. Extremely affected by the C substitution are the ^{31}P NMR spectra in which the combined γ and δ (antipodal[16]) shielding changes at the P(7) site are enormously high, decreasing from Cl (+68.1) to I (+31.3) ($\Delta\rho(^{31}P)_{\gamma+\delta}$ values in parentheses) for P(7), the effects being remarkably enhanced by the antipodal relation between B(5) and P(7). The combined γ effects on P(8) for the dihalogenated compounds are relatively smaller, decreasing from Cl (+5.3) to I (–8.9) ($\Delta\rho(^{31}P)_{\gamma}$ values in parentheses). The combined β and γ effects on P(7) and P(8) for **5** are also comparatively high at $\Delta\rho(^{31}P)_{\beta+\gamma}$ = –25.0 and –18.0 ppm, respectively.

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