Phosphacarborane Chemistry: The Synthesis of the Parent Phosphadicarbaboranes *nido*-7,8,9-$PC_2B_8H_{11}$ and [*nido*-7,8,9-$PC_2B_8H_{10}$]$^-$, and Their 10-Cl Derivatives − Analogs of the Cyclopentadienide Anion

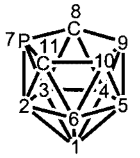
Bohumil Štíbr,*[a,b] Josef Holub,[a] Mario Bakardjiev,[a] Drahomír Hnyk,[a] Oleg L. Tok,[b] Wolfgang Milius,[b] and Bernd Wrackmeyer[b]

Keywords: Ab initio calculations / Boranes / Clusters / Phosphorus

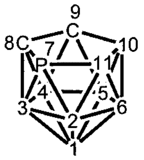
The reaction of the carborane *nido*-5,6-$C_2B_8H_{12}$ (**1**) with PCl_3 in dichloromethane in the presence of a "proton sponge" [PS = 1,8-bis(dimethylamino)naphthalene], followed by hydrolysis of the reaction mixture, resulted in the isolation of the eleven-vertex *nido*-phosphadicarbaboranes 7,8,9-$PC_2B_8H_{11}$ (**2**) and 10-Cl-7,8,9-$PC_2B_8H_{10}$ (**10-Cl-2**), depending on the ratio of the reactants. Both of these compounds can be deprotonated by PS to give the *nido* anions [7,8,9-$PC_2B_8H_{10}$]$^-$ (**2**$^-$) and [10-Cl-7,8,9-$PC_2B_8H_9$]$^-$ (**10-Cl-2**$^-$). The molecular geometries of all compounds were optimized by ab initio methods at a correlated level of theory [RMP2(fc)] using the 6-31G* basis set and their correctness was assessed by a comparison of the experimental ^{11}B NMR chemical shifts with those calculated by the GIAO-SCF/II//RMP2(fc)/6-31G* method. Moreover, the structure of **10-Cl-2**$^-$ was determined by an X-ray diffraction analysis. The anionic compounds **2**$^-$ and **10-Cl-2**$^-$ are analogs of the Cp (Cp = η^5-$C_5H_5^-$) anion.

Introduction

There is current interest in the synthesis and chemistry of phosphacarboranes since the presence of P as a B-cluster constituent gives borane clusters carborane character. The cluster P atom in these species contributes three electrons and three orbitals into the cluster bonding, as does a carborane CH group, while the remaining two electrons reside in the exopolyhedral P sp^3 orbital.[1] Recent efforts are dominated by successful attempts at the isolation of phoshacarborane analogues of tricarbollides (11-vertex *nido*-tricarbaboranes).[2] In this field of chemistry, one of our groups has recently reported preliminary results on the synthesis of the *nido*-phosphadicarbaboranes 7,8,11-$PC_2B_8H_{11}$ and [7,8,11-$PC_2B_8H_{10}$]$^-$ based on the reaction between [6,9-$C_2B_8H_{10}$]$^{2-}$ and PCl_3.[3] The first species is an analog of the neutral tricarbollide 7,8,9-$C_3B_8H_{12}$ and the second anion is analogous to [7,8,9-$C_3B_8H_{11}$]$^-$.[4] Both anions, [7,8,11-$PC_2B_8H_{10}$]$^-$ and [7,8,9-$C_3B_8H_{11}$]$^-$ are also regarded[2] as perfect Cp analogs as they are monoanionic and contain an open pentagonal face which can donate five electrons for the η^5-type coordination to metal ions. As shown in structures **I** and **II**, the presence of the P vertex in the open pentagonal face of an eleven-vertex phosphadicarbaborane anion with the general formula [$PC_2B_8H_{10}$]$^-$ allows for two possible configurations of open-face heteroatoms in adjacent positions. While Cp analogs of configuration **I** are known,[3] those of structure **II** have not yet been reported. Although Sneddon et al. have prepared neutral compounds 7-R-7,8,9-$PC_2B_8H_{10}$ (R = Me and Ph)[5] adopting configuration **II**, these cannot be regarded as Cp analogs as they are not monoanionic. We report here a simple and efficient method for the synthesis of the missing Cp analogs of structure **II**, specifically the preparation of the neutral compound 7,8,9-$PC_2B_8H_{11}$ and the anionic [7,8,9-$PC_2B_8H_{10}$]$^-$, and their 10-Cl derivatives.



I



II

Results and Discussion

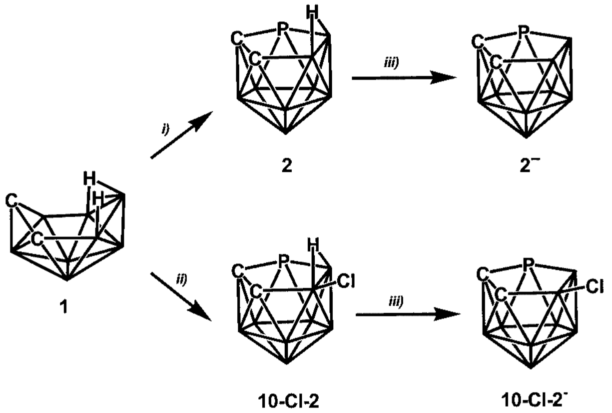
Syntheses

As shown in Scheme 1 [path *i)*] (C = CH, vertices of individual polyhedra denote BH groups), treatment of *nido*-

---

[a] Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, Research Centre for New Inorganic Compounds and Advanced Materials, University of Pardubice
25068 Rez, Czech Republic
Fax: (internat.) + 420-2/20941502
E-mail: stibr@iic.cas.cz
[b] Laboratorium für Anorganische Chemie der Universität Bayreuth,
Postfach 101251, Bayreuth, 95440, Germany
Fax: (internat.) + 49-(0)921/552157
E-mail: B.Wrack@uni-bayreuth.de

5,6-$C_2B_8H_{12}$ (**1**)[6] with excess PCl_3 in the presence of a proton sponge [PS = 1,8-bis(dimethylamino)naphthalene] (molar ratio **1**/PS = 1:1.5) in CH_2Cl_2, at room temperature for 48 h, followed by hydrolysis and chromatographic purification of the products, resulted in the isolation of the 11-vertex phosphadicarbaborane *nido*-7,8,9-$PC_2B_8H_{11}$ (**2**) in a yield of 38% (based on **1**). One of the chromatographic fractions contained the dicarbaborane *closo*-1,2-$C_2B_8H_{10}$, which justifies the overall stoichiometry as in Equation (1); otherwise the formation of **2** could not be explained [Equation (1)].



Scheme 1

$$2\,C_2B_8H_{12}\,(\mathbf{1}) + PCl_3 + 3\,PS \rightarrow PC_2B_8H_{11}\,(\mathbf{2}) + C_2B_8H_{10} + 3\,PSH^+Cl^- \qquad (1)$$

We assume that 1 equiv. of **1** is oxidized to give *closo*-1,2-$C_2B_8H_{10}$ under the formation of transient [$PHCl_2$] [Equation (2)] which then reacts with **1** according to Equation (3) to produce the phoshacarborane **2**.

$$C_2B_8H_{12} + PCl_3 + PS \rightarrow C_2B_8H_{10} + [PHCl_2] + PSH^+Cl \qquad (2)$$

$$C_2B_8H_{12} + [PHCl_2] + 2\,PS \rightarrow PC_2B_8H_{11} + 2\,PSH^+Cl^- \qquad (3)$$

In contrast to the reaction according to Equation (1), the same reaction of **1** with an excess of PCl_3, but using a different **1**/PS ratio (1:2) [Scheme 1, path *ii)*], leads to the formation of the 10-Cl-substituted derivative 10-Cl-*nido*-7,8,9-$PC_2B_8H_{10}$ (**10-Cl-2**) as a predominant product (yield 30%).

$$C_2B_8H_{12}\,(\mathbf{1}) + PCl_3 + 2\,PS \rightarrow PC_2B_8H_{10}Cl\,(\mathbf{10\text{-}Cl\text{-}2}) + 2\,PSH^+Cl^- \qquad (4)$$

From the mechanistic viewpoint, reactions according to Equations (1) and (4) are consistent with the insertion of the P vertex into the area identified by the C(6), B(7), B(8), and B(9) vertices in structure **1** (see Scheme 1). Interestingly, in the reaction corresponding to Equation (4), the Cl substituent enters a position not adjacent to the P vertex, as observed earlier in the case of the $P_2C_2B_7H_8Cl$ derivatives.[7] Both **2** and **10-Cl-2** can easily be deprotonated by reactions with stoichiometric amounts of PS in CH_2Cl_2 to give the crystalline salts PSH^+ [*nido*-7,8,9-$PC_2B_8H_{10}$]$^-$ (compound $PSH^+\mathbf{2}^-$) and PSH^+ [10-Cl-*nido*-7,8,9-$PC_2B_8H_9$]$^-$ (compound $PSH^+\mathbf{10\text{-}Cl\text{-}2}^-$) upon careful addition of pentane onto the surface of the solution. The deprotonation reaction thus generates a bare pentagonal face, a favorable feature for employing these anions as Cp analogs for metal complexation.

NMR Spectroscopic Studies

The asymmetrical structure with a contiguous P−C−C string in the open face of an 11-vertex framework (see Scheme 1) is in agreement with the NMR-spectroscopic data of all the compounds described above. The ^{11}B NMR spectra of all the isolated compounds consist of eight different resonances with some incidental overlaps. All of them are doublets, except that the spectra of the substituted compounds **10-Cl-2** and **10-Cl-2⁻** contain one B(10) singlet, the resonances being shifted downfield ($\Delta\delta$ = 11.4 and 11.8 ppm, respectively) in comparison to the unsubstituted counterparts. It is also obvious that the ^{11}B NMR signals of the anionic compounds **2⁻** and **10-Cl-2⁻** are all shifted upfield ($\Delta\delta$ = 11.2 and 11.0 ppm, respectively) in comparison to those of the neutral compounds **2** and **10-Cl-2**. Graphical comparisons of the ^{11}B NMR shifts of **2**, **10-Cl-2**, and the isostructural tricarbaboranes *nido*-7,8,9-$C_3B_8H_{12}$ (compound **3**)[4] are given in Figure 1 (bottom part) together with similar comparisons for the corresponding anionic species **2⁻**, **10-Cl-2⁻**, and [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$ (**3⁻**)[4] (top diagrams).

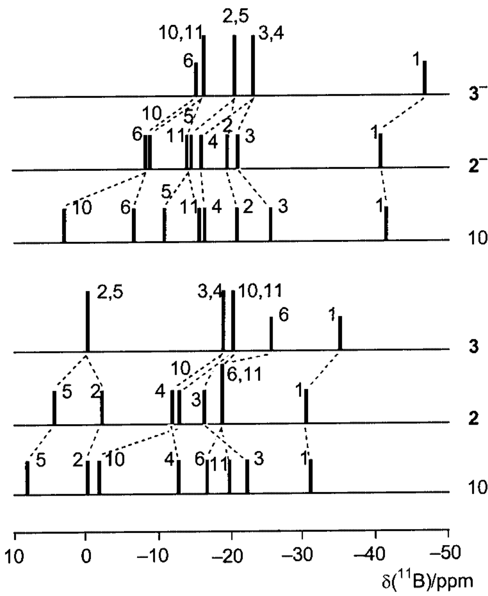


Figure 1. Stick representation and intercomparison of the $\delta(^{11}B)$ chemical shifts for neutral *nido* compounds 7,8,9-$PC_2B_8H_{11}$ (**2**), 10-Cl-7,8,9-$PC_2B_8H_{10}$ (**10-Cl-2**), and 7,8,9-$C_3B_8H_{12}$ (**3**) (bottom diagrams) and their anionic counterparts [7,8,9-$PC_2B_8H_{10}$]$^-$ (**2⁻**), [10-Cl-7,8,9-$PC_2B_8H_9$]$^-$ (**10-Cl-2⁻**), and [7,8,9-$C_3B_8H_{11}$]$^-$ (**3⁻**) (top diagrams)

Figure 1 clearly shows that the δ(^{11}B) data of individual isostructural couples **2**/**3** and **2**$^-$/**3**$^-$ are very similar (spectrum span δ = 36.4/35.5 and 35.2/31.9 ppm, respectively), but all signals of the P compounds are shifted downfield by an increment of Δδ ≈ 5 ppm. Similar deshielding effects are also observed in the corresponding ^{1}H NMR spectra. These straightforward NMR similarities between tricarbaboranes and the corresponding phosphadicarbaborane counterparts reflect the isolobal relationship between CH and bare P vertices, which is that each contribute three electrons to the cluster bonding scheme. The characteristic feature of the ^{1}H NMR spectra of all compounds isolated is the presence of one CH(9) singlet and one CH(8) doublet ($^{2}J_{\mathrm{PH}}$ coupling). The spectra of the neutral compounds **2** and **10-Cl-2** contain a typical broad, high-field μH(10,11) resonance at δ = −2.48 and −1.12 ppm, respectively. The ^{31}P NMR spectra of all compounds show one singlet and the ^{13}C NMR spectra display one doublet ($^{1}J_{\mathrm{P-C}}$ splitting) and one broader singlet (with fine multiplet $^{1}J_{\mathrm{CB}}$ splitting) due to C(8) and C(9) resonances, respectively. As in the ^{11}B NMR spectra, there are similar upfield shifts of both CH(9) (Δδ = 1.58 [9.3] and 1.79 [9.8] ppm) and CH(8) (Δδ = 1.75 [27.7] and 1.82 [28.9] ppm) resonances, in the corresponding ^{1}H and ^{13}C (data in square brackets) NMR spectra of anions **2**$^-$ and **10-Cl-2**$^-$, with respect to those of the neutral **2** and **10-Cl-2**. This effect is copied in the ^{31}P NMR spectra in which the singlet resonances of the anionic species **2**$^-$ and **10-Cl-2**$^-$ again exhibit shielding (Δδ = 33.1 and 27.7 ppm) with respect to those of the neutral compounds **2** and **10-Cl-2**. As shown in Figure 2, there is a linear correlation between δ(^{13}C) and δ(^{1}H) shifts for CH(8) (line A) and CH(9) (line B) cluster units which can be useful for further NMR-spectroscopic considerations in the fields of carborane and heterocarborane chemistry.

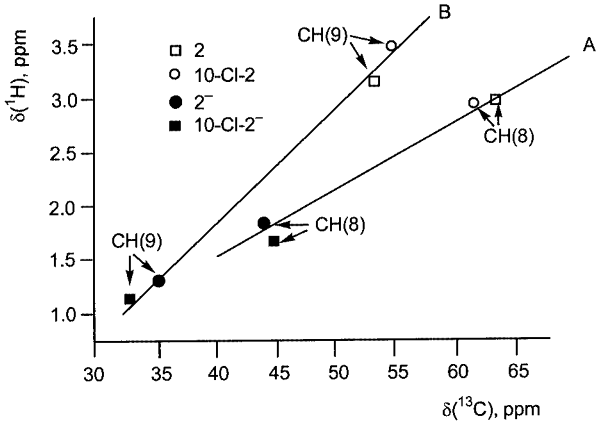


Figure 2. Plot of δ(^{1}H) versus δ(^{13}C) chemical shifts for CH(8) (line A) and CH(9) (line B) cluster units for the *nido*-phosphadicarbaboranes 7,8,9-$PC_2B_8H_{11}$ (**2**), 10-Cl-7,8,9-$PC_2B_8H_{10}$ (**10-Cl-2**), $[7,8,9\text{-}PC_2B_8H_{10}]^-$ (**2**$^-$), and $[10\text{-}Cl\text{-}7,8,9\text{-}PC_2B_8H_9]^-$ (**10-Cl-2**$^-$)

Geometry Optimization

Gimarc's topological stabilization rule[8] suggests that elements with higher electronegativity than boron, such as e.g. C and P, occupy cluster sites of the highest electronegativity of a parent boron hydride from which a corresponding isostructural heteroborane is formally derived. Indeed, the contiguous P−C−C string substitutes the analogous B−B−B string of the hypothetical $[nido\text{-}B_{11}H_{11}]^{4-}$ in its open pentagonal belt [RMP2(fc)/6-31G* natural population analysis (NPA) charge is −0.334, in contrast to −0.170 attributed to the B_5 girdle capped by B(1)].[7] The experimental NMR spectra indicate a total lack of symmetry in all compounds and, consequently, their geometries were fully optimized (see Figure 3) without any symmetry constraints beginning at the SCF level with 3-21G and 6-31G* basis sets. Frequency calculations confirmed the structures to be minima on the corresponding 6-31G* potential energy hypersurfaces. The final level of optimization was second-order Møller−Plesset perturbation theory in frozen core approximation (fc). These geometries were used for GIAO-SCF/II//RMP2(fc)/6-31G* (level of NMR theory// geometry) calculations of the ^{11}B and ^{13}C NMR shifts. Comparisons of these shifts with experimental values are in satisfactory agreement [see Exp. Sect., maximum differences for δ(^{11}B) fall within the range of 5 ppm with the exception of B(4) in **2** (δ = 7 ppm), δ(^{13}C) calculations performed slightly worse but these usually show strong dependence on the theory and basis set used[9]] and thus provide evidence for believing that the RMP2(fc)/6-31G* internal coordinates can be deemed as good representations of the molecular geometries of **2** and **10-Cl-2** and of the anionic species **2**$^-$ and **10-Cl-2**$^-$ in their solutions. The calculated geometries are depicted in Figure 3 and Table 1 offers salient computed geometrical parameters. Apparently, the presence of the P vertex is a principal source of the distortion from a regular "icosahedral-like" shape. The carbon atoms contribute to such a deformation to a lesser extent.

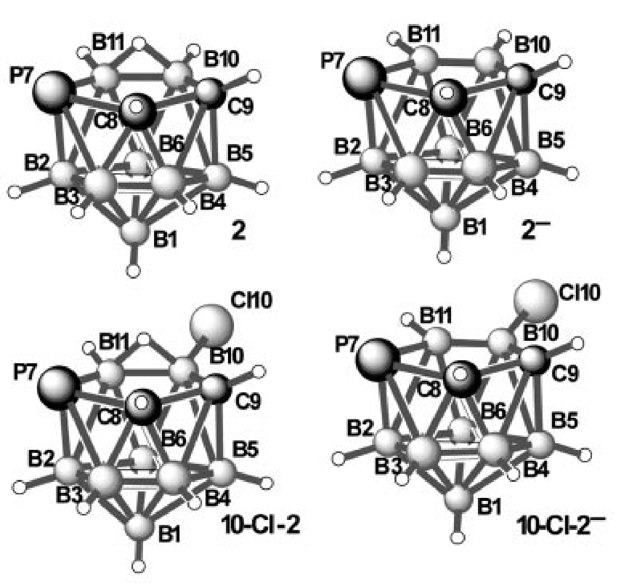


Figure 3. RMP2(fc)/6-31G*-optimized structures of the phosphadicarbaboranes 7,8,9-$PC_2B_8H_{11}$ (**2**), 10-Cl-7,8,9-$PC_2B_8H_{10}$ (**10-Cl-2**), $[7,8,9\text{-}PC_2B_8H_{10}]^-$ (**2**$^-$), and $[10\text{-}Cl\text{-}7,8,9\text{-}PC_2B_8H_9]^-$ (**10-Cl-2**$^-$)

Table 1. Salient internal coordinates at the RMP2(fc)/6-31G* level

	2	**10-Cl-2**	**2^-**	**10-Cl-2^-**
Bond lengths [Å]				
$[B(1)-B]_{mean}$ [a]	1.772	1.774	1.774	1.774
$(B-B)_{mean}$ [b]	1.777	1.776	1.777	1.776
2−7	2.028	2.026	2.051	2.051
3−7	2.025	2.023	2.060	2.057
3−8	1.748	1.747	1.748	1.743
4−8	1.712	1.713	1.710	1.711
4−9	1.700	1.701	1.726	1.726
5−9	1.693	1.698	1.719	1.724
5−10	1.795	1.799	1.787	1.790
6−10	1.797	1.796	1.788	1.783
2−11	1.826	1.823	1.821	1.816
6−11	1.778	1.784	1.768	1.776
7−8	1.888	1.890	1.871	1.871
8−9	1.528	1.529	1.528	1.527
9−10	1.658	1.647	1.620	1.612
10−11	1.834	1.837	1.741	1.727
7−11	2.027	2.035	1.949	1.950
$(B-H)_{mean}$	1.189	1.188	1.198	1.195
$(C-H)_{mean}$	1.088	1.189	1.090	1.089
10-Cl		1.790		1.834
10-H_b	1.329	1.347		
11-H_b	1.305	1.290		
Bond angles [°]				
7-8-9	120.0	120.1	113.4	113.6
8-9-10	112.8	112.7	114.7	113.8
8-7-11	91.5	91.4	94.8	94.8
Dihedral angles [°]				
7−8−9−10	−3.2	−3.4	−7.8	−7.9
9−8−7−11	8.7	8.6	13.1	13.0
8−9−10−11	−5.0	−4.8	−2.8	−2.6

[a] For atomic numbering, see Figure 3. [b] Lower pentagon.

The most remarkable features of the computed molecular structures of these systems are the considerable deformations of the open pentagonal belts. For instance, the C(8)−P(7)−B(11) angles for **2** and **10-Cl-2** are 91.5 and 91.4°, respectively. Such deviations from a regular pentagonal angle of 108° are by far the largest noticed so far in the family of heteroboranes that contain a third-row element.[7,10] In the case of the corresponding anions, **2^-** and **10-Cl-2^-**, these angles are opened by ca. 3.5° with respect to **2** and **10-Cl-2**, but still deviate substantially from 108°. On the other hand, such a pronounced narrowing in **2** and **10-Cl-2** is likely to be compensated by opening of the P(7)−C(8)−C(9) angles when compared with their smaller values for both anions. Moreover, these pentagons are not planar, as exemplified by some dihedral angles in Table 1, although such a nonplanarity is less marked in the neutral species. As found in other phosphaboranes,[7,11] the Cl-substitution brings about only marginal effects in the molecular cage geometry relative to an unsubstituted compound (see Table 1). The P−C, P−B, C−C, and B−B nearest-neighbor separations in the open pentagonal belts resemble those determined for the four $P_2C_2B_7H_9$ isomers and their Cl derivatives[7], at the same level of theory [e.g. *r*(C−C), retain their aliphatic single-bond character, which is also revealed by their Wiberg bond indices (WBI, natural atomic bond orders) calculated for **2** and **2^-**: 0.962 (0.833) and 0.946 (0.817), respectively]. Whereas the WBI for the remaining four linkages of the open pentagonal face of **2^-** span a narrow interval of <0.773, 0.866> (<0.688, 0.823>), the presence of the hydrogen bond in **2** considerably decreases electron delocalization in the open pentagonal face {WBI for *r*[B(10)−B(11)] = 0.457 (0.619)}.

X-ray Diffraction Studies

The structure of PSH$^+$**10-Cl-2^-** was determined unambiguously by an X-ray diffraction analysis (for selected crystallographic parameters see Tables 2 and 3). As seen from Figure 4, the structure of the anionic part **10-Cl-2^-** is consistent with all NMR-spectroscopic data and compares well with the calculated RMP2(fc)/6-31G* geometrical parameters. The computed and experimental structural parameters in Tables 1 and 2, respectively, are generally in good agreement. The cage P−C, P−B, C−C and C−B, B−B distances in the open pentagonal face are 1.866(4), 1.939(4), 1.517(4) and 1.596(5), 1.723(4) Å, respectively, similar to those found crystallographically for the diphosphadicarbaboranes $P_2C_2B_7H_9$, the other cluster C−B and P−B, B−B, and B−Cl separations fall within usual limits.[7] The structure determination also confirms the asymmetrical arrangement of the C and P heteroatoms within a distorted open pentagonal face. As also exhibited in the calculated structure, the distortion is due to relatively long P−B and P−C separations as demonstrated, e.g., by the torsion angle B(11)−P−C(8′)−C(9′) −13.3(2)°. Also the C(8′)−P−B(11) angle shows at 94.92(14)°, a remarkable deviation from the ideal 108° in a regular pentagon. We were even able to localize the bridging N−H−N hydrogen in the cationic (PSH$^+$) part of the molecule, which is closer to one of the nitrogen atoms by 0.7454(3) Å than to the other.

Conclusions

The neutral compound 7,8,9-$PC_2B_8H_{11}$ (**2**) and its chlorinated derivative **10-Cl-2** can now easily be prepared by phosphorus insertion from the readily available 5,6-$C_2B_8H_{12}$ (**1**) dicarbaborane.[6] We have demonstrated that the constitution of **2** is analogous to that of the neutral tricarbollide 7,8,9-$C_2B_8H_{12}$ (**3**) as the bare P vertex is isolobal with the cage CH group. The bridging hydrogen atom in **2** can be removed by deprotonation to generate anion **2^-**. This anion is analogous to the Cp anion as it is monoanionic, contains a bare pentagonal face and would then be capable of donating five electrons for η^5-type complexation of suitable metal centers. This is also justified by similar electron densities in the linkages forming the PCCBB pentagon in terms of the Wiberg and natural bond orders. Indeed, recent experiments in our laboratories[12] point to facile formation of the isomeric (cyclopentadienyl)-ferraphosphadicarbaboranes of general formula $CpFePC_2B_8H_{10}$, analogues of ferrocene and the earlier reported[2] ferratricarbollides. Apart from extending metal complexation reactions of **2^-**, we are also exploring various

Table 2. Selected intracluster bond lengths [Å] and angles [°] for PSH$^+$[10-Cl-*nido*-7,8,9-PC$_2$B$_8$H$_9$]$^-$ (PSH$^+$**10-Cl-2**$^-$)

Cl−B(10)	1.844(3)	P−C(8′)	1.866(4)
P−B(2)	2.041(3)	P−B(3)	2.038(4)
P−B(11)	1.939(4)	B(1)−B(2)	1.767(5)
B(1)−B(3)	1.761(5)	B(1)−B(4)	1.791(5)
B(1)−B(5)	1.787(4)	B(1)−B(6)	1.800(5)
B(2)−B(3)	1.812(5)	B(2)−B(6)	1.776(4)
B(2)−B(11)	1.805(4)	B(3)−B(4)	1.830(5)
B(3)−C(8′)	1.740(4)	B(4)−B(5)	1.766(5)
B(4)−C(8′)	1.749(5)	B(4)−C(9′)	1.743(4)
B(5)−B(6)	1.748(5)	B(5)−C(9′)	1.729(5)
B(5)−B(10)	1.783(5)	B(6)−B(10)	1.787(4)
B(6)−B(11)	1.770(5)	C(8′)−C(9′)	1.517(4)
C(9′)−B(10)	1.596(5)	B(10)−B(11)	1.723(4)
C(8′)−P−B(11)	92.92(14)	C(8′)−P−B(3)	52.70(13)
B(11)−P−B(3)	95.44(14)	C(8′)−P−B(2)	90.93(14)
B(11)−P−B(2)	53.84(13)	B(3)−P−B(2)	52.74(14)
C(9′)−C(8′)−B(3)	112.6(2)	C(9′)−C(8′)−B(4)	64.1(2)
B(3)−C(8′)−B(4)	63.26(19)	C(9′)−C(8′)−P	113.4(2)
B(3)−C(8′)−P	68.72(17)	B(4)−C(8′)−P	123.7(2)
C(8′)−C(9′)−B(10)	113.9(3)	C(8′)−C(9′)−B(5)	113.1(2)
B(10)−C(9′)−B(5)	64.7(2)	C(8′)−C(9′)−B(4)	64.4(2)
B(10)−C(9′)−B(4)	116.8(2)	B(5)−C(9′)−B(4)	61.1(2)
C(9′)−B(10)−B(11)	109.8(2)	C(9′)−B(10)−B(5)	61.2(2)
B(11)−B(10)−B(5)	110.1(2)	C(9′)−B(10)−B(6)	106.4(2)
B(11)−B(10)−B(6)	60.55(18)	B(5)−B(10)−B(6)	58.61(18)
B(10)−B(11)−B(6)	61.51(18)	B(10)−B(11)−B(2)	106.3(2)
B(6)−B(11)−B(2)	59.56(18)	B(10)−B(11)−P	105.8(2)
B(6)−B(11)−P	114.4(2)	B(2)−B(11)−P	65.97(15)

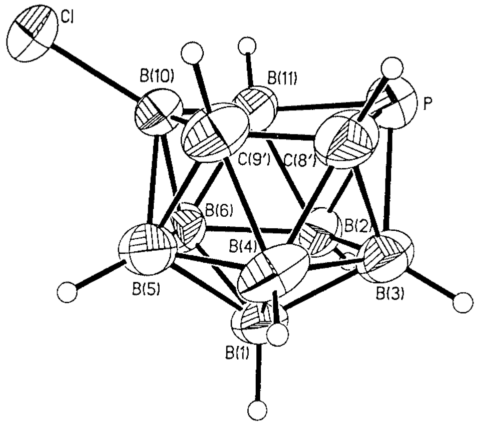


Figure 4. ORTEP representation of the crystallographically determined molecular structure of the [10-Cl-*nido*-7,8,9-PC$_2$B$_8$H$_9$]$^-$ (**10-Cl-2**$^-$) anion

isomerization and substitution reactions of the phosphadicarbaborane species outlined in this paper. Moreover, phosphorus insertion reactions with other borane and carborane compounds are also being studied with the aim of generating new types of chemically versatile heteroborane cages.

Experimental Section

General Procedures: All reactions were carried out with the use of standard vacuum or inert-gas techniques as described by Shriver,[13] although some operations, such as column LC, were carried out in air. The starting carborane **1** was prepared according to the literature.[6] Dichloromethane and hexane (both from Fluka) were dried with CaH$_2$ and freshly distilled before use. Other chemicals were reagent- or analytical grade and were used as purchased. Column chromatography was carried out using 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 diiodine vapor, followed by 2% aqueous AgNO$_3$ spray). Melting points were measured in sealed capillaries under argon 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). Proton (^{1}H) and boron (^{11}B), and phosphorus (^{31}P) NMR spectroscopy was performed at 11.75 and 5.88 Tesla with Varian XL-500, and ARX 250 instruments and the ^{13}C NMR spectra were measured with a Bruker DRX 500 spectrometer, equipped for heteronuclear ^{13}C{^{1}H,^{11}B} triple-resonance experiments. The [^{11}B-^{11}B]-COSY[14] and ^{1}H-{^{11}B(selective)}[15] NMR experiments were essentially as described in other related papers from our laboratories.[16] Chemical shifts are given in ppm to high frequency (low field) of Ξ = 32.083971 MHz (nominally F$_3$B·OEt$_2$ in CDCl$_3$) for ^{11}B (quoted ±0.5 ppm), Ξ = 25.144 MHz (SiMe$_4$) for ^{13}C (quoted ±0.5 ppm), Ξ = 40.4805 MHz (H$_3$PO$_3$) 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.[17] Solvent resonances were used as internal secondary standards. Coupling constants ^1J(^{11}B-^{1}H) are taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in Hz. The ^{11}B and ^{1}H NMR spectra of all phosphacarborane compounds discussed in this work can easily be assigned using two-dimensional [^{11}B-^{11}B]-COSY spectroscopy[14] combined with ^{1}H{^{11}B(selective)}[15] measurements. Moreover, all ^{1}H{^{11}B} resonances of individual BH and CH vertices adjacent to the cluster P vertex are spit into doublets due to $^2J_{PH}$ coupling, which helps all cluster resonances to be assigned. IR spectra were obtained with an EU 9512 Pye−Unicam Fourier transform spectrometer.

***nido*-7,8,9-PC$_2$B$_8$H$_{11}$ (2):** A solution of compound **1** (5.0 g, 40.2 mmol) in CH$_2$Cl$_2$ (50 mL) was cooled to 0 °C and treated with PS (10.0 g, 46.7 mmol) whilst stirring for 15 min. To this solution, PCl$_3$ (3.5 mL, 40.4 mmol) was added dropwise over a period of 15 min and the mixture was then stirred for 24 h at ambient temperature. The mixture was then cooled again to 0 °C and decomposed carefully with water (50 mL) whilst stirring. The CH$_2$Cl$_2$ layer was separated, the solvent evaporated and the residual materials were separated by chromatography on a silica gel column (30 × 2.5 cm) to collect a pure fraction of R_f = 0.22 which was identified by NMR spectroscopy as **2** (2.42 g, 39%). Crystallization of an analytical sample of **2** by slow concentration of a pentane solution. R_f (hexane) = 0.22; m.p. 260 °C. ^{11}B NMR (CDCl$_3$, ppm): δ = 5.7 (d, $^1J_{B-H}$ = 162 Hz, 1 B, B^5), 2.2 (d, $^1J_{B-H}$ = 158 Hz, 1 B, B^2), −12.8 (d, 1 B, B^4), −13.6 (d, $^1J_{B-\mu H}$ = 42 Hz, 1 B, B^{10}), −17.2 (d, 1 B, B^3), ca. −18.0 (d, 1 B, B^6), −18.3 (d, 1 B, B^{11}), −30.9 (d, $^1J_{B-H}$ = 158 Hz, 1 B, B^1), all theoretical [^{11}B-^{11}B]-COSY crosspeaks observed. ^{11}B NMR [calcd., GIAO-SCF/II/RMP2(fc)/6-31G*, ppm]: δ = 9.5 (B^5), 7.0 (B^2), −11.1 (B^4), −13.9 (B^{10}), −14.2 (B^3), −17.0 (B^6), −17.5 (B^{11}), −30.2 (B^1). ^{1}H{^{11}B} NMR (CDCl$_3$, ppm): δ = 3.22 (s, 1 H, H^9), 3.02 (d, $^2J_{P-H}$ = 17 Hz, 1 H, H^8),. 2.96 (s, 1 H, H^5), 2.68 (d, $^2J_{P-H}$ = 23 Hz, 1 H, H^2), 2.35 (d, $^2J_{P-H}$ = 23 Hz, 1 H, H^3), 2.34 (s, 1 H, H^4),. 2.29 (s, 1 H, H^{10}), 1.88 (s, 1 H, H^1), 1.73 (s, 1 H, H^{11}), 1.72 (s, 1 H, H^6), −2.73 (q, $^2J_{H-H}$ = 12 Hz, 1 H, μH^{10,11}). ^{13}C{^{1}H} NMR (CDCl$_3$, ppm): δ =

63.3 (d, $^1J_{P-C}$ = 72 Hz, 1 C, C^8), 53.4 (s, 1 C, C^9). ^{13}C NMR [calcd., GIAO-SCF/II/RMP2(fc)/6-31G*, ppm]: δ = 58.3 (C^8), 44.8 (C^9). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ = −60.1 (s, 1 P, P^7). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2926 (C−H), 2576 (B−H). MS (70 eV, EI): *m*/*z* (%) = 154 (9) [M]$^+$, 150 (100) [M − 4 H]$^+$; elemental analysis: calcd. (%) for $C_2H_{11}B_8P$ (152.64): B 56.71, found B 55.11.

10-Cl-*nido*-7,8,9-PC$_2$B$_8$H$_{10}$ (10-Cl-2): To a solution of **1** (2.00 g, 16.1 mmol) in CH_2Cl_2 (40 mL) was added PS (7.00 g, 32.7 mmol), followed by dropwise addition of PCl_3 (5 mL, 57.7 mmol) whilst stirring and cooling to 0 °C. The mixture was then stirred at ambient temperature for 24 h and carefully treated with water (50 mL) at 0 °C and the CH_2Cl_2 layer was concentrated to dryness. The residual solid was then separated by LC on a silica gel column (2.5 × 35 cm) using hexane as a mobile phase to collect three pure fractions of R_f (hexane) = 0.22, 0.13, and 0.07 which were concentrated to dryness and identified by ^{11}B NMR spectroscopy as **2** (130 mg, 5%), 1,2-$C_2B_8H_{10}$ (125 mg, 6%), and **10-Cl-2** (910 mg, 30%), respectively. Crystallization of **10-Cl-2** by slow concentration of a pentane solution gave an analytically pure sample. R_f (hexane) = 0.07; m.p. 150 °C. ^{11}B NMR (CDCl$_3$, ppm): δ = 7.8 (d, $^1J_{B-H}$ = 165 Hz, 1 B, B^5), −0.4 (d, $^1J_{B-H}$ = 154 Hz, 1 B, B^2), −2.2 (s, 1B, B^{10}), −13.1 (d, $^1J_{B-\mu H}$ = 177 Hz, 1 B, B^4), −16.9 (d, $^1J_{B-H}$ = 154 Hz, 1 B, B^6), ca. −19.9 (d, $^1J_{B-H}$ = 158 Hz, 1 B, B^{11}), −22.8 (d, $^1J_{B-H}$ = 173 Hz, 1 B, B^3), −31.2 (d, $^1J_{B-H}$ = 154 Hz, 1 B, B^1), all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed. ^{11}B NMR [calcd., GIAO-SCF/II/RMP2(fc)/6-31G*, ppm]: δ = 11.4 (B^5), 4.9 (B^2), −2.0 (B^{10}), −11.7 (B^4), −15.5 (B^6), −18.5 (B^3), −18.8 (B^{11}), −30.7 (B^1). ^{1}H{^{11}B} NMR (CDCl$_3$, ppm): δ = 3.48 (s, 1 H, H^9), 3.35 (s, 1 H, H^5), 2.96 (d, $^2J_{P-H}$ = 28 Hz, 1 H, H^8), 2.61 (d, $^2J_{P-H}$ = 21 Hz, 1 H, H^2), 2.39 (s, 1 H, H^4), 2.20 (d, $^2J_{P-H}$ = 14 Hz, 1 H, H^3), 1.98 (s, 1 H, H^6), 1.85 (d, $^2J_{P-H}$ = 55 Hz, 1 H, H^{11}), 1.80 (s, 1 H, H^1), −1.12 (q, $^2J_{H-H}$ = 9 Hz, 1 H, μH^{10,11}). ^{13}C{^{1}H} NMR (CDCl$_3$, ppm): δ = 61.5 (d, $^1J_{P-C}$ = 72 Hz, 1 C, C^8), 54.6 (q, $^1J_{C-B}$ ≈ 33 Hz, 1 C, C^9). ^{13}C NMR [calcd., GIAO-SCF/II/RMP2(fc)/6-31G*, ppm]: δ = 56.1 (C^8), 47.6 (C^9). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ = −67.7 (s, 1 P, P^7). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2932 (C−H), 2581 (B−H). MS (70 eV, EI), *m*/*z* (%) = 189 (5) [M]$^+$, 185 (100) [M − 4 H]$^+$. $C_2H_{10}B_8ClP$ (187.13): calcd. B 46.26; found B 45.12.

PSH$^+$[*nido*-7,8,9-PC$_2$B$_8$H$_{10}$]$^-$ (PSH$^+$2$^-$): To a solution of **2** (129 mg, 0.85 mmol) in CH_2Cl_2 (10 mL) was added PS (193 mg, 0.9 mmol) whilst stirring and cooling to 0 °C. Onto the surface of the solution, a layer of hexane (20 mL) was carefully added and the mixture was left to crystallize for 48 h. The colorless crystals were then isolated by filtration, washed with hexane, and vacuum-dried at room temperature to give PSH$^+$**2**$^-$ (290 mg, 93%). Crystallization of an analytical sample was achieved by diffusion of pentane vapors into a CH_2Cl_2 solution. R_f (CH_2Cl_2) = 0.1; m.p. 230 °C. ^{11}B NMR (CDCl$_3$, ppm): δ = −8.0 (d, 1 B, B^6), −8.3 (d, 1 B, B^{10}), −13.6 (d, 1 B, B^{11}), −14.4 (d, $^1J_{B-H}$ ≈ 150 Hz, 1 B, B^{10}), −15.5 (d, $^1J_{B-H}$ ≈ 165 Hz, 1 B, B^4), −19.0 (d, $^1J_{B-H}$ = 143 Hz, 1 B, B^2), −20.9 (d, $^1J_{B-H}$ = 158 Hz, 1 B, B^3), −41.1 (d, $^1J_{B-H}$ = 142 Hz, 1 B, B^1), all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed. ^{11}B NMR [calcd., GIAO-SCF/II/RMP2(fc)/6-31G*, ppm]: δ = −3.7 (B^6), −10.4 (B^{10}), −13.8 (B^5), −14.4 (B^{11}), −14.7 (B^4), −17.5 (B^2), −19.6 (B^3), −42.7 (B^1). ^{1}H{^{11}B} NMR (CDCl$_3$, ppm): δ = 2.16 (d, $^2J_{P-H}$ = 10 Hz, 1 H, H^3), 2.15 (s, 1 H, H^6), 2.13 (s, 1 H, H^4), 2.03 (s, 1 H, H^9), 1.81 (s, 1 H, H^5), 1.80 (s, 1 H, H^{10}), 1.46 (d, $^2J_{P-H}$ = 30 Hz, 1 H, H^8), 1.18 (d, $^2J_{P-H}$ = 40 Hz, 1 H, H^{11}), 1.18 (d, $^2J_{P-H}$ = 20 Hz, 1 H, H^2), 1.02 (s, 1 H, H^1). ^{13}C{^{11}B,^{1}H} NMR (CD$_3$CN, ppm): δ = 44.1 (s, 1 C, C^9), 35.4 (d, $^1J_{C-P}$ = 55 Hz, 1 C, C^8). ^{13}C{^{11}B} NMR (CD$_3$CN, ppm): δ = 44.1 (d, $^1J_{C-H}$ = 162 Hz, 1 C, C^9), 35.4 (dd, $^1J_{C-H}$ = 169, $^1J_{C-P}$ ≈ 60 Hz, 1 C, C^8). ^{13}C NMR [calcd., GIAO-SCF/II/RMP2(fc)/6-31G*, ppm]: δ = 38.2 (C^9), 28.6 (C^8). ^{31}P{^{1}H} NMR (CD$_3$CN, ppm): δ = −91.0 (s, 1 P, P^7). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2574 (B−H). $C_{16}H_{29}B_8N_2P$ (366.95): calcd. B 23.59; found B 22.70.

PSH$^+$[10-Cl-*nido*-7,8,9-PC$_2$B$_8$H$_9$]$^-$ (PSH$^+$10-Cl-2$^-$): To a solution of **10-Cl-2** (200 mg, 1.1 mmol) in hexane (20 mL), a solution of PS (300 mg, 1.4 mmol) in hexane was added whilst stirring and cooling to 0 °C. The colorless crystals that deposited were filtered, washed with hexane, and vacuum dried at room temperature to give PSH$^+$**10-Cl-2**$^-$ (390 mg, 91%). Crystallization of an analytical sample by diffusion of pentane vapors into a CH_2Cl_2 solution. R_f (CH_2Cl_2) = 0.04; m.p. 155 °C. ^{11}B NMR (CD$_3$CN, ppm): δ = 3.0 (s, 1 B, B^{10}), −7.3 (d, $^1J_{B-H}$ = 138 Hz, 1B, B^6), −11.8 (d, $^1J_{B-H}$ = 147 Hz, 1B, B^5), −16.4 (d, 1B, B^{11}),−17.2 (d, $^1J_{B-H}$ ≈ 165 Hz, 1 B, B^4), −20.8 (d, $^1J_{B-H}$ = 142 Hz, 1 B, B^2), −25.6 (d, $^1J_{B-H}$ = 154 Hz, 1 B, B^3), −42.2 (d, $^1J_{B-H}$ = 139 Hz, 1 B, B^1), all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed. ^{11}B NMR [calcd., GIAO-SCF/II/RMP2(fc)/6-31G*, ppm]: δ = 3.0 (B^{10}), −2.3 (B^6), −10.3 (B^5), −15.8 (B^{11}), −16.1 (B^4), −18.8 (B^2), −22.8 (B^3), −43.2 (B^1). ^{1}H{^{11}B} NMR (CD$_3$CN, ppm): δ = 1.91 (s, 1 H, H^6), 1.84 (s, 1 H, H^4), 1.69 (s, 1 H, H^9), 1.64 (s, 1 H, H^5), 1.54 (d, $^2J_{P-H}$ = 32 Hz, 1 H, H^{11}), 1.80 (s, 1 H, H^{10}), 1.14 (d, $^2J_{P-H}$ = 32 Hz, 1 H, H^8), 0.78 (d, $^2J_{P-H}$ = 40 Hz, 1 H, H^2), 0.60 (d, $^2J_{P-H}$ = 20 Hz, 1 H, H^3), 0.44 (s, 1 H, H^1). ^{13}C{^{11}B,^{1}H} NMR (CD$_3$CN, ppm): δ = 44.8 (s, 1 C, C^9), 33.0 (d, $^1J_{C-P}$ = 56 Hz, 1 C, C^8). ^{13}C{^{11}B} NMR (CD$_3$CN, ppm): δ = 44.8 (d, $^1J_{C-H}$ = 163 Hz, 1 C, C^9), 33.0 (dd, $^1J_{C-H}$ = 170, $^1J_{C-P}$ = 56 Hz, 1 C, C^8). ^{13}C NMR [calcd., GIAO-SCF/II/RMP2(fc)/6-31G*, ppm]: δ = 40.0 (C^9), 26.0 (C^8). ^{31}P{^{1}H} NMR (CD$_3$CN, ppm): δ = −91.0 (s, 1 P, P^7). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2579 (B−H). $C_{16}H_{28}B_8ClN_2P$ (401.44): calcd. B 21.56; found B 19.90.

X-ray Crystallography: A colorless crystal of PSH$^+$**10-Cl-2**$^-$ of dimensions 0.30 × 0.21 × 0.18 mm was sealed into a glass capillary under argon and measured with a Siemens P4 four-circle diffractometer at 293(2) K with Mo-K_α radiation (graphite monochromator). The crystallographic details are summarized in Table 3 and selected interatomic distances are listed in Table 2. The structure was solved by the direct methods and refined by a full-matrix least-squares procedure based on F^2 (SHELXLTL V.5.1: G. M. Sheldrick, program package SHELXTL, Göttingen). The absorption was neglected. Hydrogen atoms were localized on a difference Fourier map and refined isotropically. The final difference map had no peaks of chemical significance. Scattering factors were those implemented in the SHELXLTL V.5.1 programs. CCDC-175954 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: Geometry optimizations and frequency calculations employed standard ab initio methods incorporated[18] in the Gaussian94 suite of programs[19] and were performed with the Power Challenge XL computer of the Supercomputing Center of the Charles University in Prague. This program package also enabled us to compute both the Wiberg bond indices (WBI),[20] overlap-weighted natural atomic orbital (NAO) bond orders[21] and the chemical shifts, the latter being calculated at an SCF level using the GIAO (gauge-invariant atomic orbital) method and employing a II Huzinaga basis set[22] well-proven for the calculations of shielding tensors.[23]

Table 3. Crystal data and structure refinement for PSH$^+$ [10-Cl-*nido*-7,8,9-PC$_2$B$_8$H$_9$]$^-$ (PSH$^+$**10-Cl-2**$^-$)

Empirical formula	$C_{16}H_{28}B_8ClN_2P$
M_r	401.30
λ [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	6.4573(4)
b [Å]	24.5282(17)
c [Å]	13.8020(9)
β [°]	94.626
V [Å^3]	2178.9(2)
Z	4
$\rho_{calcd.}$ [Mg/m^3]	1.223
μ [mm^{-1}]	0.254
F(000)	840
θ range [°]	2.22−24.99
h,*k*,*l* collected	$-1 \leq h \leq 7$, $-1 \leq k \leq 29$, $-16 \leq l \leq 16$
No. of reflections collected	5131
No. of independent reflections	3806 [*R*(int) = 0.0336]
Completeness to θ = 24.99° [%]	99.0
Data/restraints/parameters	3806/0/246
GoF on F^2	1.020
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0502$, $wR2 = 0.1391$
R indices (all data)	$R1 = 0.0701$, $wR2 = 0.1531$
Extinction coefficient	0.0046(14)
max/min Δρ [e·Å^{-3}]	0.358/−0.345

Acknowledgments

This work was supported by the Alexander von Humboldt Stiftung (FRG) (B. S.), the Deutsche Forschungsgemeinschaft (B. W., O. L. T.), the Fonds der Chemischen Industrie (B. W.), the Ministry of Education of Czech Republic (project no. LN00A028). We also thank the Grant Agency of the Charles University (grant no. 203/00/B-CH/PrF) and the Supercomputing Center of the Charles University in Prague for granting computer time, and Drs. J. Fusek, Z. Plzák, and E. Vecerníková for partial NMR-spectroscopic measurements, mass and IR spectra.

---

[1] [1a] L. J. Todd, in: *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. Abel), Pergamon, **1982**, part I, chapter 5.6, pp. 543−553. [1b] L. J. Todd, in: *Metal Interactions with Boron Clusters* (Ed.: R. N. Grimes), Plenum, New York, **1982**, pp. 145−171.

[2] [2a] B. Štíbr, *Chem. Rev.* **1992**, *92*, 225−250, and references therein. [2b] B. Stíbr, J. Holub, F. Teixidor, in: *Advances in Boron Chemistry* (Ed.: W. Siebert), Royal Society of Chemistry, Cambridge, **1997**, pp. 333−340.

[3] J. Holub, D. L. Ormsby, J. D. Kennedy, R. Greatrex, B. Štíbr, *Inorg. Chem. Commun.* **2000**, *3*, 178−181.

[4] [4a] B. Štíbr, J. Holub, F. Teixidor, C. Vinňas, *J. Chem. Soc., Chem. Commun.* **1995**, 795−796. [4b] J. Holub, B. Štíbr, D. Hnyk, J. Fusek, I. Císařová, F. Teixidor, C. Viňas, Z. Plzák, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1997**, *119*, 7750−7759.

[5] M. Shedlow, L. G. Sneddon, *Inorg. Chem.* **1998**, *37*, 5269−5277.

[6] B. Štíbr, J. Holub, T. Jelínek, B. Grüner, J. Fusek, Z. Plzák, F. Teixidor, C. Viňas, J. D. Kennedy, *Collect. Czech. Chem. Commun.* **1997**, *62*, 1229−1238.

[7] J. Holub, T. Jelínek, D. Hnyk, Z. Plzák, I. Císařová, M. Bakardjiev, B. Štíbr, *Chem. Eur. J.* **2001**, *7*, 1546−1554.

[8] J. J. Ott, B. M. Gimarc, *J. Am. Chem. Soc.* **1986**, *108*, 4303−4308.

[9] M. Bühl, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1992**, *114*, 477−491.

[10] D. Hnyk, M. Hofmann, P. v. R. Schleyer, M. Bühl, D. W. H. Rankin, *J. Phys. Chem.* **1996**, *100*, 3435−3440.

[11] B. Grüner, D. Hnyk, I. Císarová, Z. Plzák, B. Stíbr, *J. Chem. Soc., Dalton Trans.*, submitted for publication.

[12] J. Holub, B. Stíbr, M. Bakardjiev, I. Císarová, O. L. Tok, B. Wrackmeyer, *Abstracts of the 2nd European Symposium on Boron Chemistry (EUROBORON 2)*, Dinard (France), 2.−6.9.**2001**, O18.

[13] D. F. Shriver, M. A. Drezdon, *Manipulation of Air Sensitive compounds*, 2nd ed., Wiley, New York, **1986**.

[14] [14a] J. D. Kennedy, in: *Multinuclear N. M. R.* (Ed.: J. Mason), Plenum Press, New York, **1987**, p. 221. [14b] W. C. Hutton, T. L. Venable, R. N. Grimes, *J. Am. Chem. Soc.* **1984**, *106*, 29−37. [14c] Schraml, J. M. Bellama, *Two-Dimensional NMR Spectroscopy*, Wiley, New York, **1982**.

[15] X. L. R. Fontaine, J. D. Kennedy, *J. Chem. Soc., Dalton Trans.* **1987**, 1573.

[16] J. Plešek, B. Štíbr, X. L. R. Fontaine, J. D. Kennedy, S. Heřmánek, T. Jelínek, *Collect. Czech. Chem. Commun.* **1991**, *56*, 1618−1635.

[17] W. McFarlane, *Proc. R. Soc. London, Ser. A* **1968**, *306*, 185.

[18] W. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab initio Molecular Orbital Theory*, Wiley, New York, **1986**.

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zahrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkra, M. Challacombe, C. Y. Peng, P. Y. Ayala, Y. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomprets, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, L. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, J. A. Pople, *Gaussian94*, Revision B.2. Gaussian Inc., Pittsburg, PA, **1995**.

[20] K. Wiberg, *Tetrahedron* **1968**, *24*, 325.

[21] [21a] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Phys. Chem.* **1985**, *83*, 735. [21b] A. E. Reed, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899. [21c] A. E. Reed, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 1434.

[22] S. Huzinaga, *Approximate Atomic Wave Functions*, University of Alberta, Edmonton, Canada, **1971**.

[23] W. Kutzelnigg, M. Schindler, U. Fleischer, *NMR, Basic Principles and Progress*, Springer-Verlag, Berlin, New York, **1990**; vol. 23.

Received March 14, 2002
[I02133]