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Heterocycles

Carbaborane-Substituted 1,2,3-Triphospholanes and 1-Aza-2,5-diphospholane: New Synthetic Approaches

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Abstract: New phosphorus-containing, five-membered P,P,P and P,N,P heterocycles were synthesized and fully characterized. The P,P,P heterocycles, 1,2,3-triphospholanes, can be synthesized by two different facile pathways, whereas the P,N,P compound, a 1-aza-2,5-diphospholane, can only be obtained with silylamine.

Introduction

Strained phosphorus-containing heterocycles have attracted considerable interest due to their unusual reactivity and structures,[1] and also as ligands for transition metals.[2] However, the synthesis of stable four- and five-membered phosphorus-containing heterocycles with endocyclic P–P bonds remains a challenge.[3,7] The first triphospholane, namely, 1,2,3-triphenyl-1,2,3-triphosphaindane, was obtained by Mann and Pragnell in 1966[4] from the reduction of dichlorophenylphosphane with lithium followed by reaction with 1-bromo-2-iodobenzene; 5,10-dihydro-5,10-diphenylphosphanthrene was obtained as a byproduct.

X-ray structure analysis showed a *trans* arrangement of the three phenyl groups.[5] Further studies by Mann and Mercer accessed new synthetic routes and illustrated the chemistry of these interesting compounds.[6] In 1985, Sheldrick and co-workers prepared 1,2,3-triphospholane-2-ide from *o*-phenylene-bis-(lithiumphenylphosphanide) and white phosphorus in good yield.[7] This anionic species can then be treated with different halogenated substrates to give the corresponding 1,2,3-triphospholanes.[7]

Besides 1,2,3-triphospholanes, several two-element 1,3-diphospholanes have been reported. One of the first P,As,P heterocycles was synthesized by the reaction of a dilithiodiphosphanide species with different arsenic dichlorides.[8] Extensive studies of *o*-phenylenebisphosphanes by Issleib et al. revealed that these are versatile reagents that allow easy access to a variety of five-membered C–P–E–P–C heterocycles (E = BR, AlR, CR_2, SiR_2, SnR_2, NR, AsR, S; R = alkyl, aryl, $N(alkyl)_2$, $N(aryl)_2$).[9] In 1976, Heinicke et al. described the synthesis of different C–E1–E2–E3–C heterocycles (E1 = NR; E2 = BR, SiR_2, PR, AsR, SnR_2; E3 = AsR; R = alkyl, aryl).[10]

1,2-Dicarba-*closo*-dodecaborane(12) [*ortho*-carbaborane][11] is an interesting electron-poor C_2-symmetrical backbone for bisphosphanes.[12] Most research is focused on disubstituted derivatives, in which the *ortho*-carbaborane imitates an ethylene or phenylene system, but acts more like a rigid backbone.[13] When combined with the electron-withdrawing and -delocalizing ability of the carbaborane moiety the properties of phosphorus(III) compounds change dramatically. Furthermore, when the carbaborane backbone was employed, cyclic 1,2-diphosphetanes could be obtained.[14] In this work, we extend this synthetic approach to carbaborane-based five-membered heterocycles, namely, 1,2,3-triphospholanes and 1-aza-2,5-diphospholane.

Results and Discussion

Synthesis of 4,5-dicarba-*closo*-dodecaboranyl-1,2,3-triphospholanes

4,5-Dicarba-*closo*-dodecaboranyl-1,2,3-triphospholanes can be obtained by two different routes.

Synthesis from carbaborane-based 1,2-diphosphetanes

Carbaborane-based 1,2-diphosphetanes,[14] which can be prepared in a facile way and with excellent yield, have proved to be highly versatile starting materials for a variety of P-substituted carbaboranes.[15] Alkali metals,[16] lithium alkyls,[17] and platinum(0) complexes[18] were reported to cleave the P–P bond of phosphorus heterocycles. Thus, the *tert*-butyl-substituted 1,2-diphosphetane **1a** (Scheme 1) reacts with elemental lithium in THF with cleavage of the P–P bond to give a deep-red solution of the dianionic lithium salt, which offers access to novel open-chain or cyclic derivatives.[19] Treatment with one equivalent of dichlorophenylphosphane gave the first five-

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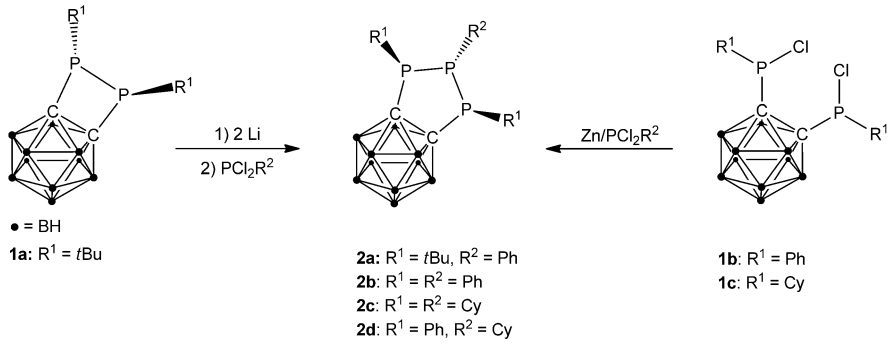


Scheme 1. Synthetic routes to *trans*,*trans*-4,5-dicarba-*closo*-dodecaboranyl-1,2,3-triphospholanes **2a**–**d**.

membered 4,5-dicarba-*closo*-dodecaboranyl-1,3-di-*tert*-butyl-2-phenyl-1,2,3-triphospholane (**2a**) in moderate yield (Scheme 1).

Synthesis from 1,2-bis(halophosphanyl)-1,2-dicarba-closo-dodecaborane(12)s

An alternative synthetic route is the reaction of 1,2-bis(halophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)s[12a,13c,l,m,20] with dichlorophosphanes and a reducing agent (Scheme 1). The starting materials 1,2-bis(chlorophenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**1b**)[12a] and 1,2-bis(chlorocyclohexylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (**1c**) (see the Supporting Information for X-ray structures) are easily accessible by reaction of the dilithiated carbaborane with dichlorophenylphosphane or dichlorocyclohexylphosphane. Reduction of the diastereomeric mixture of **1b** or **1c** with zinc followed by addition of dichlorophenyl- or dichlorocyclohexylphosphane exclusively gave the all-*trans* isomers of the 1,2,3-triphospholanes **2b**–**d** (Scheme 1), shown by $^{31}P\{^1H\}$ NMR spectroscopy of the reaction solutions. Apparently, the electron-withdrawing and -delocalizing ability of the cluster and the long C–C bond stabilize the five-membered heterocycles **2a**–**d**.[12b] Compounds **2a**–**d** were obtained in good to moderate yield as colorless crystals. They are highly soluble in nonpolar solvents, water stable, and moderately air stable due to the reduced electron density at phosphorus.[21]

Table 1. Chemical shifts (δ) and coupling constants (J) of the C_2P_3 system in **2a**–**d**.

	$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ [ppm]	^1J(P,P) [Hz]	$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ABX spin system) [ppm]	^1J(C,P)+^2J(C,P) [Hz]
2a	−21.0 (t), 50.8 (d)	172.8	80.4 (m)	89.5
2b	−7.3 (t), 28.1 (d)	184.0	83.7 (m)	79.2
2c	5.5 (t), 34.0 (d)	225.0	88.8 (m)	78.1
2d	2.4 (t), 23.0 (d)	201.0	85.3 (m)	75.7

Molecular structures of 2a–d

X-ray structure analyses[22] were carried out for **2a**–**d**. The five-membered rings of the unsymmetrically substituted compounds **2a** and **2d** (Figure 1) have an envelope conformation, illustrated by the large torsion angles (Table 2), in contrast to **2b** and **2c**, which show almost planar rings (Figure 2). The endocyclic P–C bond lengths (185.6(2)–188.1(4) pm) of **2a**–**d** are larger than those found in cyclic phosphanes, for example, 1,2,3-triphenyl-1,2,3-triphospholane (average P–C bond length = 182.5 pm),[5,23] whereas the P–P bonds (220.4(1)–222.0(1) pm) compare well with the standard value (222 pm) for P–P bonds.[24] The C1–C2 bond lengths (167.4(2)–169.9(2) pm) of the five-membered heterocycles are in the same range as those of the parent four-membered 1,2-diphosphetane **1a** (164.5(4) pm), but shorter than in the parent 1,2-bis(halophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)s **1b**

Spectroscopic properties of 2a–d

The ^{31}P NMR spectra of **2a**–**d** in $CDCl_3$ exhibit a doublet and a triplet signal for the A_2B spin system with ^1J(P,P) coupling constants that range from 170 to 225 Hz. The $^{13}C\{^1H\}$ NMR spectra of **2a**–**d** show a complex coupling pattern for the ABX spin system of the PCCP moiety (^1J(C,P)+^2J(C,P) ≈ 80 Hz (Table 1)), which is generally observed for 1,2-bisphosphanyl-substituted carbaboranes.[12] The dynamic cyclohexyl substituents in **2c** and **2d** appear as broad multiplets in the ^1H NMR spectra, thus, no assignment is possible.

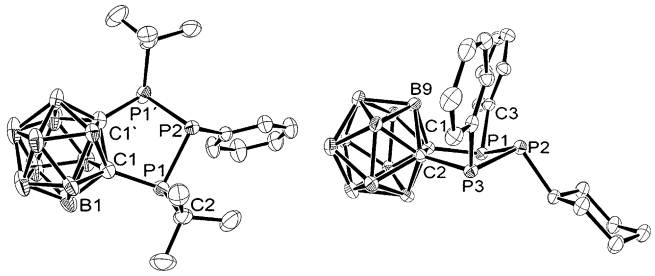


Figure 1. Molecular structures of the unsymmetrically substituted 1,2,3-triphospholanes **2a** (left) and **2d** (right) with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths [pm], angles [°], and torsion angles [°] for **2a–d**.

	2a[a]	**2b**	**2c**	**2d**
C1–C2	168.4(7)	167.5(4)	169.9(2)	167.4(2)
C1–P1	187.1(3)	186.2(3)	186.6(2)	187.0(2)
C2–P3	188.1(4)	186.5(3)	185.6(2)	186.2(2)
P1–P2	220.4(1)	221.0(1)	220.68(6)	220.76(8)
P2–P3	220.4(1)	222.0(1)	220.45(6)	221.66(8)
P1–C_{Sub}[b]	188.1(4)	182.5(3)	187.3(2)	182.8(3)
P2–C_{Sub}	183.2(4)	185.4(3)	186.9(2)	186.6(3)
P3–C_{Sub}	188.1(4)	182.5(3)	187.3(2)	182.8(3)
C1-P1-P2	97.0(1)	100.4(1)	99.40(5)	98.53(7)
P1-P2-P3	96.14(7)	101.83(4)	102.91(2)	99.70(2)
P2-P3-C2	97.0(1)	100.4(1)	99.80(5)	98.53(7)
P3-C2-C1	115.2(1)	118.5(2)	118.0(1)	117.3(2)
C2-C1-P1	115.2(1)	117.9(2)	118.1(1)	117.3(2)
P1-P2-P3-C2	38.8(1)	9.0(1)	12.0(5)	26.29(7)
P2-P1-C1-C2	27.6(1)	6.2(1)	8.5(1)	18.5(1)
P1-C1-C2-P3	0.09(3)	0.5(2)	0.0(1)	0.6(2)

[a] C2 and P3 are C1′ and P1′ in the case of **2a**. [b] Sub = substituent.

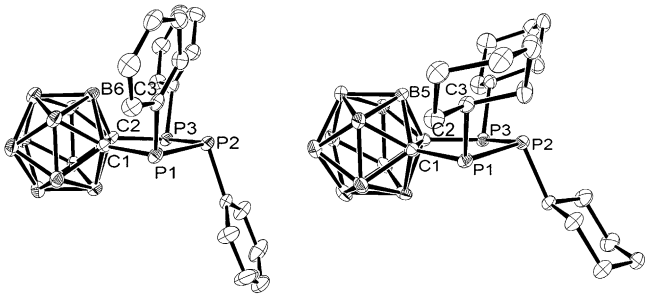


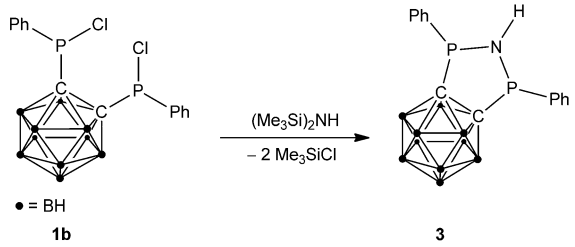
Figure 2. Molecular structures of **2b** (left) and **2c** (right) with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

and **1c** (170.2(3) and 173.7(2) pm, respectively). In contrast to the C–C bond length in 1,2,3-triphenyl-1,2,3-triphospholane (141.6(8) pm),[5] the C–C bond lengths in 4,5-dicarba-*closo*-dodecaboranyl-1,2,3-triphospholanes are significantly longer, which may explain the higher stability of these compounds.[12b] The endocyclic bond angles at the phosphorus atoms vary, with the smallest value of 96.14(7)° for **2a** and largest of 102.91(2)° for **2c**. Nevertheless they compare well with the average angles found in $(PPh)_5$ (101.3°)[25] and 1,2,3-triphenyl-1,2,3-triphospholane (100.2°).[5] In summary, the geometries of all 1,2,3-triphospholanes are similar: they occur as *trans*,*trans* isomers and have similar bond lengths and angles.

Synthetic approach to P,N,P heterocycles

Among the routes to generate P–N bonds, the most frequently used method is aminolysis of halophosphanes because halophosphanes are readily accessible from commercial sources.[26] The liberated HCl forms an insoluble salt with an added base (the amine reagent, triethylamine, or 1,8-diazabicyclo-[5.4.0]undec-7-ene [DBU]), which leads to facile separation and purification of the desired products.

An attempt to synthesize five-membered P,N,P heterocycles from **1b** and primary amines (RNH_2; R = *t*Bu, Cy, Ph) failed. The formation of the disubstituted aminobisphosphane derivatives was always preferred,[27] and the strong base leads to decapping of the boron cluster. Compound **3** was previously prepared from **1b** and gaseous ammonia but the product was only characterized by elemental analysis.[12a] However, in a facile alternative method,[28] elimination of $SiMe_3Cl$ in the reaction of chlorophosphanes and bis(trimethylsilyl)amine gave the desired P,N,P heterocycle, 4,5-dicarba-*closo*-dodecaboranyl-1-aza-2,5-diphospholane (**3**; Scheme 2), as a white powder in moderate yield. Diphospholane **3** was fully characterized, is air stable in the solid state, and highly soluble in nonpolar solvents.



Scheme 2. Synthesis of 4,5-dicarba-*closo*-dodecaboranyl-1-aza-2,5-diphenyl-diphospholane (**3**).

The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits one singlet signal at $\delta = 87.6$ ppm (cf. $\delta = 80.9$ ppm in **1b**),[12a] which indicates the formation of only one isomer. A triplet signal at $\delta = 2.21$ ppm ($^2J(H,P) = 18.5$ Hz) was observed for the N–H proton in the ^1H NMR spectrum. The N–H stretching mode was detected at $\tilde{\nu} = 3368\ cm^{-1}$ in the IR spectrum. In the $^{13}C\{^1H\}$ NMR spectrum, a complex coupling pattern was observed for the ABX spin system of the $PC_{Carb}C_{Carb}P$ group (Carb = carbaborane) at $\delta =$ 84.2 ppm. The $^{11}B\{^1H\}$ NMR spectrum showed three broad signals at $\delta = -3.0$, -5.1, and -11.1 ppm (2:2:6).

Colorless crystals of **3** were obtained from *n*-hexane. An X-ray structure analysis showed the expected five-membered C_2PNP heterocycle, however, one phosphorus atom is partially oxidized (ca. 16%, P(2)/P(2)O(1) = 0.84(1):0.16(1), see the Supporting Information). Partial oxidation of compound **3** (ca. 5%) was also observed in the $^{31}P\{^1H\}$ NMR spectrum of the obtained crystals.

Conclusions

Two versatile routes to 4,5-dicarba-*closo*-dodecaboranyl-1,2,3-triphospholanes were developed: 1) reductive P–P bond cleavage of 1,2-diphosphetanes with lithium and subsequent reaction with dichlorophosphane; 2) reduction of bis(halophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12)s with zinc in the presence of dichlorophosphanes. Furthermore, less basic silylamines seem to be suitable precursors to P,N,P heterocycles. Thus, diphospholane **3** could be obtained by reaction of bis-(chlorophenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) with bis(trimethylsilyl)amine.

Compared to the corresponding benzene analogues,[4–6] the carbaboranyl backbone offers several possibilities for further functionalization.[11a] These include selective substitution of the hydrogen atom of boron atom B9[29] or deboronation of the *closo* cluster to give *nido* derivatives.[30] Preliminary NMR spectroscopic studies have shown that **2b** reacts with tetra-*n*-butylammonium fluoride (TBAF) in THF at room temperature to form the corresponding *nido* species without P–P bond cleavage. The resulting *nido* cluster should be an interesting ligand in transition metal chemistry because it combines the features of a *nido*-carbaborane ligand with those of an oligophosphane. These studies are now underway.

Experimental Section

General

All reactions were carried out under dry high-purity nitrogen by standard Schlenk techniques. Solvents were purified and degassed with an MBraun SPS-800 solvent purification system. NMR spectra were recorded at 25 °C with a Bruker Avance DRX 400 MHz spectrometer (^{1}H NMR: 400.13 MHz, ^{11}B NMR: 128.38 MHz, ^{13}C NMR: 100.63 MHz, ^{31}P NMR: 161.98 MHz). TMS was used as an internal standard in the ^{1}H NMR spectra and all other nuclei spectra were referenced to TMS by using the Ξ scale.[31] ^{13}C{^{1}H} NMR spectra were obtained as APT (attached proton test) spectra, mass spectra (EI) with a VG12–250 apparatus, and FTIR spectra with a Perkin Elmer Spectrum 2000 FTIR spectrometer in the range of $\tilde{\nu}$ = 400–4000 cm^{-1} with samples dispersed in KBr. Elemental analyses were performed with a Heraeus VARIO EL CHN-O-S Analyzer. Melting points were determined in glass capillaries that were sealed under nitrogen on a Gallenkamp apparatus and are uncorrected. Carbaborane derivatives **1a**[14] and **1b**,[12a] and dichlorocyclohexylphosphane[32] were prepared by literature methods. $PPhCl_2$, 1,2-dicarba-*closo*-dodecaborane(12), lithium in mineral oil, hexamethyldisilazane, and zinc are commercially available.

X-ray crystallographic analysis

The data were collected on an Agilent Technologies CCD Xcalibur-S diffractometer. Data collection and data reduction were performed with the CrysAlis Pro software package, and the programme SCALE3 ABSPACK was used for empirical absorption correction.[33] The structures were solved by direct methods with SHELXS-97 or SIR-92 programmes and the anisotropic refinement of all non-hydrogen atoms was performed with the SHELXL-97 programme.[34] Hydrogen atoms of all structures were located on difference Fourier maps calculated at the final stage of the structure refinement. Structure figures were generated with ORTEP.[35] The data are collected in Table 3.

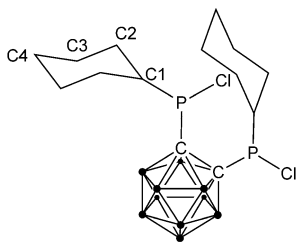
Table 3. Crystal data for compounds **2a–d**.

Compound	**2a**	**2b**	**2c**	**2d**
empirical formula	$C_{16}H_{33}B_{10}P_3$	$C_{20}H_{25}B_{10}P_3$	$C_{20}H_{43}B_{10}P_3$	$C_{20}H_{31}B_{10}P_3$
formula weight	426.43	466.41	484.55	472.46
T [K]	130(2)	130(2)	130(2)	130(2)
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pnma*	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [pm]	1373.65(7)	954.69(4)	1060.03(3)	1399.91(8)
b [pm]	1347.57(7)	1926.30(6)	1242.48(3)	1005.04(4)
c [pm]	1328.61(6)	1329.07(4)	2068.12(5)	1911.6(1)
α [°]	90	90	90	90
β [°]	90	93.392(3)	95.562(2)	111.436(7)
γ [°]	90	90	90	90
V [nm^3]	2.4594(2)	2.4399(2)	2.7110(1)	2.5035(2)
Z	4	4	4	4
ρ_{calcd}	1.152	1.270	1.187	1.254
θ_{max}	25.35	26.37	30.51	30.51
F(000)	896	960	1032	984
reflns collected	16043	21584	29887	35939
independent reflns	2350	4971	8275	7833
$R1/wR2$ [$I > 2\sigma(I)$]	0.0591/0.1360	0.0563/0.1138	0.0524/0.0936	0.0432/0.0807
$R1/wR2$ (all data)	0.0608/0.1368	0.0854/0.1244	0.0797/0.1024	0.0603/0.0875

Synthesis of compound 2a

Compound **1a** (2.0 g, 6.3 mmol) was added to lithium powder (0.1 g in mineral oil, 14.5 mmol) suspended in THF (40 mL). The reaction mixture was stirred for 12 h and dichlorophenylphosphane (1.1 g, 6.3 mmol) was slowly added. The reaction mixture was stirred for 24 h and LiCl was filtered off. The solvent was removed under vacuum and the yellow residue extracted with toluene (3× 20 mL). The solution was concentrated, cooled to −20 °C, and crystals of compound **2a** (1.3 g, 50%) were obtained. M.p. 208–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, J(P,H) = 14.0 Hz, 18H; C(CH_3)$_3$), 1.20–3.60 (m, 10H; $B_{10}H_{10}$), 7.26–7.80 ppm (m, 5H; C_6H_5); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = −10.8 (br s, 2B), −7.9 (br s, 2B), −6.2 (br s, 2B), −3.3 (br s, 1B), −2.5 ppm (br s, 3B); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 27.4 (dd, J(C,P) = 9.2, 21.1 Hz, C(CH_3)$_3$), 35.2 (dd, J(C,P) = 45.5, 16.4 Hz; C(CH_3)$_3$), 80.4 (m, ^1J(C,P) + ^2J(C,P) = 89.5 Hz; $C_2B_{10}H_{10}$), 128.8 (d, J(C,P) = 8.2 Hz; *m*-C, C_6H_5), 130.1 (s; *p*-C, C_6H_5), 133.2 (dt, J(C,P) = 25.6, 16.3 Hz; *ipso*-C, C_6H_5), 136.3 ppm (dt, J(C,P) = 7.6, 21.3 Hz; *o*-C, C_6H_5); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −21.0 (t, J(P,P) = 172.8 Hz; P2), 50.8 ppm (d, J(P,P) = 172.8 Hz; P1, P3); IR (KBr): $\tilde{\nu}$ = 3070 (w; CH), 2991 (m; CH), 2976 (w; CH), 2934 (s; CH), 2922 (s; CH), 2862 (s), 2620 (s; BH), 2579 (s; BH), 1656 (w; C=C), 1572 (w; C=C), 1469 (s), 1459 (s), 1436 (s), 1392 (s), 1365 (s), 1262 (w), 1175 (s), 1070 (s), 1026 (w), 932 (w), 800 (s), 745 (s), 694 (s), 626 (w), 578 (w), 503 (w), 456 (m), 410 cm^{-1} (m); MS (EI+, 70 eV): *m/z* (%): 426 [*M*]$^+$ (25), 370 [*M*-*t*Bu]$^+$ (30), 314 [*M*-2×*t*Bu]$^+$ (45), 57 [*t*Bu]$^+$ (100); elemental analysis calcd (%) for $C_{16}H_{33}B_{10}P_3$: C 45.06, H 7.80; found: C 43.76, H 7.65.

Synthesis of compound 1c



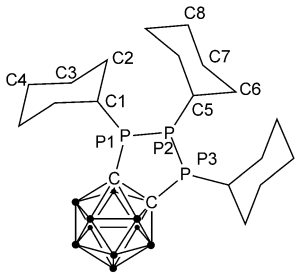
1,2-Dicarba-*closo*-dodecaborane(12) (2.5 g, 17.3 mmol) was dissolved in Et_2O (40 mL) and dilithiated by addition of *n*-butyllithium (20.4 mL, 1.7 M) at 0 °C. The reaction mixture was warmed to rt, stirred for 2 h and then added, over a period of 1 h, to a solution of dichlorocyclohexylphosphane (6.4 g, 34.6 mmol) in Et_2O (30 mL).

After stirring for 24 h, LiCl was filtered off and the solvent removed under vacuum. Compound **1c** (5.7 g, 75%) crystallized at −20 °C from *n*-hexane (see the Supporting Information for X-ray structure). M.p. 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09–2.14 (br m, 22H; C_6H_{11}), 1.65–3.30 ppm (m, 10H; $B_{10}H_{10}$); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = −9.7 (br s, 6B), −6.3 (br s, 2B), 0.51 ppm (br s, 2B); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 26.4 (m), 27.1 (s), 30.1 (m), 41.9 (m; C1 [*rac*]), 42.3 (m; C1 [*meso*]), 84.1 ppm (m, ^1J(C,P)+^2J(C,P) = 91.3 Hz; $C_2B_{10}H_{10}$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 106.9 (s; *rac*), 107.6 ppm (s; *meso*); IR (KBr): $\tilde{\nu}$ = 2931 (s; CH), 2850 (s; CH), 2617 (s; BH), 2571 (s; BH), 1448 (s; CH), 1345 (w), 1289 (w), 1269 (w), 1175 (m), 1072 (s), 1043 (m), 996 (s), 890 (w), 845 (w), 802 (w), 728 (m), 624 (w), 510 (s), 500 cm^{-1} (s); MS (EI+, 70 eV): *m/z* (%): 441.3 [*M*]$^+$ (30), 358.3 [*M*-C_6H_{11}]$^+$ (40), 83.2 [C_6H_{11}]$^+$ (100); elemental analysis calcd (%) for $C_{14}H_{32}B_{10}Cl_2P_2$: C 38.10, H 7.43; found: C 38.45, H 7.43.

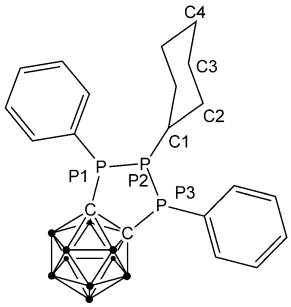
General procedure for the synthesis of 2b–d

Zinc dust was activated with 1,2-dibromoethane and suspended in toluene (50 mL). 1,2-Bis(halophosphanyl)-1,2-dicarba-*closo*-dodecaborane(12) (1 equiv) and dichlorophosphane (excess) were added and the reaction mixture was heated at reflux until the ^{31}P NMR spectrum of the solution showed full conversion of the starting material. The zinc dust was filtered off and the solvent was evaporated under vacuum. The product was dissolved in *n*-hexane/toluene. Residual LiCl was removed by filtration. The solution was concentrated and cooled to −20 °C to give **2b–d** as colorless crystals.

Compound 2b: Compound **1b** (1.0 g, 2.3 mmol), dichlorophenylphosphane (1.0 g, 5.6 mmol), zinc dust (3.3 g, 50 mmol). Yield: 0.64 g (60%); m.p. 198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00–3.20 (m, 10H; $B_{10}H_{10}$), 7.24–8.00 ppm (m, 15H; C_6H_5); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = −10.3 (br s, 2B), −9.0 (br s, 2B), −6.0 (br s, 2B), −3.6 ppm (br s, 4B); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 83.7 (m, ^1J(C,P)+^2J(C,P) = 79.2 Hz; $C_2B_{10}H_{10}$), 129.1 (m; C_6H_5), 130.2 (s; C_6H_5), 131.3 (m; *ipso*-C, C_6H_5), 131.7 (s; C_6H_5), 143.8 ppm (m; C_6H_5); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −7.3 (t, *J*(P,P) = 184.0 Hz; P2), 28.1 ppm (d, *J*(P,P) = 184.0 Hz; P1, P3); IR (KBr): $\tilde{\nu}$ = 3070 (w; CH), 3056 (w), 2598 (s; CH), 2571 (s; CH), 1948 (w; BH), 1880 (w; BH), 1583 (m), 1482 (s; C=C), 1434 (s; C=C), 1304 (C=C), 1262 (w; C=C), 1188 (m), 1161 (w), 1076 (s), 1025 (s), 998 (s), 801 (w), 737 (s), 692 (s), 488 (s), 419 (s), 690 cm^{-1} (s); MS (EI+, 70 eV): *m/z* (%): 466.5 [*M*]$^+$ (100), 389.3 [*M*-C_6H_5]$^+$ (20); elemental analysis calcd (%) for $C_{20}H_{25}B_{10}P_3$: C 51.50, H 5.40; found: C 51.43, H 5.10.



Compound 2c: Compound **1c** (0.8 g, 1.7 mmol), dichlorocyclohexylphosphane (0.50 g, 2.7 mmol), zinc dust (3.1 g, 47 mmol). Yield: 0.35 g (43%); m.p. 237 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99–2.02 (br m, 33H; C_6H_{11}), 1.50–3.35 ppm (m, 10H; $B_{10}H_{10}$); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = −9.5 (br s, 6B), −3.6 ppm (br s, 4B); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 25.8 (br s; C_6H_{11}), 26.3 (br m; C_6H_{11}), 27.2 (br m; C_6H_{11}), 30.9 (m; C2, C_6H_{11}), 33.0 (m; C6, C_6H_{11}), 36.8 (m; C5, C_6H_{11}), 38.2 (dd, *J*(C,P) = 25.0, 13.9 Hz; C1, C_6H_{11}), 88.8 ppm (m, ^1J(C,P)+^2J(C,P) = 78.1 Hz; $C_2B_{10}H_{10}$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 5.5 (t, *J*(P,P) = 225.0 Hz; P2), 34.0 ppm (d, *J*(P,P) = 225.0 Hz; P1, P3); IR (KBr): $\tilde{\nu}$ = 2923 (s; CH), 2851 (s; CH), 2601 (s; BH), 2573 (s; BH), 1447 (s), 1340 (w), 1294 (w), 1264 (m), 1188 (w), 1172 (w), 1075 (m), 998 (m), 885 (w), 849 (w), 801 (w), 739 cm^{-1} (w); MS (EI+, 70 eV): *m/z* (%): 484.4 [*M*]$^+$ (60), 402.3 [*M*−C_6H_{11}]$^+$ (20), 320.2 [*M*−2×C_6H_{11}]$^+$ (100); elemental analysis calcd (%) for $C_{20}H_{43}B_{10}P_3$: C 49.57, H 8.94; found: C 49.30, H 8.83.



Compound 2d: Compound **1b** (1.0 g (2.3 mmol), dichlorocyclohexylphosphane (0.55 g, 3.0 mmol), zinc dust (3.3 g, 50 mmol). Yield: 0.33 g (30%); m.p. 198.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00–2.51 (m, 11H; C_6H_{11}), 1.10–3.50 (m, 10H; $B_{10}H_{10}$), 7.47–8.31 ppm (m, 10H; C_6H_5); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = −10.1 (br s, 4B), −5.8 (br s, 2B), −3.9 (br s, 2B), −3.0 ppm (br s, 2B); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 25.6 (s; C4), 26.5 (d, *J*(C,P) = 10.9 Hz; C3), 32.8 (m; C2), 36.6 (m; C1), 85.3 (m, ^1J(C,P)+^2J(C,P) = 75.7 Hz; $C_2B_{10}H_{10}$), 128.8 (s; *p*-C, C_6H_5), 131.3 (s; *m*-C, C_6H_5), 132.0 (dd, *J*(C,P) = 30.0, 12.3 Hz; *ipso*-C, C_6H_5), 134.6 ppm (dd, *J*(C,P) = 12.9, 22.4 Hz; *o*-C, C_6H_5); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 2.4 (t, *J*(P,P) = 201.0 Hz; P2), 23.0 ppm (d, *J*(P,P) = 201.0 Hz; P1, P3); IR (KBr): $\tilde{\nu}$ = 3055 (w; CH), 2928 (s; CH), 2852 (w; CH), 2576 (s; BH), 1628 (w; C=C), 1435 (s; C=C), 1263 (s), 1077 (s), 803 (s), 742 (s), 693 (s), 489 cm^{-1} (w); MS (EI+, 70 eV): *m/z* (%): 472 [*M*]$^+$ (40), 390 [*M*-C_6H_{11}]$^+$ (100); elemental analysis calcd (%) for $C_{20}H_{31}B_{10}P_3$: C 50.84, H 6.61; found: C 50.03, H 6.44.

Synthesis of compound 3

Hexamethyldisilazane (0.20 g, 1.21 mmol) was added at rt to a solution of **1b** (0.52 g, 1.21 mmol) in THF (30 mL). The reaction mixture was heated at 60 °C for 12 h. The solvent was evaporated under vacuum and the residue extracted with *n*-hexane (3×10 mL). The *n*-hexane fractions were cooled at −20 °C to give **3** (0.25 g, 55%) as a white powder. M.p. 189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15–3.13 (m, 10H; $B_{10}H_{10}$), 2.21 (t, *J*(P,H) = 18.5 Hz, 1H; N*H*), 7.39–7.59 ppm (m, 10H; C_6H_5); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = −11.1 (br s, 6B), −5.1 (br s, 2B), −3.0 ppm (br s, 2B); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 84.2 (m, ^1J(C,P)+^2J(C,P) = 70.6 Hz; $C_2B_{10}H_{10}$), 128.6 (m; *o*-C, C_6H_5), 130.2 (d, *J*(C,P) = 12.9 Hz; *m*-C, C_6H_5), 131.3 (s; *p*-C, C_6H_5), 136.9 ppm (d, *J*(C,P) = 30.2 Hz; *ipso*-C, C_6H_5); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 87.6 ppm (s); IR (KBr): $\tilde{\nu}$ = 3368 (s; NH), 3074 (m; CH), 3056 (m; CH), 3005 (w; CH), 2552 (s; BH), 1958 (w), 1587 (w), 1572 (w; C=C), 1482 (s; C=C), 1425 (s; C=C), 1308 (m), 1246 (s), 1231 (s), 1080 (s), 998 (m), 969 (m), 850 (s), 806 (s), 740 (s), 707 (s), 692 (s), 629 (s), 561 (m), 490 (s), 476 (s), 426 cm^{-1} (s); MS (EI+, 70 eV): *m/z* (%): 373 [*M*]$^+$ (100); elemental analysis calcd (%) for

$C_{14}H_{21}B_{10}P_2N$: C 45.03, H 5.67; N 3.75; found: C 45.08, H 5.87; N 3.36.

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