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Phosphine–boranes incorporating the carborane cluster

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Abstract

The high stability of the *closo*-carboranylmonophosphines and the low basicity and nucleophilicity are attributed to the electron-withdrawing character of the *closo* cluster. On the contrary, the *nido* cluster has an electron-donor character, which induces high electronic density on the phosphorus atom, then increasing the basicity and nucleophilicity of these ligands. In this way, the *nido*-carboranylmonophosphines react with ethanol to give the *tertiary* phosphonium salts and are readily oxidized by air in solution. They readily react with transition metals to form the corresponding metallacarboranes. To learn more of the distinct behavior of the *closo*-and *nido*-carboranylmonophosphines, the reaction of some of them with the $BH_3 \cdot THF$ Lewis acid has been carried out. In this communication, we report the reaction of *closo*- and *nido*-carboranylmonophosphines with $BH_3 \cdot THF$ leading to the formation of new phosphine–borane adducts. In the case of the *nido*-carboranylmonophosphines, all of them have shown a similar behavior irrespective of the nature of the R and R′ groups. However, the *closo*-carboranylmonophosphines have demonstrated to be less basic and only one of them has been able to form the corresponding phosphine–borane adduct. The crystal structure of $[NBu_4]^+[7\text{-}P^iPr_2 \cdot BH_3\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}]^-$ has also been described. The coordination chemical shift (**ccs**) has been calculated and a relation established between the coupling constants (^{11}B–^{1}H and ^{31}P–^{11}B) obtained by the $^{11}B\{^1H\}$- and $^{31}P\{^1H\}$-NMR and the Lewis basicity of the phosphines. © 2002 Published by Elsevier Science B.V.

Keywords: *Nido*-carboranylphosphines; Lewis basicity of the phosphines; *Tertiary* phosphonium salts

1. Introduction

The different reactivity of *closo* and *nido*-carboranylmonophosphines towards metal ions motivated us to know further their differences comparing their basicity and nucleophilicity [1]. The *nido*-derivatives $[NMe_4][7\text{-}PR_2\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]$ (R = Ph, Et, ^{i}Pr; R′ = Me, Ph) react with ethanol or acids to give the tertiary phosphonium salts, they are readily oxidized by air in solution and react with metallic complexes to give metallacarborane compounds. In contrast, the *closo*-carboranylmonophosphines do not react with ethanol, acids or metal complexes and are very stable in solid state and in solution [2]. Besides, the latter react with iodine to form charge transfer complexes or zwitterionic species depending on the solvent used [3]. To complete the study, we have compared their behavior towards a Lewis acid such as $BH_3 \cdot THF$. It is well known that the phosphine–boranes show peculiar chemical properties such as their inertness towards oxygen, moisture and even sometimes to strong acids and bases, which has been attributed to the low polarity and polarizability of the P–B and B–H bonds [4]. This stability has permitted to use borane complexation as a temporary protection or activation of the Lewis base [5]. The phosphine–boranes have been used as hydroboration agents, [6] reagents in organic synthesis as for radical reactions, [7] and precursors for synthesis of chiral phosphines for asymmetric catalysis [8]. Taking into account that $PR_3 \cdot BH_3$ adducts are isoelectronic with $[BH_4]^-$ and with methane, they have also been used in organometallic chemistry for the preparation of complexes containing an B–H–M bond (M = Cr, Mo, W) [9].

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2. Results

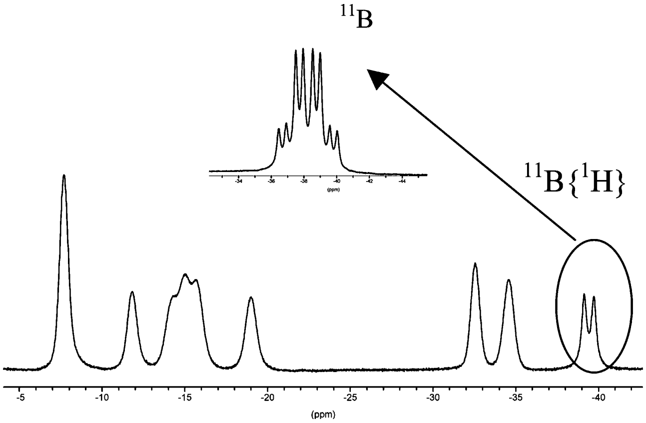
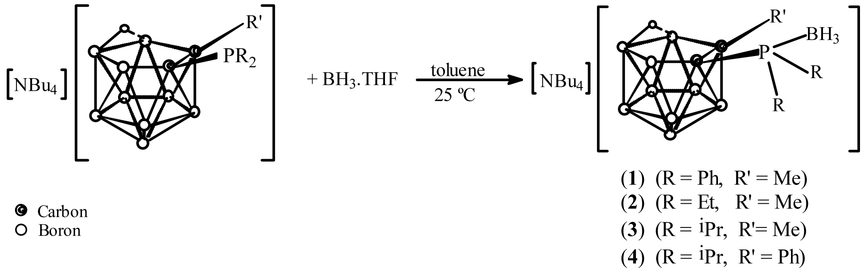


Fig. 1. $^{11}B\{^1H\}$-NMR and fragment of the ^{11}B spectrum of compound (**3**).

The reaction of the *nido*-carboranylmonophosphines $[NBu_4][7\text{-}PR_2\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]$ with $BH_3{\cdot}THF$ in a 1:2.5 ratio in toluene for 16 h at room temperature produces, in high yield, the corresponding *nido*-carboranylmonophosphine–borane adducts $[NBu_4]^+[7\text{-}PR_2{\cdot}BH_3\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = Ph, Et, ^{i}Pr; R′ = Me) (**1**), (**2**), (**3**) and (R = ^{i}Pr, R′ = Ph) (**4**). The general reaction is shown in Scheme 1. The spectroscopic data and elemental analysis are consistent with the proposed formula. The IR spectra of these complexes display ν(B–H) absorptions between 2520 and 2550 cm^{-1}, which are characteristic of *nido* $[7,8\text{-}C_2B_9H_{12}]^-$ derivatives. Generally, B–H bond stretching frequencies for the BH_3 group in phosphine–boranes, are displayed as a strong absorption between 2450 and 2350 cm^{-1}, and a shoulder at 2380–2330 cm^{-1}. The exact frequency depends on the nature of the substituents on phosphorous [5a] In the compounds reported here, bands between 2390 and 2330 indicate the presence of the BH_3 group. The ^1H-NMR spectra display broad resonances in the negative region around −2.0 ppm corresponding to the bridging hydrogen B–H–B, which are very close to those observed for the free ligands, which appear between −2.2 and −2.3 ppm. The existence of this B–H–B evidences the presence of the *nido* cluster. A broad quartet between 0.5 and 1.5 ppm assigned to BH_3 and due to ^{11}B–^1H coupling is also observed. It is sharpened into a doublet in the $^1H\{^{11}B\}$-NMR spectra, due to the ^{31}P–^1H coupling (between 13 and 20 Hz) depending on the compound, which is similar to those observed in other phosphine–borane complexes [10]. The $^{13}C\{^1H\}$-NMR spectra display resonances that exhibit phosphorous coupling, typically with the largest J(P, C) near 35 Hz, for the carbon atom directly bonded to the phosphorous. The coupling constants are somewhat larger than those observed for the free ligand, consistent with the four-coordination of the P atoms [11]. The $^{11}B\{^1H\}$-NMR spectra patterns indicate the presence of ten boron atoms in the molecule for all compounds. Fig. 1 shows the $^{11}B\{^1H\}$-NMR and a fragment of the ^{11}B-NMR spectra of (**3**). The $^{11}B\{^1H\}$ pattern is 2:1:1:1:1:1:1:1:1, in which the highest field resonance at −39.4 ppm is split into a doublet due to the ^{31}P–^{11}B coupling (^1J(P, B) = 58 Hz). This signal is converted into a quartet of doublets in the ^{11}B-NMR, due to both the ^{11}B–^1H coupling (^1J(B, H) = 92 Hz) and the ^{31}P–^{11}B coupling (^1J(P, B) = 58 Hz). The absorption corresponding to the BH_3 group is found in the same region for all compounds (−35 ± 5 ppm) (Table 1), a position common in other phosphine–borane adducts $(PR_3{\cdot}BH_3)$ [11,12]. For compound (**1**) the coupling constants with other nucleus was not calculated, because, it was overlapped with resonances corresponding to the B(1) and B(10). The $^{31}P\{^1H\}$-NMR spectra of these compounds displayed only one signal. The $^{31}P\{^1H\}$-NMR spectrum of (**2**) is presented in Fig. 2, as an example, in which a quartet shaped resonance is observed with a coupling constant ^1J(P, B) = 60 Hz. For the other compounds, the $^{31}P\{^1H\}$-NMR shows a not so-well defined doublet attributed to the J coupling

Table 1
^1H, $^{11}B\{^1H\}$ chemical shift (in ppm) and coupling constants between the P and H atoms in absolute values (in Hz) for the BH_3 group

Compounds	δ^1H	$\delta^{11}B$	^1J(B, H)
(**1**)	1.15	−33.8	–
(**2**)	0.54	−36.9	96
(**3**)	0.46	−39.4	92
(**4**)	0.49	−38.5	95
(**5**)	0.72	−38.3	100



Scheme 1. General reaction for preparing *nido*-carboranylphosphine–borane adducts (**1**–**4**) using $BH_3{\cdot}THF$.

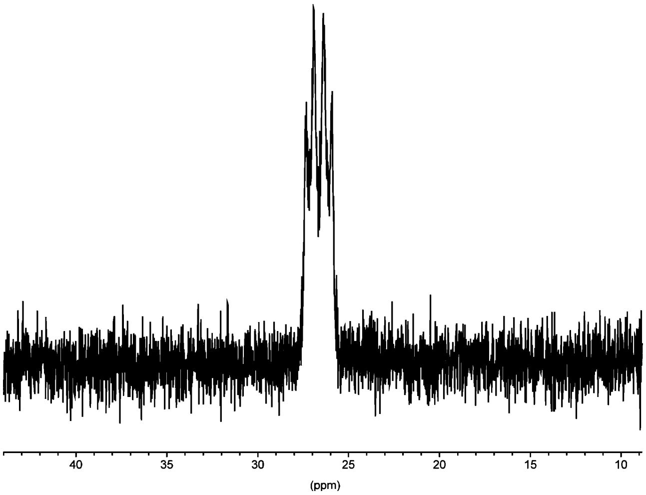


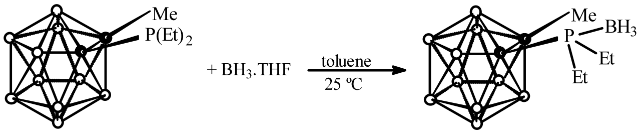
Fig. 2. $^{31}P\{^1H\}$-NMR spectrum of compound (**2**).

between ^{31}P and ^{11}B, identical to those observed in the respective $^{11}B\{^1H\}$-NMR spectra (see Table 2). All these data support the formation of the B–P bond.

As a matter of comparison the same studies were conducted with *closo*-carboranylphosphines ($1-PR_2-2-R'-1,2-C_2B_{10}H_{10}$) (see Scheme 2). The results were, however, completely different in evidencing the dissimilarity between *closo* and *nido*-carboranylmonophosphines. In only one case, for R = Et and R′ = Me the reaction with $BH_3 \cdot THF$ took place yielding compound **5**. In all other cases, the unreacted starting *closo* was recovered. The ^1H-NMR spectrum of **5** displayed a broad quartet due to $^{11}B-^1H$ coupling, corresponding to the BH_3 group, which sharpened into a doublet at 0.72 ppm ($^3J(P, H) = 13.4$ Hz) in the $^1H\{^{11}B\}$-NMR. No major chemical shift discrepancy was observed with regard to the corresponding *nido*-carboranylmonophosphine–borane adducts. The rest of the spectrum was very similar to the free carboranylphosphine. The $^{11}B\{^1H\}$-NMR spectrum shows a pattern of 1:1:6:2 in the *closo*-cluster region from 0 to −15 ppm, and an additional doublet, due to the $^{31}P-^{11}B$ coupling ($^1J(P, B) = 43$ Hz) (Table 2), of global intensity 1 is observed at −38.3 ppm that corresponds to the BH_3 group. In the ^{11}B-NMR, it is converted in a quartet of doublets due to the $^{11}B-^1H$ coupling ($^1J(B, H) = 100$ Hz) (Table 1). A quartet is also observed in the $^{31}P\{^1H\}$ NMR spectrum with the same $^1J(P, B)$ to that observed in the $^{11}B\{^1H\}$-NMR.

Table 2
Coupling constants between the P and B atoms in absolute values (in Hz)

Compounds	$\delta^{31}P$	$^3J(P, H)$	$^1J(P, B)$
(1)	27.47	14.5	63
(2)	27.75	13.8	60
(3)	42.46	13.8	56
(4)	45.40	14.2	55
(5)	47.12	18.0	43



Scheme 2. General reaction for preparing the *closo*-carboranylphosphine–borane adduct (**5**) using $BH_3 \cdot THF$.

To confirm the formation of the carboranylmonophosphine–borane adducts some colourless crystals of **3**, suitable for the X-ray diffraction, were isolated from a solution 1:1 of CH_2Cl_2–diethyl ether at room temperature. Asymmetric unit of the structure of **3** consists of two *nido*-carboranylmonophosphine–borane adducts (anions **A** and **B**) and two $[N(Bu)_4]^+$ ions. Selected bond lengths and angles for **3** are listed in Table 4 and a drawing of anion **A** is shown in Fig. 3. The anions are ca. mirror images of each other. In each anion the P1–B13 bond is ca. parallel with the C8–C12 bond and the bridging hydrogen atom is connected to B10 and B9. Corresponding bond parameters of the anions are very similar, almost all of them being equal within experimental errors. The C7–C8 distances of 1.592(3) and 1.594(3) Å, for **A** and **B,** fall in the range found for the *nido*-carboranes but the P1–B13 bonds of 1.946(3) and 1.948(3) Å are slightly longer than comparable P–B distances for teminal BH_3 groups in $dppf(BH_3)_2$ [1.922(4) Å] [11] and $Ph_2PH(BH_2)PPh_2 \cdot BH_3$ [1.932(2) Å] [12c]. Bond angles around phosphorous atoms vary from *ca*. 103 to 122° (*cf*. Table 4). Opening of the C7–P1–B13 angles to ca. 122° possibly originates of the need to avoid close contact between the BH_3 group and the CH_3 group at C12.

The bond parameters of the $[N(Bu)_4]^+$ ions are normal and do not need any comment.

3. Discussion

The H_3B–P generation causes a modification of the ^{31}P chemical shift with respect to the free ligand. The

Table 3
^{31}P chemical shifts (in ppm) for the starting *closo* and *nido*-carboranylphosphines and the corresponding carboranylphosphine–boranes, including the **ccs**

Carboranylphosphine	$\delta^{31}P\{^1H\}$		
	Free	Adduct	ccs
$[7-PPh_2-8-Me-7,8-C_2B_9H_{10}]^-$	12.79	27.47	14.68
$[7-PEt_2-8-Me-7,8-C_2B_9H_{10}]^-$	−8.29	27.75	36.04
$[7-P^iPr_2-8-Me-7,8-C_2B_9H_{10}]^-$	15.73	42.46	26.73
$[7-P^iPr_2-8-Ph-7,8-C_2B_9H_{10}]^-$	16.86	45.40	29.34
$1-PEt_2-2-Me-1,2-C_2B_{10}H_{10}$	5.37	47.12	41.75

Table 4
Selected bond lengths (Å) and angles (°) for compound (**3**)

Anion	**A**	**B**
Bond lengths		
P1–C7	1.844(2)	1.843(2)
P1–B13	1.946(3)	1.948(3)
P1–C14	1.843(2)	1.843(2)
P1–C17	1.841(3)	1.847(3)
C7–C8	1.592(3)	1.594(3)
C7–B11	1.625(3)	1.621(4)
C8–B9	1.622(4)	1.621(4)
C8–C12	1.515(3)	1.511(4)
B9–B10	1.848(5)	1.837(5)
B10-B11	1.811(4)	1.817(4)
Bond angles		
C7–P1–B13	122.37(13)	121.78(12)
C7–P1–C14	103.64(10)	103.36(11)
C7–P1–C17	103.41(11)	103.71(11)
B13–P1–C14	108.81(14)	109.19(13)
B13–P1–C17	110.26(15)	110.58(14)
C14–P1–C17	107.36(11)	107.21(12)

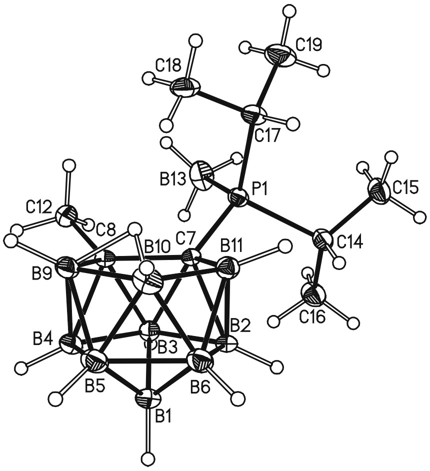


Fig. 3. Perspective drawing of anion **A** of compound (**3**).

difference between the chemical shift of the free phosphine and the chemical shift of its borane adduct is known as coordination chemical shift (**ccs**) [13] which is dependent on the nature of the phosphorus substituents. In general, trialkyl- and triarylphosphines complexation with borane ($PhMe_2P \cdot BH_3$, $Me_3P \cdot BH_3$, $Me_2HP \cdot BH_3$, etc) results in a rather strong deshielding (**ccs** = 95–133 ppm) [10]. A **ccs** deshielding is also found upon the adduct formation between the *nido*-carboranylmonophosphine and BH_3. It is, however, smaller and between 14 and 36 ppm (see Table 3) comparable to the **ccs** (31 ppm) found for PPh_3 [14]. Contrarily, the **ccs** found for the unique *closo*-carboranylmonophosphine–borane adduct is slightly larger (42 ppm).

3.1. Can the small **ccs** found in nido-carboranylmonophosphine–borane be rationalized?

The *nido*-carboranylmonophosphines are comparatively better coordinating ligands than organic phosphines, in the same way as *nido*-carboranylthioethers are better than organic thioethers. Based on this assumption, and considering that **ccs** has been taken as an indication of coordinating ability, it is highly surprising that **ccs** for *nido*-carboranylmonophosphines are smaller than **ccs** for common organic phosphines.

We have found two possible explanations for this, a priori, discordant result. The first makes use of only the σ_d component of the shielding constant. If coordination of P to B is considered, as a first approach, independent of the third ligand (R), a low field shift due to **ccs** is expected. Upon the coordination a partial positive charge on phosphorus is generated. Considering the capacity of the *nido*-carboranyl cluster to dissipate the negative charge on the substituent on C(cage), a charge neutralization will take place, which would not take place with neutral R groups, therefore, shielding in some extent the P and shifting it upfield, overall producing a smaller **ccs** (see Fig. 4).

The second explanation that can be complementary to the former one makes use of the σ_p term. It considers that this is largely influenced by the *nido*-cage, thus shifting the ^{31}P-NMR chemical shifts to lower field. This is in agreement with experimental evidence. For instance, the ^{31}P-NMR chemical shifts of two conceptually similar monophosphines $Ph_2P–Ph$ and $[7\text{-}Ph_2P\text{-}7,8\text{-}C_2B_9H_{11}]^-$ are found at −8 and 12.79 ppm, respectively. As a consequence, the chemical shift position of the free *nido*-carboranylphosphines should be artificially modified to remove the σ_p contribution, then making the starting points of the *nido*-carboranylmonophosphines and conventional phosphines comparable. The large σ_p contribution is what causes the large **ccs** upon coordination to BH_3.

3.2. The J(B, H) coupling and the P–B strength

It has also been reported that the ^1J(B, H) values are related to the electronegativity of the phosphorous

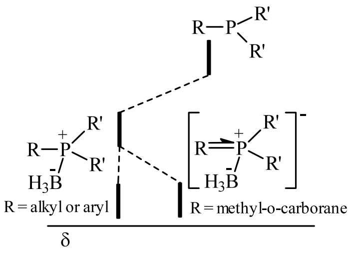


Fig. 4. Graphical representation of the $^{31}P\{^1H\}$ chemical shift and the **ccs**.

substituents, in the sense that the placement of electronegative substituents on phosphorous leads to an increase in the ^{1}J(B, H) [10]. Practically all *nido*-alkylcarboranylmonophosphine–borane adducts show very constant ^{1}J(B, H)'s, between 92 and 96 Hz, (see Table 1) very similar to the values found for $Me_3P\cdot BH_3$ (^{1}J(B, H) = 97.4 Hz) [10]. On the other hand, the higher ^{1}J(B, H) value (100 Hz) for the *closo*-carboranylphosphine–borane adduct evidences the higher electronegativity of the *closo*-cluster versus the *nido*-one.

It has already been studied, [10] by selected displacement reactions, the existence of a correlation between ^{1}J(P, B), the coordinate dative bond strength and the Lewis basicity of a phosphine towards the borane unit [10,15]. For example $(MeO)_3P$ with ^{1}J(P, B) = 97.2 Hz for the borane complexe is more basic that $MePH_2$ with ^{1}J(P, B) = 43.5 Hz for the adduct. In our case, all the *nido*-carboranylphosphine–borane adducts show coupling constant ^{1}J(P, B) values, between 55 and 63 Hz, whereas we found the smaller ^{1}J(P, B) for the *closo*-carboranylmonophosphine–borane (43 Hz), indicating a lower basicity of the latter with respect to the *nido*-carboranylmonophosphine–boranes.

If we compare the easy reaction of BH_3 with *nido*-carboranylmonophosphines and the practically non-reactivity of the *closo*-carboranylmonophosphines, and the NMR indicators based on ^{1}J(B, H) and ^{1}J(P, B) are considered, it is clear that the *nido*-carboranylmonophosphines are much better coordinating ligands than the corresponding *closo*-ones, a fact that we had already evidenced in coordinating to metals, but not with conventional Lewis acids. Although both types of coordination are equivalent, conceptually they are different in the sense that *nido*-carboranylmonophosphines are negative and the *closo* are neutral. Thus, the reactivity towards a metal in a positive oxidation state was different than reactions towards a Lewis acid that would leave the original charge of the ligand unaffected in the end product. With these experiments we have proven the superior coordinating capacity of the *nido* versus the *closo* species in any circumstance.

4. Experimental

4.1. Instrumentation

Microanalyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyser. IR spectra (KBr pellets) were obtained on a Nicolet 710-FT spectrophotometer. The $^{1}H\{^{11}B\}$-NMR (300.13 MHz), ^{11}B-NMR (96.29 MHz), $^{31}P\{^{1}H\}$-NMR (121.4 MHz) and $^{13}C\{^{1}H\}$-NMR (75.47 MHz) spectra were obtained on a Bruker ARX 300 instruments. All NMR measurements were performed in deuterated solvents at 22 °C. The ^{11}B-NMR shifts are referenced to external $BF_3\cdot O(Et)_2$, while the δ ^{1}H and δ ^{13}C data are referenced to $Si(Me)_4$ and the δ ^{31}P data to the 85% H_3PO_4, positive values of the shifts, according to the IUPAC convention, are to high frequency.

4.2. Materials

Before use, 1-methyl-*o*-carborane, *o*-carborane and decaborane (Katchem Ltd. Prague) were sublimed under high vacuum. Phenyl-*o*-carborane was prepared from decaborane according to a method reported previously [16]. The started *closo*-carboranylphosphines: 1-PPh_2-2-Me-1,2-$C_2B_{10}H_{10}$, [17] 1-P(^{i}Pr)$_2$-2-Me-1,2-$C_2B_{10}H_{10}$, [18] 1-PEt_2-2-Me-1,2-$C_2B_{10}H_{10}$ were prepared from methyl-*o*-carborane and 1-P(^{i}Pr)$_2$-2-Ph-1,2-$C_2B_{10}H_{10}$ [19] from phenyl-*o*-carborane according to the literature, previously to prepare the corresponding *nido*-carboranylmonophosphines. The *nido*-carboranylmonophosphines: [NBu_4][7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$], [NBu_4][7-PEt_2-8-Me-7,8-$C_2B_9H_{10}$], [NBu_4][7-P(^{i}Pr)$_2$-8-Me-7,8-$C_2B_9H_{10}$], and [NBu_4][7-P(^{i}Pr)$_2$-8-Ph-7,8-$C_2B_9H_{10}$], were prepared according to the literature [20]. A 1 M solution of $BH_3\cdot THF$ in THF from Aldrich was used as purchased. Unless mentioned elsewhere, the reactions are carried out under N_2 atmosphere and used solvents (toluene and diethyl ether) were oxygen free and dry.

4.3. Synthesis of tetrabutylammonium diphenyl[7-(8-methyl-7,8-dicarba-nido-undecaborate)]phosphine–borane (1)

To a three-necked round bottom flask (50 ml) containing toluene (10 ml) was added [NMe_4][7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$] (130 mg, 0.32 mmol) and a solution of $BH_3\cdot THF$ 1 M in THF (0.80 ml, 0.80 mmol). The mixture was stirred for 16 h at room temperature (r.t.). After this time, a rubish-solid was observed. This was separated by decantation and more toluene was added to obtained a white powder which was filtered to yield (105 mg, 78%). Calc. elemental analysis for $C_{19}H_{38}B_{10}PN$: C, 54.42; H, 9.07; N, 3.34. Found: C, 54.09; H, 8.28; N, 2.82%; IR, ν(cm^{-1}): 2522, 2399, 2345 (B–H). ^{1}H-NMR ($(CD_3)_2CO$, δ, ppm): −2.20 (br, 1B, B–H–B), 2.32 (s, 3 H, CH_3), 3.42 (s, 12 H, N–CH_3), 8.03–7.19 (m, 10 H, C_6H_5). $^{1}H\{^{11}B\}$-NMR ($(CD_3)_2CO$, δ, ppm): −2.20 (s, 1B, B–H–B), 1.15 (d, 3 H, ^{2}J(P, H) = 14.5 Hz, BH_3), 2.32 (s, 3 H, CH_3), 3.42 (s, 12 H, CH_3), 8.03–7.19 (m, 10 H, C_6H_5). ^{11}B-NMR ($(CD_3)_2CO$, δ, ppm): −6.9 (d, 2 B, ^{1}J(B, H) = 126 Hz); −10.4 (d, 1 B, ^{1}J(B, H) = 162 Hz); −13.7 (d, 1 B, ^{1}J(B, H) = 146 Hz); −15.4 (d, 2 B, ^{1}J(B, H) = 155 Hz); −21.5 (d, 1 B, ^{1}J(B, H) = 156 Hz), −32.9 (d, 1 B, ^{1}J(B, H) = 138 Hz), −33.8 (1 B), −34.6 (d, 1 B, ^{1}J(B, H) = 139 Hz). $^{31}P\{^{1}H\}$-NMR ($(CD_3)_2CO$, δ, ppm): 27.47 (br d, 1 P, ^{1}J(P, B) = 63 Hz).

4.4. Synthesis of tetrabutylammonium diethyl[7-(8-methyl-7,8-dicarba-nido-undecaborate)]phosphine–borane (2)

The same procedure as before using [NBu$_4$][7-PEt$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$] (180 mg, 0.38 mmol) in toluene (10 ml) and a solution of BH$_3$·THF 1 M in THF (0.94 ml, 0.94 mmol) added dropwise. The mixture was stirred 16 h at r.t. to obtain a white oily precipitate. The solid was washed with toluene and ethyl ether to give a white powder (140 mg, 75%). Calc. elemental analysis for C$_{23}$H$_{62}$B$_{10}$NP: C, 56.22; H, 12.63; N, 2.85; Found: C, 55.96; H, 12.44; N, 2.55%. IR ν(cm^{-1}): 2515, 2392, 2337 (B–H). ^{1}H{^{11}B}-NMR ((CD$_3$)$_2$CO, δ, ppm): −2.21 (s, 1B, B–H–B), 0.54 (d, 3 H, ^{2}J(P, H) = 13.8 Hz, BH$_3$), 0.99 (t, 12 H, ^{3}J(H, H) = 7, Hz CH$_3$), 1.15 (m, 6 H, CH$_3$), 1.44 (hex, 8 H, ^{3}J(H, H) = 7 Hz, CH$_2$), 1.67 (s, 3 H, CH$_3$), 1.81 (q, 8 H, ^{3}J(H, H) = 7 Hz, CH$_2$), 2.06 (m, 4 H, CH$_2$), 3.44 (t, 8 H, ^{3}J(H, H) = 8 Hz, NCH$_2$). ^{11}B-NMR ((CD$_3$)$_2$CO, δ, ppm): −6.8 (d, 1 B, ^{1}J(B, H) = 156 Hz); −8.6 (d, 1 B, ^{1}J(B, H) = 132 Hz); −11.6 (d, 1 B, ^{1}J(B, H) = 125 Hz); −14.2 (d, 1 B, ^{1}J(B, H) = 144 Hz); −16.2 (d, 2 B, ^{1}J(B, H) = 168 Hz); −20.4 (d, 1 B, ^{1}J(B, H) = 161 Hz), −33.2 (d, 1 B, ^{1}J(B, H) = 168 Hz), −35.3 (d, 1 B, ^{1}J(B, H) = 168 Hz), −36.9 (dquartet, 1 B, ^{1}J(P, B) = 60 Hz, ^{1}J(B, H) = 96 Hz). ^{31}P{^{1}H}-NMR ((CD$_3$)$_2$CO, δ, ppm): 27.75 (quartet, 1 P, ^{1}J(P, B) = 60 Hz). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO, δ, ppm): 7.2 (s); 7.8(s); 13.1 (s); 19.4 (s); 19.9 (s); 20.2 (s); 23.5 (s); 23.8 (d, ^{1}J(P, C) = 36 Hz); 58.1 (s).

4.5. Synthesis of tetrabutylammonium diisopropyl[7-(8-methyl-7,8-dicarba-nido-undecaborate)]phosphine–borane (3)

The same procedure as before using [NBu$_4$][7-P(^{i}Pr)$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$] (125 mg, 0.25 mmol) in toluene (10 ml) and a solution of BH$_3$·THF 1 M in THF (0.62 ml, 0.62 mmol) added dropwise. The mixture was stirred 16 h at r.t. to obtain a crystalline white solid, which is washed with toluene and dried to yield 100 mg, 77%. Calc. elemental analysis for C$_{25}$H$_{66}$B$_{10}$NP: C, 57.80; H, 12.72; N, 2.70. Found: C, 57.69; H, 12.57; N, 2.51%; IR ν(cm^{-1}): 2522, 2355 (B–H). ^{1}H{^{11}B}-NMR ((CD$_3$)$_2$CO, δ, ppm): −2.20 (s, 1B, B–H–B), 0.46 (d, 3 H, ^{2}J(P, H) = 13.8 Hz, BH$_3$), 1.00 (t, 12 H, ^{3}J(H, H) = 7 Hz, CH$_3$), 1.20 (m, 6 H, CH$_3$), 1.28 (m, 6 H, CH$_3$), 1.45 (hex, 8 H, ^{3}J(H, H) = 7 Hz, CH$_2$,), 1.68 (s, 3 H, CH$_3$), 1.83 (q, 8 H, ^{3}J(H, H) = 7 Hz, CH$_2$), 2.30 (m, 2 H, CH), 3.47 (t, 8 H, ^{3}J(H, H) = 8 Hz, NCH$_2$). ^{11}B-NMR ((CD$_3$)$_2$CO, δ, ppm): −7.7 (d, 2 B, ^{1}J(B, H) = 132 Hz); −11.8 (d, 1 B, ^{1}J(B, H) = 169 Hz); −14.4 (1 B); −15.1 (1 B); −15.7 (1 B,); −19.0 (d, 1 B, ^{1}J(B, H) = 153 Hz), −32.6 (d, 1 B, ^{1}J(B, H) = 162 Hz), −34.6 (d, 1 B, ^{1}J(B, H) = 152 Hz), −39.4 (dquartet, 1 B, ^{1}J(P, B) = 56 Hz, ^{1}J(B, H) = 92 Hz). ^{31}P{^{1}H}-NMR ((CD$_3$)$_2$CO, δ, ppm): 42.46 (br d, 1 P, ^{1}J(P, B) = 56 Hz). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO, δ, ppm): 12.9 (s); 17.6 (s); 18.1 (d, ^{2}J(P,C) = 18 Hz); 19.2 (s); 19.5 (s); 23.5 (s); 25.3 (s); 27.3 (d, ^{1}J(P,C) = 34 Hz); 58.5 (s).

4.6. Synthesis of tetrabutylammonium diisopropyl[7-(8-phenyl-7,8-dicarba-nido-undecaborate)]phosphine–borane (4)

The same procedure as before using [NBu$_4$][7-P(^{i}Pr)$_2$-8-Ph-7,8-C$_2$B$_9$H$_{10}$] (103 mg, 0.18 mmol) in toluene (10 ml) and a solution of BH$_3$·THF 1 M in THF (0.45 ml, 0.45 mmol) added dropwise. The mixture was stirred 16 h at r.t. After this time, a precipitate is observed. The solution was concentrated, the solid was filtered, washed with toluene and dried to vacuum. Yield (80 mg, 77%). Calc. elemental analysis for C$_{30}$H$_{68}$B$_{10}$NP: C, 61.97; H, 11.70; N, 2.41; Found: C, 61.70; H, 11.44; N, 2.55%. IR ν(cm^{-1}): 2526, 2360 (B–H). ^{1}H{^{11}B}-NMR ((CD$_3$)$_2$CO, δ, ppm): −2.16 (s, 1B, B–H–B), 0.49 (d, 3 H, ^{2}J(P, H) = 14.2 Hz, BH$_3$), 1.20 (t, 12 H, ^{3}J(H, H) = 7 Hz, CH$_3$), 1.30 (m, 12 H, CH$_3$), 1.48 (hex, 8 H, ^{3}J(H, H) = 7 Hz, CH$_2$), 1.85 (q, 8 H, ^{3}J(H, H) = 7 Hz, CH$_2$), 2.35 (m, 2 H, CH), 3.45 (t, 8 H, ^{3}J(H, H) = 8 Hz, NCH$_2$,), 7.17–7.53 (m, 5 H, C$_6$H$_5$). ^{11}B-NMR ((CD$_3$)$_2$CO, δ, ppm): −6.2 (d, 1 B, ^{1}J(B, H) = 143 Hz); −7.5 (d, 1 B, ^{1}J(B, H) = 150 Hz); −9.9 (d, 1 B, ^{1}J(B, H) = 140 Hz); −14.2 (d, 2 B, ^{1}J(B, H) = 173 Hz); −15.8 (d, 1 B, ^{1}J(B, H) = 176 Hz); −22.4 (d, 1 B, ^{1}J(B, H) = 151 Hz), −30.2 (d, 1 B, ^{1}J(B, H) = 136 Hz), −33.7 (d, 1 B, ^{1}J(B, H) = 144 Hz), −38.5 (dquartet, 1 B, ^{1}J(P, B) = 55 Hz, ^{1}J(B, H) = 95 Hz). ^{31}P{^{1}H}-NMR ((CD$_3$)$_2$CO, δ, ppm): 45.40 (br d, 1 P, ^{1}J(P, B) = 55 Hz). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO, δ, ppm): 12.9 (s); 16.4 (d, J(P, C) = 18 Hz); 17.9 (s); 18.8 (s); 19.5 (s); 23.1 (d, J(P, C) = 37 Hz); 23.5(s); 23.9 (s); 58.6 (s); 128.1 (s); 128.5 (s); 128.9 (s); 133.0 (s).

4.7. Synthesis of diethyl[1-(2-methyl-1,2-dicarba-closo-dodecaborane)]phosphine–borane (5)

The same procedure as before using 1-PEt$_2$-2-Me-1,2-C$_2$B$_{10}$H$_{10}$] (150 mg, 0.60 mmol) in toluene (10 ml) and a solution of BH$_3$·THF 1 M in THF (1.80 ml, 1.80 mmol) added dropwise. The mixture was stirred 2 days at r.t. The solvent was evaporated and a solid was obtained, which was washed with ethyl ether. Yield (125 mg, 80%). Calc. elemental analysis for C$_7$H$_{26}$B$_{11}$P: C, 32.33; H, 10.01. Found: C, 32.03; H, 9.95%. IR ν(cm^{-1}): 2570 (B–H). ^{1}H{^{11}B}-NMR ((CD$_3$)$_2$CO, δ, ppm): 0.72 (d, 3 H, ^{2}J(P, H) = 13.4 Hz, BH$_3$), 1.27 (t, 3 H, ^{3}J(H, H) = 8 Hz, CH$_3$), 1.30 (t, 3 H, ^{3}J(H–H) = 7 Hz, CH$_3$), 2.18 (m, 4 H, CH$_2$), 2.33 (s, 3 H, CH$_3$). ^{11}B-NMR ((CD$_3$)$_2$CO, δ, ppm): 0.6 (d, 1 B, ^{1}J(B, H) = 144Hz); −4.8 (d, 1 B, ^{1}J(B, H) = 149 Hz); −8.9 (d, 6 B, ^{1}J(B, H) = 140 Hz); −10.3 (2B); −38.3 (dquartet, 1 B, ^{1}J(P, B) = 43 Hz,

^1J(B, H) = 100 Hz). ^{31}P{^{1}H}-NMR ((CD$_3$)$_2$CO, δ, ppm): 47.12 (quartet, 1 P, ^1J(P, B) = 43 Hz). ^{13}C{^{1}H}-NMR ((CD$_3$)$_2$CO, δ, ppm): 7.3 (s); 10.0(d, J(P, C) = 21 Hz); 19.7 (d, J(P, C) = 32 Hz); 20.8 (d, J(P, C) = 17 Hz,); 24.9 (s); 71.9 (s);79.4 (s).

4.8. X-Ray studies of tetrabuthylammonium diisopropyl[7-(8-methyl-7,8-dicarba-nido-undecaborate)]phosphine–borane (3)

Single-crystal data collection for (**3**) was performed at −80 °C on a CAD4 diffractometer using graphite monochromatized Cu–K$_\alpha$ radiation. The unit cell parameters were determined by least-squares refinement of 25 carefully centered reflections. A total of 10232 reflections, giving 10 012 independent reflections ($R_{\text{int}} = 0.0365$) were collected by $\omega - \theta$ scans. The data obtained were corrected for Lorentz and polarization effects, and for absorption (ψ scan). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 techniques using the SHELX-97 program package [21]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters or refined isotropically (hydrogen atoms at B9, B10, B11 and B13). Crystallographic data are listed in Table 5.

Table 5
Crystallographic data for compound (**3**)

Empirical formula	$C_{25}H_{66}B_{10}NP$
Formula weight	519.86
Wavelength (Å)	1.54184
Crystal system	Monoclinic
Space group	$P2_1/c$ (number 14)
Unit cell dimensions	
a (Å)	18.320(3)
b (Å)	11.931(2)
c (Å)	31.663(5)
β (°)	90.73(2)
V (Å^3)	6920(2)
Z	8
D_{calc} (g cm^{-3})	0.998
μ (cm^{-1})	7.81
Number of unique reflections	10012
Number of parameters	727
Goodness-of-fit on F^2	1.004
$R_1(F_o)$ [a] $[I > 2\sigma(I)]$	0.0476
$wR_2(F_o^2)$ [b] $[I > 2\sigma(I)]$	0.1386
Largest differential peak and hole (e Å^{-3})	0.340 and −0.344

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 167914 for **3**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.)+44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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