12-Vertex Zwitterionic Bis-phosphonium-*nido*-carborates via Ring-opening Reaction of 1,2-Diphosphetanes

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Dedicated to Professor Narayan Hosmane on the occasion of his 70th birthday.

Abstract: Carborane-substituted 1,2-diphosphetanes (**Ia,b**) react with elemental lithium in THF with cleavage of the P−P bond to give a deep red solution from which red crystals of a lithiated intermediate, [{1-P*t*BuLi(THF)-6-P*t*Bu-4,1,6-*closo*-Li(THF)$C_2B_{10}H_{10}${Li(THF)$_3$}]$_2$· 2 THF (**2**), were obtained. The compound is dimeric, C_2-symmetric and contains six lithium and four phosphorus atoms. Two lithium atoms are capping the six-membered C_2B_4 faces resulting in two 13-vertex *closo*-clusters (according to Wade's rules) with docosahedral geometry. Addition of methyl iodide resulted in formation of the zwitterionic bis-phosphonium-*nido*-carborates, 7,10-bis(*tert*-butyl-dimethylphosphonium)-dodecahydro-7,10-dicarba-*nido*-dodecaborate(2–) (**1a**) and 7,10-bis(*N,N*-diisopropylamino-dimethylphosphonium)-dodecahydro-7,10-dicarba-*nido*-dodecaborate(2–) (**1b**) in moderate to good yields. **1a** and **1b** exhibit short $C_{cluster}$–P bonds and large $C_{cluster}\cdots C_{cluster}$ distances in the solid state. Further insight into the ring opening and reduction potential of the alkyl halide was obtained from methylation reactions of different 1,2-bis-phosphinocarboranes. Reaction of *rac/meso*-1,2-bis(*tert*-butyl-methylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**3a**) with two equivalents of methyl iodide resulted in formation of **1a** as well (as shown by NMR spectroscopy) while the reaction of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) with methyl triflate afforded the phosphonium salt 1-methyl-diphenylphosphonium-2-diphenylphosphino-1,2-dicarba-closo-dodecaborane(12) triflate (**4**) without reduction of the cluster.

Introduction

The chemistry of carboranes is dominated by 1,2-dicarba-*closo*-dodecaborane(12) [*closo*-1,2-$C_2B_{10}H_{12}$] due to its commercial availability and thermodynamic stability.[1] Under strongly basic conditions (e.g. alcoholic potassium hydroxide), the icosahedral *ortho*-carborane can be deboronated selectively to give the 7,8-dicarba-*nido*-dodecahydro-undecaborate(1–), [*nido*-7,8-$C_2B_9H_{12}$]$^-$, which can be further deprotonated to the dicarbollide ion, [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$.[2] A different synthetic route for the preparation of *nido*-carboranes is the two-electron reduction of

any of the dicarba-*closo*-dodecaborane(12) isomers (1,2-(*ortho*), 1,7- (*meta*) or 1,12-dicarba-*closo*-dodecaborane(12) (*para*)) with alkali metals such as lithium, sodium or potassium.[3–5] While the reduction of either *o*- or *m*-carborane yields the same dianion [*nido*-7,9-$C_2B_{10}H_{12}$]$^{2-}$, the reduction of *p*-carborane affords [*nido*-7,10-$C_2B_{10}H_{12}$]$^{2-}$ instead.[3–5] These *nido*-12-vertex clusters are the gateway to carboranes and metallacarboranes with vertices higher than 12.[6] For instance, if they are reacted with metals, a capitation occurs to afford *closo*-13-vertex metallacarboranes.[7]

A reversible and mild cluster opening reaction was reported by Pringle et al. in 2008.[8] Reaction of carborane-based 1,2-bis-phosphanes with ethereal HCl afforded the zwitterionic *nido*-12-vertex species *nido*-7-C(PH*t*Bu$_2$)-10-C(PClEt$_2$)$B_{10}H_{10}$ (**II**). Reversion of the reaction was achieved by addition of NEt$_3$. Additionally, they established that the unusual *nido*-12-vertex polyhedron of **II** is not unique, by obtaining the crystals of *nido*-7-C(P*n*Bu*t*Bu$_2$)-10-C(PHEt$_2$)$B_{10}H_{10}$ (**III**).
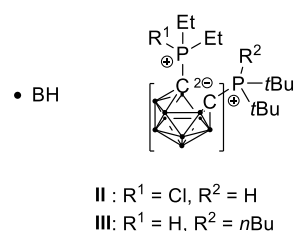

Figure 1. Structure of the zwitterionic *nido*-12-vertex species **II** and **III**.

We here report the reductive ring opening reaction of *ortho*-carborane-based 1,2-diphosphetanes[9] with lithium and further reaction with methyl iodide resulting in zwitterionic *nido*-12-vertex clusters 7,10-bis(phosphonium)-dodecahydro-7,10-dicarba-*nido*-dodecaborate(2–) (**1a,b**).

We have previously reported several syntheses incorporating the cleavage of the P–P bond by reaction of 1,2-diphosphetane **Ia** with lithium (Scheme 1),[10,11] we herein report the synthesis and crystal structure of **2**, a lithiated intermediate from this reaction.

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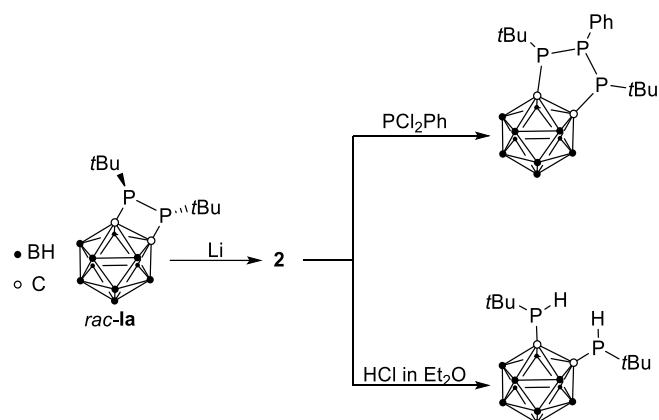
Scheme 1. Synthetic routes incorporating the cleavage of the P–P bond in **Ia** with elemental lithium with formation of the lithiated intermediate **2**.

Results and Discussion

Zwitterionic *nido*-12-vertex clusters

Carborane-based 1,2-diphosphetanes, which can be prepared by a facile route in excellent yields,[9] have proved to be highly versatile starting materials for a variety of P-substituted carboranes. Reactions with diaryl dichalcogenides bearing a pyridinyl or anilyl moiety lead to multidentate P,N ligands.[12] If reacted with elemental lithium in THF the *tert*-butyl- and diisopropylamino-substituted 1,2-diphosphetanes **Ia** and **Ib** react with cleavage of the P–P bond to give a deep red solution of the corresponding lithium salt. This lithiated intermediate (vide infra) offers access to novel open-chain (addition of HCl)[10] or cyclic (addition of dichlorophosphines)[11] derivatives (Scheme 1). Addition of methyl iodide resulted in formation of zwitterionic bis-phosphonium-*nido*-carborates, namely 7,10-bis(*tert*-butyl-dimethylphosphonium)- (**1a**) and 7,10-bis(*N,N*-diisopropylamino-dimethylphosphonium)-dodecahydro-7,10-dicarba-*nido*-dodecaborate(2–) (**1b**) (Scheme 2), which were obtained as colourless crystals in moderate to good yields [72% (**1a**) and 55% (**1b**)].
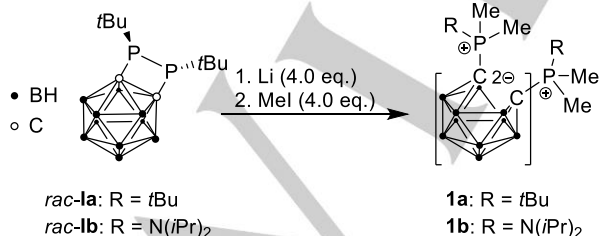
Scheme 2. Synthesis of zwitterionic *nido*-12-vertex bis-phosphonium carborates **1a,b** via ring-opening reaction and methylation of carborane-based 1,2-diphosphetanes **Ia,b**.

Apparently, lithium not only cleaves the P–P bond reductively in this reaction, but also facilitates a two-electron reduction of the *closo*-carborane in **Ia,b**, resulting in a bis-ylide structure when methyl iodide is added.

The $^{31}P\{^1H\}$ NMR spectra exhibit singlets at 35.6 ppm (**1a**) and 50.3 ppm (**1b**), which are shifted upfield compared to the starting materials (41.2 ppm (**Ia**), 58.8 ppm (**Ib**)). The methyl groups appear as doublets in the ^1H NMR spectrum at ca. 1.6 ppm ($^2J(H,P)$ = 15.5 or 12.3 Hz), and as doublets in the $^{13}C\{^1H\}$ NMR spectrum at 6.4 ppm ($^1J(C,P)$ = 58.0 Hz, **1a**) and 15.9 ppm ($^1J(C,P)$ = 69.2 Hz, **1b**). The carbon atoms of the cluster display singlets at 66.9 ppm (**1a**) and 67.9 ppm (**1b**).
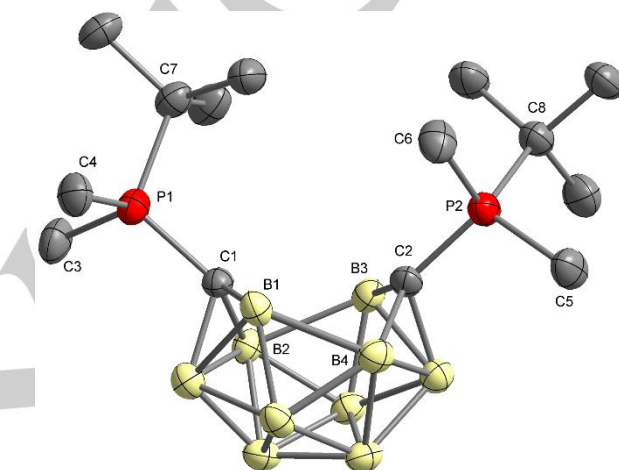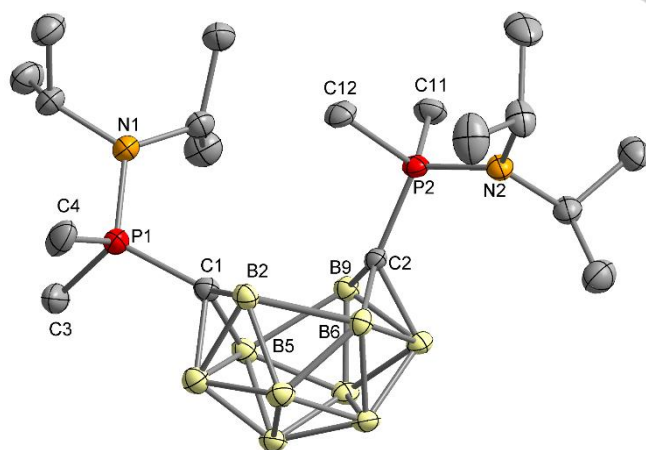

Figure 2. Molecular structure of **1a** in the solid state with ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Both products were obtained from toluene as colourless crystals suitable for X-ray structure analysis. Compound **1a** crystallises in the orthorhombic space group $P2_12_12_1$, compound **1b** in the monoclinic space group $P2_1/n$, both with four molecules in the unit cell and one disordered toluene molecule in the asymmetric unit. The short $C_{cluster}$–P bond [174.0(2) to 175.0(3) pm] and the large C1···C2 distance [290.8(4), 286.7(4) pm] in **1a** and **1b** (Table 1) compare well with those in *nido*-7-C(PH*t*Bu$_2$)-10-C(PClEt$_2$)B$_{10}$H$_{10}$ (**II**) [$C_{cluster}$–P 176.7(4) pm, C1···C2 285.4(8) pm]) and *nido*-7-C(P*n*Bu*t*Bu$_2$)-10-C(PHEt$_2$)B$_{10}$H$_{10}$ (**III**) [$C_{cluster}$–P 176.3(3) pm, C1···C2 289.2(4) pm], and are in general agreement with ylid bonds.[8,13] The P1···P2 distances of 525.5(1) pm (**1b**) and 549.6(1) pm (**1a**) indicate no interaction of the phosphorus atoms and are in unison with the distances in **II** and **III** as well. Both phosphorus atoms are coordinated in a tetrahedral fashion (Table 1). In contrast to the 1,2-diphosphetanes **Ia,b**,[9] the C–B bonds are shorter, while the B1–B4 and B2–B3 bonds [197.9(5), 202.0(5) pm **1a**; 198.8(4), 200.9(4) pm in **1b**] are much longer. In comparison, the C–B and B–B bond lengths found in the *nido*-12-vertex cluster **II** and **III** are very similar.

Table 1. Selected bond lengths [pm] and angles [°] for **1a** and **1b**.

Compound	**1a**	**1b**
C1···C2	290.8(4)	286.7(4)
P1···P2	549.6(1)	525.5(1)
C1–P1	174.8(3)	174.0(2)
C2–P2	175.0(3)	174.3(2)
C1–B1	153.6(4)	154.4(4)
C1–B2	161.7(4)	162.3(4)
C2–B3	153.5(4)	153.1(3)
C2–B4	161.9(4)	161.7(4)
B1–B4	197.9(5)	198.8(4)
B2–B3	202.0(5)	200.9(4)
P1–C7/N1	181.5(3)	165.5(2)
P2–C8/N1	183.3(3)	164.6(2)
B1–C1–P1	123.6(2)	123.0(2)
B3–C2–P2	132.8(2)	127.0(2)
C1–P1–C3	112.0(1)	110.3(1)
C1–P1–C4	109.8(1)	109.3(1)
C3–P1–C4	107.1(2)	105.6(2)
C1–P1–C7/N1	112.0(1)	113.5(1)
C2–P2–C8/N2	115.3(1)	115.5(1)

Figure 3. Molecular structure of **1b** in the solid state with ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Lithiated Intermediate

The lithiated intermediate [{1-P*t*BuLi(THF)-6-P*t*Bu-4,1,6-*closo*-Li(THF)C$_2$B$_{10}$H$_{10}$}{Li(THF)$_3$}]$_2$·2 THF (**2**) was isolated from the reaction of 1,2-diphosphetane **1a** and an excess of elemental lithium. This is somewhat surprising, since the reaction of 1,2-diphosphetanes with lithium usually yields bis-phosphanides.[14] **2** crystallises in the monoclinic space group *C*2/*c* with four molecules in the unit cell. It is a dimeric, C$_2$-symmetric compound with six lithium and four phosphorus atoms (Figure 4).
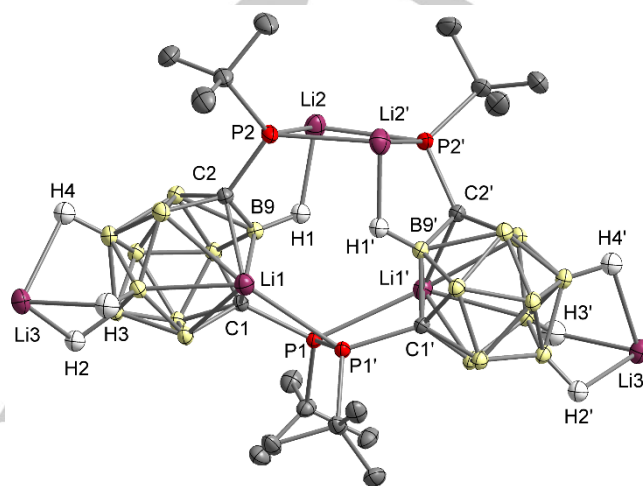
Figure 4. Molecular structure of **2** in the solid state with ellipsoids drawn at 50% probability level. Hydrogen atoms not interacting with lithium, THF molecules coordinating at lithium (Li1: 1 THF, Li2: 1 THF, Li3: 3 THF) and 2 non-coordinating THF molecules are omitted for clarity.

The P–P bond in the starting material is broken during the reaction, yet unexpectedly, one P–P bond (P1–P1') is formed in the product, resulting in a lithium phosphanide which forms a typical four-membered, almost planar ring [Li2–P2–Li2'–P2', torsion angle 3.8(1)°] with Li–P bond lengths [247.6(4) and 247.3(3) pm] and bond angles [Li–P–Li 73.68(1)°, P–Li–P 106.19(1)°] (Table 2) in the range of known dimeric lithium organophosphanides (P–Li 247–265 pm, Li–P–Li–P 4–17°, Li–P–Li 65–80°, P–Li–P 100°–110°).[15] The coordination sphere of Li2 and Li2' is completed by one THF molecule and interaction with a cluster hydride. The second P*t*Bu–P*t*Bu group (P1–P1') is now located between two clusters indicating that the reductive cleavage of the 1,2-diphosphetane was apparently followed by intermolecular coupling. The P1–P1' bond length [223.8(9) pm] is similar to that in 1,2-diphosphetane **1a** [24.6(3) pm] and bonds found in 1,2,3-triphospholanes or other cyclic phosphanes.[11,16]

The phosphorus atoms interact with Li1 (P1') or Li1' (P1) [P1'–Li1 269.6(3) pm] resulting in two four-membered only slightly puckered rings [P1–P1'–Li1–C1 and P1'–P1–Li1'–C1', dihedral angle 7.8(1)°] folded along the common P–P bond [angle between both planes 48.63(4)°]. Additionally, the lithium atoms Li1 and Li3 interact with the carborate cluster. Li1 is capping the six-membered C$_2$B$_4$ face resulting in a 13-vertex metallacarborane *closo*-cluster according to Wade's rules [each cluster in **2** has 28 skeletal electrons (2n+2 = 28, n = 13)], which adopt a docosahedral geometry (Figure 5).[17] The lithium cation

Li3 interacts with the three hydrogen atoms of a triangular B_3H_3 face, forming the counter ion of the monoanionic LiC_2B_{10} *closo*-cluster. Li3 is additionally coordinated by three THF molecules.
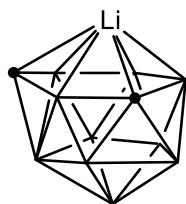

Figure 5. Docosahedral 13-vertex metallacarborane clusters in **2** (• = C).

Table 2. Selected bond lengths [pm], angles [°] and torsions angles [°] for **2**.

P1–P1'	223.8(9)	Li3–H4	234.02
Li1–P1'	269.6(3)	Li2····Li2'	296.8(7)
C1–P1	185.1(1)	Li1–P1'–P1	86.8(7)
C1–Li1	249.7(4)	P1'–P1–C1	97.5(6)
Li1–C2	221.8(4)	P2–Li2'–P2'	106.2(1)
C2–P2	178.9(2)	Li1–C1–P1	102.1(1)
P2–Li2'	247.6(4)	Li2–P2–Li2'	73.7(1)
Li3–H2	217.6(2)	P2–Li2–P2'–Li2'	3.8(1)
Li3–H3	217.2(3)	P1–C1–Li1–P1'	7.8(1)

The extraordinary sensitivity of **2** made it impossible to obtain NMR spectra without small amounts of decomposition products present.

Table 3. $^7Li\{^1H\}$ and $^{31}P\{^1H\}$ NMR data for **2**.[25]

A$_2$X$_2$ spin system	δ (P) = 88.4 ppm δ (Li) = 1.59 ppm	^1J(P,Li) = 56.0 Hz
AA'XX' spin system	δ (P) = 87.9 ppm δ (Li) = –2.45 ppm	^1J(P,P) ≤ –350 Hz ^1J(P,Li) = 39.4 Hz ^2J(P,Li) = 0 Hz ^3J(Li,Li) = 0 Hz
Li3/Li3'	δ (Li) = –0.37 ppm	

The NMR spectra of **2** are in good accordance with the molecular structure observed in the solid state. Both, the $^{31}P\{^1H\}$ and the $^7Li\{^1H\}$ NMR spectra show two multiplets for the two Li$_2$P$_2$ groups (Table 3, for details see ESI). The four-membered ring (Li2-P2-Li2'-P2') gives a simple A$_2$X$_2$ spin system, which leads to a triplet in the $^7Li\{^1H\}$ NMR and a 1:2:3:4:3:2:1 septet in the $^{31}P\{^1H\}$ NMR spectrum due to I(^7Li) = $^3/_2$. In contrast, the

binding mode in the second group (Li1-P1-P1'-Li1') renders the two P atoms magnetically inequivalent leading to a more complicated AA'XX' spin system. The J(P,P) coupling constant obtained from simulating the spectrum[25] supports the direct connection of the P atoms. In addition to the two multiplets, a third signal in the $^7Li\{^1H\}$ NMR spectrum corresponds to the atoms Li3/Li3' which are presumably solubilised.

In order to examine reactive sites of the lithiated intermediate density functional theory (DFT) calculations were performed on a simplified model of **2**, namely [{1-PtBuLi(OMe$_2$)-6-PtBu-4,1,6-*closo*-Li(OMe$_2$)C$_2$B$_{10}$H$_{10}$}]$_2$$^{2–}$ (**2'**), and the frontier molecular orbitals studied. The MULLIKEN atomic charges (from population analysis) reflect what is already proposed from chemical intuition: the atoms P1/P1' both have an atomic charge of about zero (+0.077277 or –0.002352), whereas the atoms P2/P2' have a partially negative charge (–0.206065 or –0.212165). The highest occupied molecular orbital (HOMO) as well as the HOMO–1 are located at the atoms P2/P2' where the highest contributions come from the p_x orbitals and to a minor extent from the p_y and p_z orbitals. The HOMO–2 and HOMO–3 lie mostly on the carborane cluster pointing towards the coordinated lithium cation, which is located above the six-membered ring. HOMO–4 is represented by the two lone pairs of electrons at atoms P1/P1' and a slipped-π bond with a high contribution of the p_x and p_y orbitals. The lone pairs of electrons at atoms P2/P2' are considerably higher in energy [1.3853 eV (HOMO–1) or 1.6437 eV (HOMO)] than the ones at P1/P1'. Due to their partial negative charge, it can be assumed that the atoms P2/P2' are attacked by electrophiles like MeI or HCl and, on the other hand, P1/P1' by nucleophiles. This assumption is supported by the findings that intermediate **2** can be isolated and reacted with electrophiles and nucleophiles leading to different products.

Like HOMO–4, HOMO–6 incorporates the lone pairs of electrons at P1/P1' but with opposite signs relative to each other. HOMO–5 and HOMO–10 are quite interesting since they consist mainly of the p_z orbitals of P2/P2' pointing towards each other, whereby HOMO–5 is the antibonding situation and HOMO–10 the bonding. The HOMO–LUMO gap is relatively large with about 5.02 eV suggesting intrinsic stability, albeit this is a highly reactive compound.
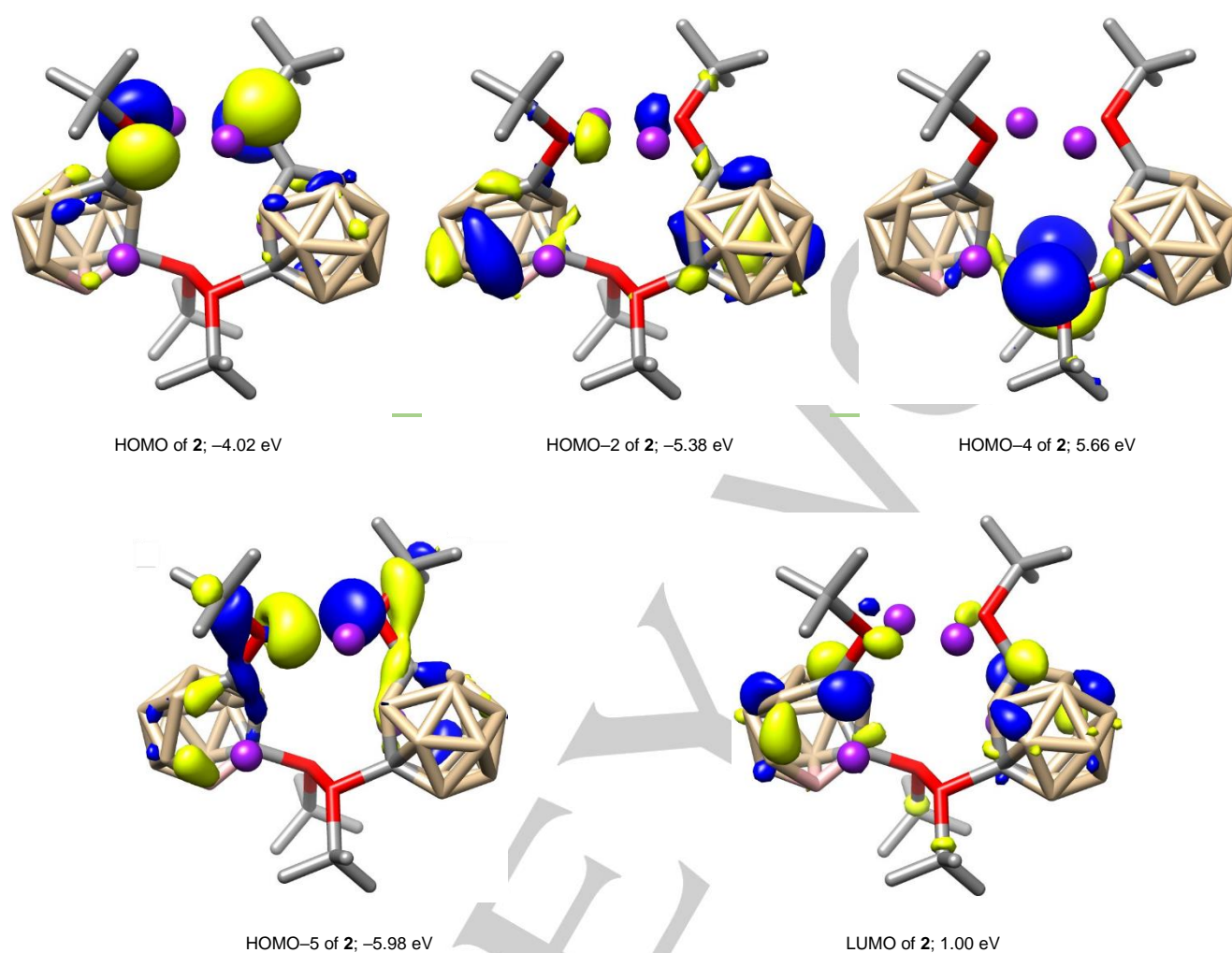
HOMO of **2**; –4.02 eV

HOMO–2 of **2**; –5.38 eV

HOMO–4 of **2**; 5.66 eV

HOMO–5 of **2**; –5.98 eV

LUMO of **2**; 1.00 eV

Figure 6. Optimised structures and frontier molecular orbitals of the lithiated intermediate **2**. P: red; C: grey; B: pink; Li: purple. Surface isovalue XXX

Methylation of 1,2-Bis-phosphanes

In order to gain further insight into the possible reduction of the carborane cluster by an alkyl halide, a mixture of *rac-* and *meso-* 1,2-bis(*tert*-butyl-methylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**3a**) was reacted with two equivalents of methyl iodide in THF at room temperature (Scheme 3).
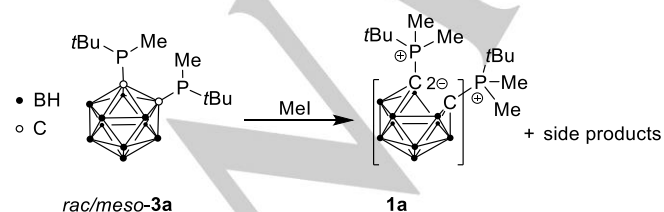

Scheme 3. Redox reaction of **3a** with methyl iodide to yield **1a**.

The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After two hours, multiple new signals emerged, the most prominent appearing at 35.6 ppm, indicating the formation of **1a**. After 24 hours, signals of the starting material were still present besides those of **1a**, with a reactant to product ratio of roughly 2:1. Therefore, an additional two equivalents of methyl iodide were added. This led, however, to the formation of new compounds with signals in the range of 25 to 45 ppm, indicating decomposition of **1a** with excess methyl iodide.

Subsequently, other attempts to form zwitterionic bis-phosphonium *nido*-carborates via reaction of 1,2-bis-phosphanes with methyl iodide were made. 1,2-bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) reacted similar to **3a** (formation of new compounds while the signal of the starting material was still present). 1,2-Bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) did not react with methyl iodide, but the stronger methylating agent MeOTf in

dichloromethane gave phosphonium salt **4** (Scheme 4). Only mono-methylation occurs regardless of the amount of MeOTf used. During the reaction, the C–C bond in **4** remained intact, which supports the necessity of iodide in the reduction of the cluster.
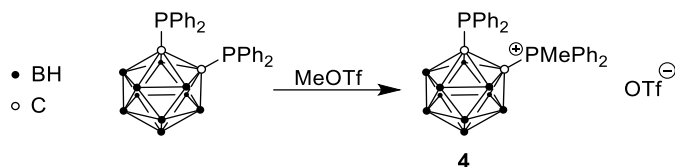
Scheme 4. Synthesis of **4** via methylation of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) with methyl triflate.

In the $^{31}P\{^{1}H\}$ NMR spectrum, **4** exhibits two doublets at 12.1 and 24.7 ppm ($^{3}J(P,P) = 28.5$ Hz). The coupling constant is much smaller compared to those of other unsymmetric carborane-based bis-phosphanes,[12,18] since the splitting is highly influenced by the lone-pair overlap and decreases significantly after partial oxidation.[19]
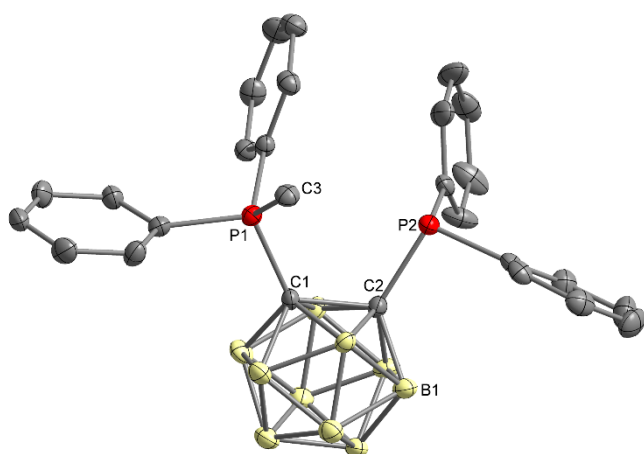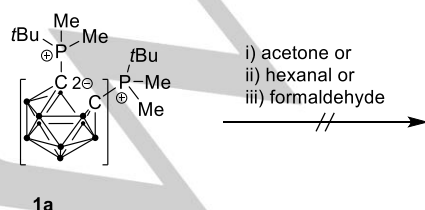

Figure 6. Molecular structure of **4** in the solid state with ellipsoids drawn at 50% probability level. The triflate anion and hydrogen atoms are omitted for clarity.

Wittig-type reactions

To utilise the two ylide groups in **1a**, Wittig-type reactions were performed of **1a** with various aldehydes and ketones (Scheme 5).

1a

Scheme 5. Reactions of **1a** with ketones and aldehydes

The reaction conditions, including the solvent, temperature, reaction time and pH, were altered. However, monitoring by ^{1}H and ^{31}P NMR spectroscopy showed no reaction.

In order to gain insight into the reactivity of the zwitterion, DFT calculations have been carried out at the RI-TPSS-D3/def2-TZVP level of theory. The solid-state structure of the zwitterion served as a starting point for the geometry optimisation. The calculations showed that the negative charge is widely delocalised over the cluster. The values for the natural charge of the carbon atoms in the cluster are only insignificantly higher than those of the methyl groups attached to the phosphorus atoms. This could explain why a nucleophilic attack of the carbanion does not take place. The zwitterion is probably too stabilised by the electron-withdrawing cluster and hence does not attack the carbonyl group.

Furthermore, the steric hindrance of the phosphonium groups and their substituents is enormous and the bulky cluster is further obstructing any reactant from approaching the backside of the molecule, as is apparent from the space-filling model of **1a** (Figure 7).
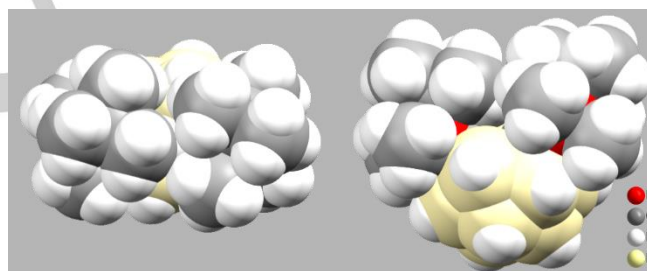
Figure 7. Space-filling model of **1a**.

Conclusions

Two zwitterionic *nido*-12-vertex bis-phosphonium carborates **1a** and **1b** were obtained via ring-opening reaction and subsequent methylation of 1,2-diphosphetanes with lithium and methyl iodide. Additionally, the lithiated intermediate **2** was obtained from the reaction of **Ia** with lithium and provides insight in this reaction and other syntheses previously reported by us.[10,11] Methylation reactions of 1,2-bis(phosphino)-1,2-dicarba-*closo*-dodecaboranes(12) also resulted in phosphonium salts and proved the crucial role of the iodide anion in the reduction of the carborane cluster.

Experimental Section

General

All reactions were carried out under dry high purity nitrogen using standard Schlenk techniques. Solvents were purified and degassed with an MBRAUN Solvent Purification System SPS-800 or dried and stored according to common procedures.[20] Compounds **Ia/Ib**,[9] 1,2-bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane(12),[21] 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12),[22] and 1,2-Bis(*tert*-butylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12)[23] were prepared according to the literature. Lithium was used as purchased. The NMR spectra were recorded with a BRUKER Avance III HD or BRUKER Avance DRX 400 MHz NMR spectrometer at room temperature (^{1}H NMR 400.13 MHz, ^{7}Li NMR 155.51 MHz, ^{11}B NMR 128.38 MHz, ^{13}C NMR 100.63 MHz, ^{31}P NMR 161.98 MHz). TMS was used as the internal standard in the ^{1}H NMR spectra and all other nuclei spectra were referenced to TMS using the Ξ scale.[24] Simulation of spectra were carried out with SPINWORKS.[25] Mass spectra were recorded with a Finnigan MAT MAT8200 (EI) or with a Micromass LCT. FTIR spectra were recorded with a PerkinElmer System 2000 FTIR spectrometer in the range of 4000–400 cm^{-1} in KBr disks. Elemental analyses were performed with a Heraeus VARIO EL instrument CHN-O-S Analyzer. The melting points were determined in glass capillaries sealed under nitrogen using a Gallenkamp apparatus and are uncorrected.

DFT Calculations

Density functional theory (DFT) calculations for the lithiated intermediate [{1-PtBuLi(THF)-6-PtBu-4,1,6-*closo*-Li(THF)C$_2$B$_{10}$H$_{10}$}$_2$·2 THF (**2**) were performed using the ORCA 3.0.3 software package.[26] The simplified model compound [{1-PtBuLi(OMe)$_2$-6-PtBu-4,1,6-*closo*-Li(OMe)$_2$C$_2$B$_{10}$H$_{10}$}]$_2^{2-}$ (**2'**) was employed. The geometry optimisation was performed based on the atomic coordinates from X-ray single crystal diffraction for **2** on the BP86 density functional (Becke 88 exchange function[27] and Perdew 86 correlation function[28]) utilising the atom-pairwise dispersion correction with Becke-Johnson damping scheme (D3BJ)[29] and Alrichs def2-TZVP basis set.[30] For the frequency calculations the same settings as for the geometry optimization were used as it was performed on the optimized geometry. Density fitting techniques, also called resolution-of-identity approximation (RI),[31] were applied throughout to speed up the calculations. Based on the optimized geometry a single-point energy evaluation using the M06-2x[32] level of theory again with the Ahlrichs def2-TZVP basis sets[30] was performed, from which the molecular orbitals were also taken. Within the used RIJCOSX approximation the COSX can additionally accelerate the numerical integration for the HF exchange in the hybrid functional, where it needed to have a higher COSX grid (GridX6).[33] In order to consider solvent effects (THF) the conductor-like screening model (COSMO) by Klamt, where the solvent is represented by a dielectric polarisable continuum, was used, as implemented in ORCA 3.0.3.[34] The convergence thresholds for SCF and geometry optimisations were set to VeryTightSCF, the FinalGrid was turned off (NoFinalGrid) and a large damping factor for the SCF converger (SlowConv) activated. The frontier orbitals (isosurface = 0.04) are visualised using the UCSF Chimera visualisation system.[35] The LOEWDIN reduced orbital population analysis was used for discussing each molecular orbital, and the MULLIKEN atomic charges were taken from the MULLIKEN population analysis.

X-ray Crystallography

The data were collected on a Gemini diffractometer (Agilent Technologies) using Mo-K$_\alpha$ radiation (λ = 71.073 pm) and ω-scan rotation. Data reduction was performed with CrysAlis Pro[36] including the program SCALE3 ABSPACK[37] for empirical absorption correction. All structures were solved by direct methods (SHELXS-97[38]: **1a**, **2**; SIR-92[39]: **1b**), and the refinement of all non-hydrogen atoms was performed with SHELXL-97.[38] With the exception of disordered solvent molecules, all non-

hydrogen atoms were refined with anisotropic thermal parameters, and a difference-density Fourier map was used to locate all hydrogen atoms for non-disordered regions of the structure (Table 4). Structure figures and the space-filling model were generated with DIAMOND (version 3.2k).[40]

Table 4. Crystal data for compounds **1a**, **1b** and **2**.

Compound	**1a** · 1 toluene	**1b** · 1 toluene	**2** · 12 THF
empirical formula	C$_{21}$H$_{48}$B$_{10}$P$_2$	C$_{25}$H$_{58}$B$_{10}$P$_2$N$_2$	C$_{68}$H$_{152}$B$_{20}$P$_4$Li$_6$O$_{12}$
formula weight	470.63	556.77	1543.62
T [K]	130(2)	130(2)	130(2)
crystal system	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$C2/c$
a [pm]	976.69(5)	890.31(4)	2380.37(5)
b [pm]	1257.99(7)	2494.9(1)	1293.20(2)
c [pm]	2350.1(1)	1602.9(1)	3077.76(4)
α [°]	90	90	90
β [°]	90	100.403(5)	103.385(2)
γ [°]	90	90	90
V [nm^3]	2.8874(3)	3.5019(3)	9.2169(3)
Z	4	4	4
ρ_{calcd}	1.083	1.056	1.112
θ_{max}	26.37	26.37	30.51
$F(000)$	1016	1208	3336
reflns collected	22401	23903	46641
independent reflns	5890	7144	14074
$R1/wR2$ [$I>2\sigma(I)$]	0.0549/0.1178	0.0639/0.1045	0.0493/0.1153
$R1/wR2$ (all data)	0.0766/0.1293	0.1103/0.1213	0.0683/0.1241

Synthesis of 7,10-bis(*tert*-butyl-dimethylphosphonium)-dodecahydro-7,10-dicarba-*nido*-dodecaborate(2–) (1a)

Small chunks of lithium (44 mg, 6.3 mmol) were added to a solution of **Ia** (505 mg, 1.6 mmol) in THF (25 ml) to give a dark red solution. After stirring for 12 h at rt MeI (0.9 g, 6.3 mmol) was added dropwise and the reaction mixture was stirred for another 12 h at rt to give a light green solution and a colourless solid. The slurry was filtered through celite, then the solvent was removed under reduced pressure. The resulting yellow residue was washed with toluene (2x10 ml) to give bis-phosphonium *nido*-carborate **1a** as a colourless solid (429 mg, 72%); m.p. 226°C; ^{1}H NMR (CDCl$_3$): δ = 0.52–2.10 (m, 10H, BH), 1.36 (d, ^3J(P,H) = 15.5 Hz, 18H, C(CH$_3$)$_3$), 1.57 ppm (d, ^3J(P,H) = 12.1 Hz, 12H, CH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 6.4 (d, ^1J(C,P) = 58.0 Hz, *C*H$_3$), 24.3 (s, C(CH$_3$)$_3$), 30.3 (d, ^1J(C,P) = 51.5 Hz, *C*(CH$_3$)$_3$), 66.9 ppm (s, C$_2$B$_{10}$H$_{10}$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 35.6 ppm (s); ^{11}B{^{1}H} NMR (CDCl$_3$): δ = –19.4 (s br, 2B), –17.3 (s br, 4B), 2.4 (s br, 2B), 22.5 ppm (s br, 2B); IR (KBr): $\tilde{v}$ = 2963 (m,

CH), 2501 (s, BH), 1635 (w), 1420 (w), 1261 (s), 1180 (m), 1097 (s), 1020 (s), 913 (w), 804 (s), 742 (w), 524 cm^{-1} (w); MS (EI, pos., 70 eV): m/z (%): 378 (60) [M^+], 321 (80) [M^+–C(CH$_3$)$_3$], 265 (100) [M^+–2×C(CH$_3$)$_3$]$^+$; elemental analysis calcd (%) for C$_{14}$H$_{40}$B$_{10}$P$_2$: C 44.42, H 10.65; found: C 44.51, H 9.64.

Synthesis of 7,10-bis(*N,N*-diisopropylamino-dimethylphosphonium)-dodecahydro-7,10-dicarba-*nido*-dodecaborate(2–) (1b)

Small chunks of lithium (50 mg, 7.2 mmol) were added to a solution of **Ib** (730 mg, 1.8 mmol) in THF (30 ml) to give a dark red solution. After stirring for 12 h at rt MeI (1.0 g, 7.2 mmol) was added dropwise and the reaction mixture was stirred for another 12 h at rt. The slurry was filtered through celite, then the solvent was removed under reduced pressure. The resulting yellow residue was washed with toluene (2x10 ml) to give bis-phosphonium *nido*-carborate **1b** as a colourless solid (460 mg, 55%); m.p. 210°C; ^{1}H NMR (CDCl$_3$): δ = 0.60–2.40 (m, 10H, BH), 1.20 (d, ^3J(H,H) = 6.6 Hz, 24H, N{CH(CH_3)$_2$}$_2$), 1.75 (d, ^3J(P,H) = 12.3 Hz, 12H, CH$_3$), 3.75 ppm (m, 4H, N{CH(CH$_3$)$_2$}$_2$); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 15.9 (d, ^1J(C,P) = 69.2 Hz, CH$_3$), 23.5 (s, N{CH(CH_3)$_2$}$_2$), 47.5 (d, ^2J(C,P) = 3.6 Hz, N{CH(CH$_3$)$_2$}$_2$), 67.9 ppm (s, C$_2$B$_{10}$H$_{10}$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 50.3 ppm (s); ^{11}B{^{1}H} NMR (CDCl$_3$): δ = –20.4 (s br, 2B), –17.4 (s br, 4B), 1.9 (s br, 2B), 21.5 ppm (s br, 2B); IR (KBr): $\tilde{v}$ = 2973 (m, CH), 2502 (s, BH), 1626 (s), 1459 (w), 1410 (m), 1292 (s), 1260 (s), 1178 (s), 1170 (m), 999 (s), 912 (m), 805 cm^{-1} (m); MS (EI, pos., 70 eV): m/z (%): 464 (20) [M^+], 364 (100) [M^+–N{CH(CH$_3$)$_2$}$_2$], 303 (20) [M^+–(CH$_3$)$_2$N{CH(CH$_3$)$_2$}$_2$].

Synthesis of the lithiated intermediate 2

Small chunks of lithium (17 mg, 2.51 mmol, 8.00 eq.) were added to a solution of **Ia** (200 mg, 0.63 mmol) in THF (2 ml). After stirring for 12 h the orange slurry was filtered through a frit (G3) to give **2** as a bright orange solid (ca. 200 mg). The yield could not be determined precisely, since **3** is very sensitive and can neither be purified nor dried without partial decomposition.

Orange prisms of **3** were obtained by using a larger amount of THF (7 ml) and leaving the reaction solution at rt after stirring for 12 h; ^{1}H NMR ([D$_8$]THF): δ = 1.00–1.50 (m, 20H, BH), 1.29–1.34 (m, 36H, C(CH$_3$)$_3$), 1.38–1.43 ppm (m, 36H, C(CH$_3$)$_3$); ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 36.0–36.4 (m), 36.7–37.0 (m), 37.6–37.8 (m), 43.5–44.0 ppm (m); ^{31}P{^{1}H} NMR ([D$_8$]THF): δ = 86.5–87.5 (m, P1/P1'), 87.5–89.5 ppm (sept, ^1J(P,Li) = 56.0 Hz, P2/P2'); ^{7}Li{^{1}H} NMR ([D$_8$]THF): δ = –2.4 (X, Li1/Li1'), –0.4 (s, Li3/Li3'), 1.6 ppm (t, ^1J(P,Li) = 56.0 Hz, Li1/Li1').

Synthesis of *rac/meso*-1,2-bis(*tert*-butyl-methylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (3a)

1,2-Bis(*tert*-butylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (600 mg, 1.5 mmol) was dissolved in Et$_2$O (20 ml) and methyllithium (2.0 ml, 3.0 mmol; 1.5 M) was added at –78°C. After stirring for 12 h at rt, LiCl was filtered off and the solvent was removed under reduced pressure. The remaining solid was recrystallised from toluene to give *rac/meso*-**3a** (300 mg, 57%); m.p. 158–160°C; ^{1}H NMR (CDCl$_3$): δ = 1,00–3.10 (m, 10H, BH), 1.13 (d, ^3J(P,H) = 6.5 Hz, 9H, C(CH$_3$)$_3$), 1.17 (d, ^3J(P,H) = 6.5 Hz, 9H, C(CH$_3$)$_3$), 1.23 ppm (*pseudo* t, ^2J(P,H) = 2.6 Hz, 3H, CH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 27.5 (m, CH$_3$), 27.8 (m, CH$_3$), 29.3 (s, C(CH$_3$)$_3$), 29.6 (s, C(CH$_3$)$_3$), 32.7 (m, C(CH$_3$)$_3$), 33.4 (s, C(CH$_3$)$_3$), 86.4 ppm (m, ^1J(P,C) + ^2J(P,C) = 73.4 Hz, C$_2$B$_{10}$H$_{10}$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 14.3 (s); 12.1 ppm (s); ^{11}B{^{1}H} NMR (CDCl$_3$): δ = –10.4 (s br, 6B), –7.1 (s br, 2B), –0.1 ppm (s, br, 2B); IR (KBr): $\tilde{v}$ = 2997 (m, CH), 2969 (s, CH), 2900 (m, CH), 2646 (s, BH), 2617 (s, BH), 2563 (s, BH), 1473 (s), 1463 (s), 1424 (s), 1393 (m), 1368 (s), 1368 (s), 1286 (m), 1262 (s), 1173 (s), 1072 (s), 1019 (s), 877 (s), 804 (s), 732 (m), 693 (m), 623 cm^{-1} (w); MS (EI, pos., 70 eV): m/z (%): 348 (2) [M^+], 291 (100) [M^+–C(CH$_3$)$_3$], 235 (80) [M^+–2×C(CH$_3$)$_3$]; elemental analysis calcd (%) for C$_{20}$H$_{43}$B$_{10}$P$_2$: C 41.36, H 9.83; found: C 39.51, H 9.67.

Synthesis of 1-(methyl-diphenylphosphonium)-2-diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (4)

A solution of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (204 mg, 0.4 mmol) in CH$_2$Cl$_2$ (4 ml) was cooled to 0°C and MeOTf (0.09 ml, 0.8 mmol) was added dropwise. The reaction mixture was allowed to warm to rt and was left stirring for 7 d. Subsequently, the solvent was removed under reduced pressure and the crude product was purified via column chromatography (50% EtOAc/*n*-hexane) to yield phosphonium salt **4** as a colourless solid (215 mg, 80%). Crystals were obtained from CDCl$_3$ at rt; ^{1}H NMR (CDCl$_3$): δ = 0.20–3.30 (m, 10H, BH), 2.78 (m, 3H, CH$_3$), 7.04–7.25 (m, 8H, C$_6$H$_5$), 7.33–7.55 (m, 10H, C$_6$H$_5$), 7.88–7.98 ppm (m, 2H, C$_6$H$_5$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 12.1 (d, ^3J(P,P) = 28.6 Hz, PPh$_2$), 24.7 ppm (d, ^3J(P,P) = 28.6 Hz, PPh$_2$Me); ^{11}B{^{1}H} NMR (CDCl$_3$): δ = –32.5 (2B), –22.0 (2B), –13.8 (3B), –7.4 ppm (3B); IR (KBr): $\tilde{v}$ = 3054 (w, CH), 2920 (m, CH), 2562 (s, BH), 2523 (s, BH), 1586 (m, C=C), 1479 (m), 1438 (s), 1415 (m), 1385 (w), 1309(w), 1289 (m), 1188 (w), 1157 (w), 1116 (s), 1101 (s), 1027 (m), 999 (m), 959 (w), 893 (s), 848 (w), 768 (w), 741 (s), 713 (m), 687 (s), 626 (m), 569 (w), 532 (w), 502 (s), 482 (s), 450 (m), 411 cm^{-1} (w).

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FULL PAPER

Graphic bitte anpassen an Platz

Two zwitterionic *nido*-12-vertex bis-phosphonium carborates were obtained via ring-opening reaction and subsequent methylation of 1,2-diphosphetanes with lithium and methyl iodide. Additionally, the lithiated intermediate was isolated and DFT calculations provided insight in the reaction with nucleophiles and electrophiles.

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12-Vertex Zwitterionic Bis-phosphonium-nido-carborates via Ring-opening Reaction of 1,2-Diphosphetanes

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