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1,3,2-Dioxaphospholanes with an Annelated 1,2-Dicarba-*closo*-dodecaborane(12) Unit: Formation and Dimerization

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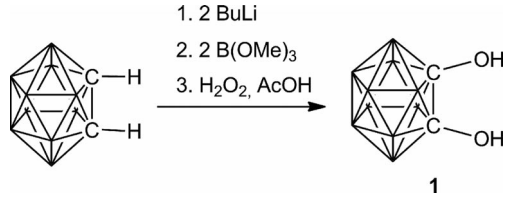
By using 1,2-hydroxy-1,2-dicarba-*closo*-dodecaborane(12) and the corresponding dilithium salt [1,2-$(LiO)_2$-1,2-$C_2B_{10}H_{10}$] for the synthesis of 1,3,2-dioxaphospholanes, it was shown that these species are short-lived with few exceptions. The phosphorus halides undergo disproportionation reactions towards phosphite derivatives, whereas the P-organo-substituted five-membered rings dimerize to give ten-membered rings. Even the *P*-diethylamino and the *P*-ethoxy compounds dimerize slowly. Dimerization is the favored process when using the dilithium salt together with ether. The reactions were monitored by multinuclear magnetic resonance spectroscopy (^1H, ^{11}B, ^{13}C, ^{31}P NMR). The gas-phase structures were optimized by DFT methods [B3LYP/6-311+G(d,p) level of theory], and NMR spectroscopic parameters were calculated. One dimer was characterized by X-ray analysis. All products were found to be sensitive to hydrolysis and oxidation. Thus, crystals of 1-[(1,1-dimethylethyl)hydroxyphosphinyl]oxy-2-hydroxy-1,2-dicarba-*closo*-dodecaborane(12) could be isolated and characterized by X-ray analysis, as well as the starting material 1,2-hydroxy-1,2-dicarba-*closo*-dodecaborane(12) (with $HNEt_2$/HCl). In all three solid-state structures, the C–C(carborane) bond lengths are elongated with respect to all other neutral *ortho*-carborane derivatives bearing second-row substituents at one or both carbon atoms.

Introduction

Vicinal diols play an important role in many fields of chemistry, and countless variations of the carbon skeleton are known. However, surprisingly little attention has been paid to 1,2-dihydroxy-1,2-dicarba-*closo*-dodecaborane(12) (**1**), although the chemistry of the parent "*ortho*-carborane" in general is well developed.[1,2] Indeed, the synthesis of **1** was reported only in 2007.[3] Before **1** had been the subject of theoretical treatment,[4] its solid-state structure is unknown, and its chemistry has remained almost unexplored as yet.[5] By contrast, monohydroxy-*ortho*-carboranes[3,5,6] and their derivatives[6,7] (including the carborane–phosphites[8]) are much better known. We have managed to reproduce the synthesis of **1** (Scheme 1) by observing carefully controlled conditions.

Extending our interest beyond derivatives of the heavy congeners of **1**,[9–12] we have tried to start from **1** to prepare and study 1,3,2-dioxaphospholanes with an annelated 1,2-dicarba-*closo*-dodecaborane unit. It is well known that many 1,3,2-dioxaphospholane derivatives tend to dimerize or polymerize.[13–17] In this context, the presence of the three-dimensional rigid carborane framework might have a distinctive influence.



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Scheme 1. Synthesis of 1,2-dihydroxy-1,2-dicarba-*closo*-dodecaborane(12) (**1**).

Results and Discussion

Synthesis and NMR Spectroscopy

Although reactions of **1** with phosphorus halides could work, we preferred after some preliminary experiments (Scheme 1; see the Supporting Information) the transformation of **1** into the dilithium derivatives **2** or **2**($n$$Et_2O$) (Scheme 2) prior to reactions with phosphorus halides (Schemes 3, 4, 5, 6, and 7). The dilithium compounds are colorless powders, slightly soluble in toluene, and were characterized by their ^{13}C and ^7Li NMR spectroscopic data (Table S1 in the Supporting Information). The broad ^{13}C(carborane) NMR spectroscopic signals, which are at higher frequency relative to **1**, indicate changes in the C–O bonding situation as well as association and exchange equlibria in solution.

In all reactions of **2** with phosphorus trihalides, the formation of the desired 1,3,2-dioxaphospholanes **3** was accompanied by **4**, which became the major product after re-

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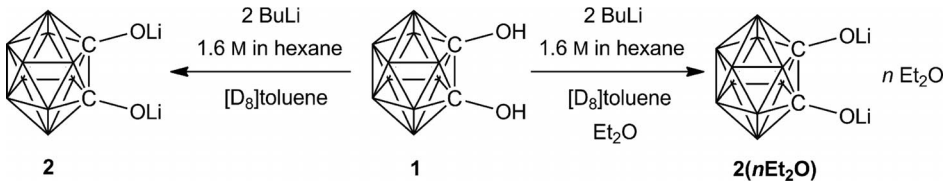
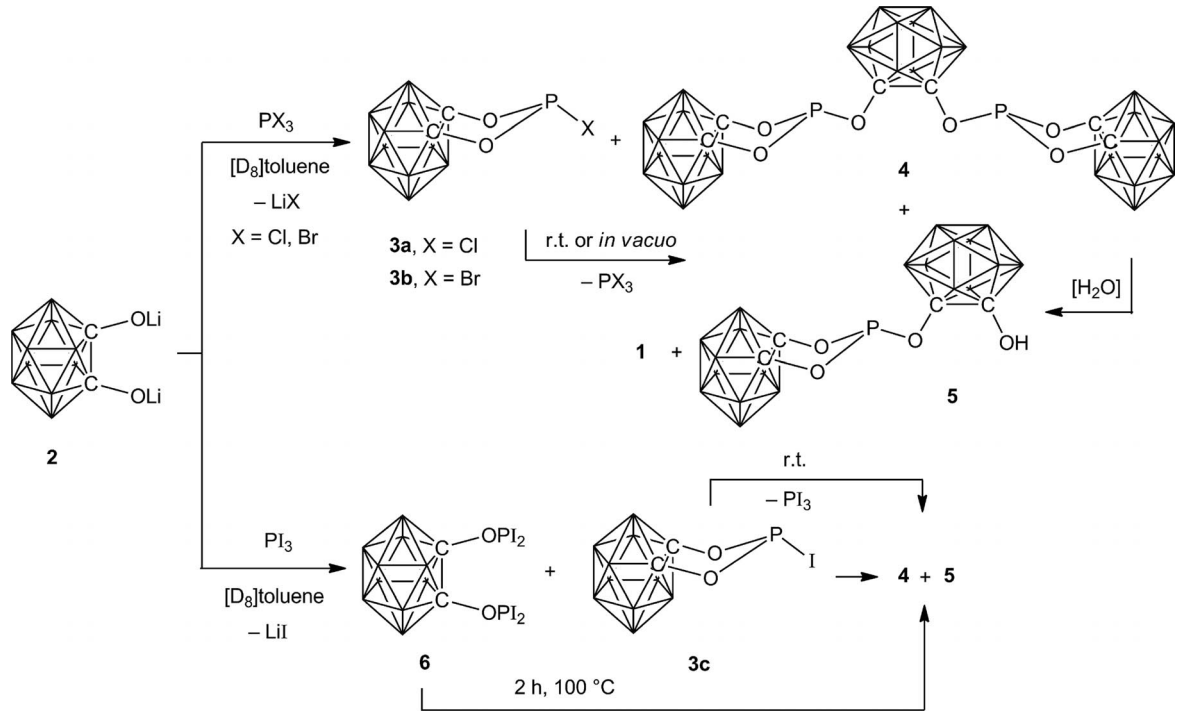


Scheme 2. Transformation of *ortho*-carborane–diol **1** into the dilithiated derivatives.



Scheme 3. Reaction of **2** with phosphorus trihalides.

moval of the volatile materials in a vacuum (Scheme 3). Frequently, a small amount of compound **5** was present, because of partial hydrolysis of **4**. Some NMR spectroscopic data of **3**–**5** could be obtained (Table 1). The equilibrium is slowly shifted towards **4** even in the absence of PX_3, and as the result of the small scale of the preparative work, hydrolysis cannot be avoided and might even become dominant (see Figure 1). In the case of iodide **3c**, the ^{31}P NMR spectra of the reaction solution clearly indicate the existence of **6**, which after some time is converted completely into **4**, accompanied by **5**. In the cases of the reaction solutions that contain chloride **3a** and bromide **3b**, there are weak ^{31}P NMR spectroscopic signals of small intensity that might belong to intermediates analogous to **6**. Signals for an appreciable amount of oxidized products could not be observed in the ^{31}P NMR spectra.

All attempts to obtain the P-organo-substituted 1,3,2-dioxaphospholanes **7**–**10** (Scheme 4) revealed their formation followed by rather fast (a few hours) conversion, mainly into dimers **11**–**14**, together with small amounts of other products, possibly oligomers, as readily shown by ^{31}P NMR spectroscopy (see also Tables 1 and 2). The formation of **7**–**10** is typically accompanied by noncyclic derivatives in various amounts (in repeated experiments) such as diastereomers $B_{10}H_{10}C_2[OP(R)X]_2$ (see also **6**), which give **7**–**10** or the dimers **11**–**14**, respectively (see Figure 2). Neither the *tert*-butyl group nor the bulky 3,5-Me_2-benzyl group prevented dimerization. Apparently, only one diastereomer of the dimers is formed, most likely for steric reasons. Purification of the dimers turned out to be difficult. However, in the case of **13**, crystalline material could be isolated that was suitable for X-ray structural analysis (see below).

The reaction of **2** in toluene with diethylamino- or ethoxyphosphorus dichloride proceeds straightforwardly to give the 1,3,2-dioxaphospholanes **15** and **16**, respectively (Scheme 5), which were sufficiently stable in solution to record a fairly complete set of NMR spectroscopic data (Table 1).

When some of reactions shown in Schemes 4 and 5 were carried out using **2**($n$$Et_2O$), only the dimers **11**–**14** were formed immediately as major products instead of the monomers **7**–**10**. Under these conditions (in the presence of ether) even the *P*-diethylamino **15** or the *P*-ethoxy derivative **17** rearranged slowly into the respective dimers **17** or **18** (Scheme 6; NMR spectroscopic data in Table 2).

Table 1. ^{13}C and ^{31}P NMR spectroscopic data[a] of the *ortho*-carborane derivatives (O_2PR monomer).

R		A′ (exp.)				A (calcd.)	A′ (calcd.)		
	Solvent	$\delta^{13}C$ [C(carb)]	$^2J(^{31}P,^{13}C_{carb})$	other $\delta^{13}C$	$\delta^{31}P$	$\delta^{31}P$	$\delta^{13}C$ [C(carb)]	$\delta^{31}P$	$^2J(^{31}P,^{13}C_{carb})$
H						263.9[b]	no min.		
Cl (**3a**)	[D$_8$]toluene	100.5	12.5	–	238.3	no min.	105.2	300.2	–16.2
Br (**3b**)	[D$_8$]toluene	100.6	12.5	–	265.5	no min.	105.1	343.3	–15.9
I (**3c**)	[D$_8$]toluene	n.o.	n.o.	–	312.7	–	–	–	–
($C_2B_{10}O_2PO$–)$_2$(C_2B_{10}) (**4**)	[D$_8$]toluene	99.4 (4COP) 95.5 (2COP)	12.5 11.0	–	183.8				
($C_2B_{10}O_2PO$–)(C_2B_{10})OH (**5**)	[D$_8$]toluene	99.9 (2COP) 97.2 (COP) 100.8 (COH)	12.7 10.3	–	184.4	no min.	110.5 103.4 104.5	214.7	not calcd.
Me						no min.	107.0	356.0	–11.1
*i*Pr (**7**)	[D$_8$]toluene	102.6	12.3	12.8 (23.6) 35.7 (44.9)	296.6	no min.	107.4	357.3	–11.3
*t*Bu (**8**)	[D$_8$]toluene	101.8	10.4	23.2 (21.2) 36.7 (46.9)	287.7	no min.	106.2	347.8	–7.4
(3,5-Me$_2$–C_6H_3)–CH_2– (**9**)	[D$_8$]toluene	n.o.	n.o.	n.o.	287.7	no min.	107.6	341.3	–11.6
Ph (**10**)	[D$_8$]toluene	102.6	10.3	129.0 (29.6) C_o 132.5 (7.0) C_m 132.9 C_p 139.2 (54.8) C_i	264.2	no min.	107.2	316.1	–11.2
NH_2						no min.	104.5	226.2	–16.2
NEt_2 (**15**)	[D$_8$]toluene	99.9	7.7	14.8 (3.1) 39.8 (23.8)	194.2	no min.	103.2	237.9	–10.0
	CD_2Cl_2	99.8	7.5	15.2 (3.3) 40.3 (23.6)	194.6				
OEt (**16**)	[D$_8$]toluene	100.9	12.5	16.6 (5.2) 63.1 (19.8)	192.8	no min.	105.2	241.3	–15.6

[a] $^nJ(^{31}P,^{13}C)$ are given in parentheses (±0.5 Hz); n.o.: not observed; no min.: calculations did not converge. [b] $^2J(^{31}P,^{13}C_{carb})$ = –11.7 Hz, $^1J(^{31}P,^1H)$ = +107.2 Hz.

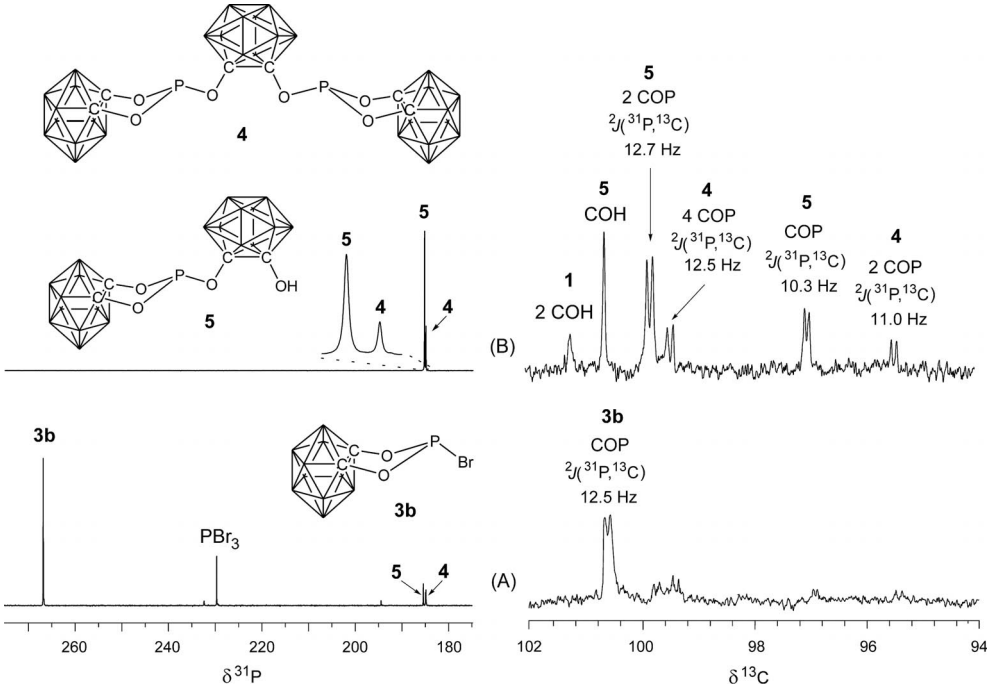
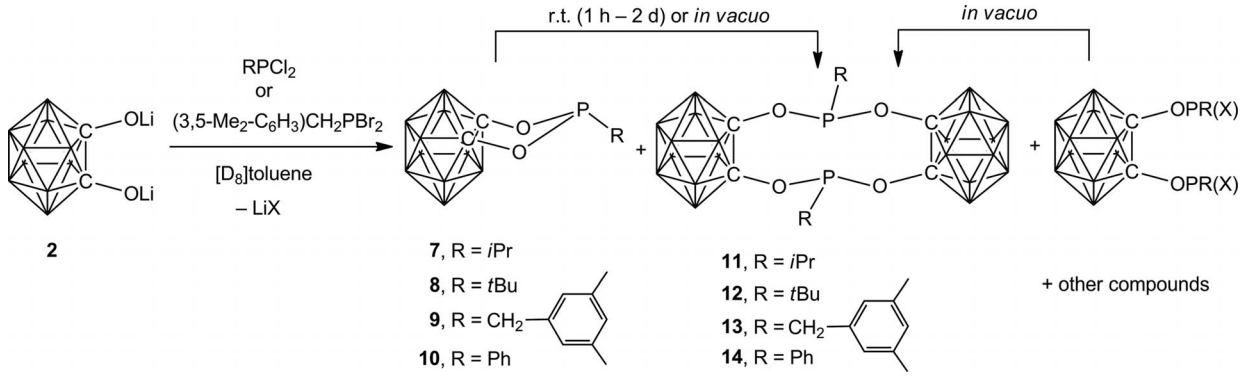


Figure 1. 202.5 MHz $^{31}P\{^1H\}$ and 125.8 MHz $^{13}C\{^1H\}$ NMR spectra of the reaction solution obtained from the reaction of **2** with PBr_3. (A) The mixture of **3b**, **4**, **5**, and PBr_3 (after 1 h at room temp. in [D$_8$]toluene). (B) The mixture **4**, **5**, and **1** after 20 h at room temp. and removing volatiles in a vacuum (in [D$_8$]toluene).



Scheme 4. Reaction of **2** with organophosphorus dihalides.

Table 2. ^{13}C and ^{31}P NMR spectroscopic data[a] of the *ortho*-carborane derivatives (O_2PR dimer).

R	Solvent	Dimer (exp.) $\delta^{13}C$[C(carb)]	$^2J(^{31}P,^{13}C_{carb})$	Other $\delta^{13}C$	$\delta^{31}P$	Dimer (calcd.) $\delta^{13}C$[C(carb)]	$\delta^{31}P$
H						107.6	215.6[b]
*i*Pr (**11**)	[D8]toluene	103.2	15.8	13.6 (17.9) 35.0 (16.1)	216.8	109.5	258.8
	CD_2Cl_2				218.2		
*t*Bu dimer (**12**)	[D8]toluene	103.0	14.0	22.9 (19.7) 37.2 (30.5)	211.0	107.6	256.1
*t*Bu trimer (**12′**)	[D8]toluene	102.9	14.0	22.9 (19.7) 37.9 (30.5)	210.5		
(3,5-Me_2–C_6H_3)–CH_2– (**13**)	[D8]toluene	102.8	16.4		206.6	108.6	246.0
	[D8]THF	103.5	15.6	21.4 45.1 (22.7) 128.9 (6.2) C_o 129.7 (8.0) C_i 130.0 (3.4) C_p 139.5 (2.7) C_m	208.3		
Ph dimer (**14**)	CD_2Cl_2	102.5	19.0	129.5 (8.4) C_m 129.7 (27.0) C_o 133.5 C_p 137.4 (14.3) C_i	190.3	107.2	203.7
Ph trimer (**14′**)	CD_2Cl_2	103.4	19.5	129.8 (9.3) C_m 130.4 (27.9) C_o 135.0 C_p 136.8 (14.7) C_i	196.6 (br)		
NEt_2 (**17**)	[D8]toluene	102.2	19.7	14.3 (3.9) 38.7 (22.8)	152.2	107.8	182.6
OEt (**18**)	[D8]toluene	99.6	16.0	16.1 (3.7) 64.7 (9.8)	134.0	104.8	190.9

[a] $^nJ(^{31}P,^{13}C)$ are given in parentheses (±0.5 Hz). [b] $^2J(^{31}P,^{13}C_{carb})$ = +21.2 Hz, $^1J(^{31}P,^1H)$ = +203.1 Hz, $^3J(^{13}C_{carb},^1H)$ = –0.7 Hz.

In addition to marked differences in $\delta^{31}P$ data for monomers and dimers, the ^{13}C(carborane) NMR spectroscopic signals show different splitting due to $^2J(^{31}PO^{13}C)$ (see, for example, Figure 3). The values $|^2J(^{31}PO^{13}C)|$ in the monomers appear to be smaller than for the dimers. Calculations have indicated a negative sign for $^2J(^{31}PO^{13}C)$ in the monomers, opposite to that for dimers (>0). This can be traced to the influence of the assumed orientation of the lone pair of electrons at phosphorus. In phosphites, ideal *syn* positions of the lone-pair orientation and O–C bond vector are expected to give rise to large and positive values $^2J(^{31}PO^{13}C)$, in contrast to ideal *anti* positions, for which the values become absolutely smaller and negative[18] (see also Figure S1 in the Supporting Information).

When samples that contain **17** in CD_2Cl_2 were left for some time, slow hydrolysis and decomposition took place (Scheme 7) and small amounts of crystalline materials could be isolated that were suitable for X-ray structural

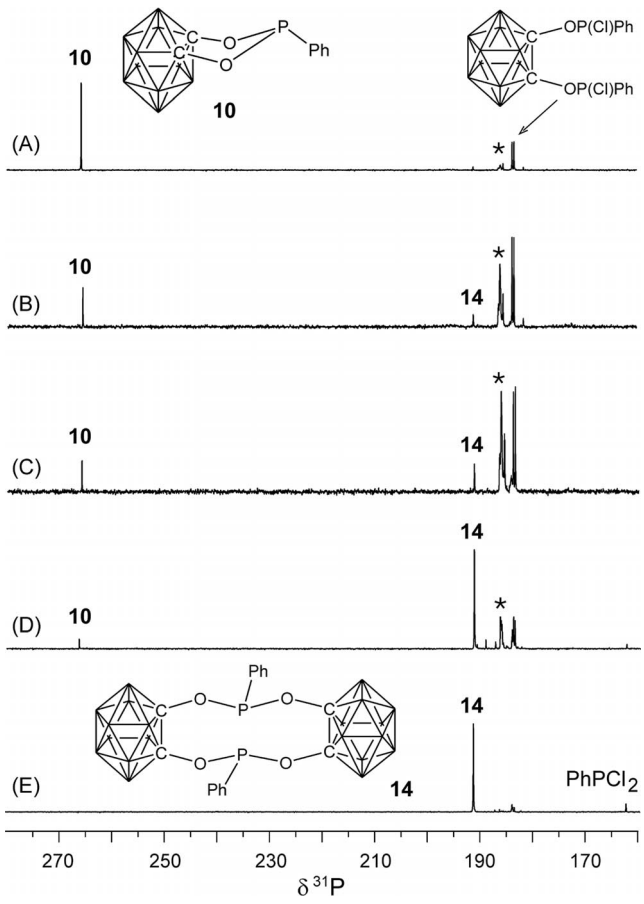


Figure 2. 202.5 MHz $^{31}P\{^{1}H\}$ NMR spectra of the reaction solution obtained from the reaction of **2** with $PhPCl_2$. (A) $^{31}P\{^{1}H\}$ NMR spectrum (in $[D_8]$toluene, at 25 °C), the mixture of **10** and $B_{10}H_{10}C_2[OP(Ph)Cl]_2$ together with unidentified intermediate products (marked by an asterisk) (after 1 d at room temp. in $[D_8]$-toluene). (B) The same spectrum as in (A) after 20 h at room temp. (C) After removing volatiles in a vacuum (in $[D_8]$toluene). (D) The same mixtures as in (C) in CD_2Cl_2 (at 25 °C). (E) The same spectrum as in (D) after 20 h at room temp. (in CD_2Cl_2, at 25 °C).

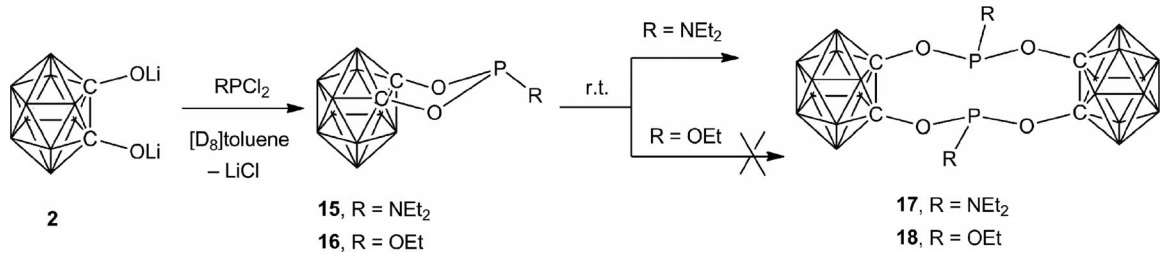
analysis. The crystal structure showed the 1,2-dihydroxy-1,2-dicarba-*closo*-dodecaborane(12) (**1**) together with $HNEt_2$/HCl.

The question of reversibility of the dimerization is addressed in Scheme 8 for the *P*-*t*Bu derivatives **12** and **8**. Upon prolonged heating of a solution of the dimer **12** in boiling toluene, the ^{31}P NMR spectroscopic signal of the monomer **8** slowly grew. By keeping the solution at 80 °C for 2 d, the equilibrium was shifted completely again towards the dimer. Apparently, oxidation and hydrolysis, to a small extent, accompanied this experiment, and the formation of **19** and **20** was observed, of which **19** could be isolated as a crystalline material, which was just suitable for X-ray analysis (see below).

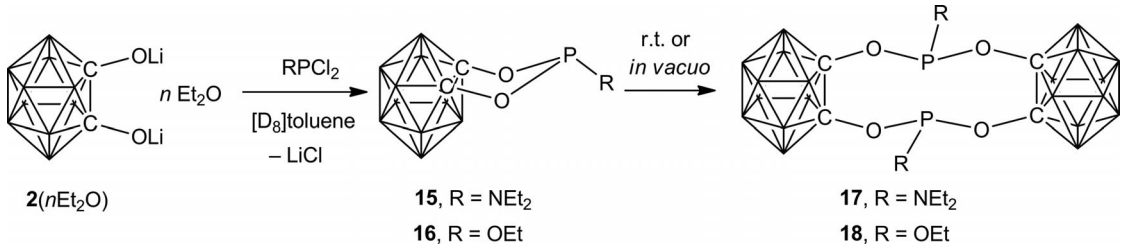
MO Calculations: Molecular Geometries, NMR Spectroscopic Parameters

The five-membered C_2O_2P rings in **3**–**5**, **7**–**10**, **15**, and **16** can in principle adopt the structures **A** or **A′** (Scheme 9). When the gas-phase structures were optimized at the B3LYP/6-311+G(d,p) level of theory[19] minima in energy were found only for **A′**. The compound with R = H, experimentally not accessible as yet, is the sole exception, for which the structure **A** was found as a minimum. This is remarkable, since according to structural evidence so far available for 1,3,2-dioxaphospholanes with an annelated benzo ring[20] an envelope structure with phosphorus in the flap is indicated, whereby the substituent R occupies the axial position (as in **A**) and leaves equatorial space for the lone pair of electrons at phosphorus.

The five-membered ring in 1,3,2-dioxaphospholanes is strained for various reasons: (1) bond angles at phosphorus are unfavorable; (2) short C–O bond lengths force the phosphorus into close distance to the carbon atoms and their substituents; (3) this is tolerated to some extent by flattening of the ring and the axial position of R; however, the annelated carborane skeleton is rigid and cannot avoid repulsive steric interactions with an axial group R, even if R is of moderate size. Thus, R = H is the only substituent that might prefer the axial position as in **A**. In **A′**, as a sort of a bad compromise, the lone pair of electrons fills the axial space around phosphorus, which might also increase the ring strain. Increasingly bulky substituents R in an equatorial position further increase the carborane/P lone-pair repulsion, which explains why bulky substituents R fail to kinetically stabilize the monomers. Indeed, the calculations show that the energies of all dimers are significantly lower than those of two monomers. The smallest difference is observed for **16**/**18** (–5.4 kcal mol^{-1}), followed by **15**/**17** (–10.7 kcal mol^{-1}), and the organo-substituted derivatives **7**/**11**, **8**/**12**, **9**/**13**, and **10**/**14** (all <–15 kcal mol^{-1}). The ^{31}P nuclei in the five-membered rings are significantly deshielded with respect to those in the dimers, which might reflect in part the ring strain and repulsive effects in the small rings.



Scheme 5. Synthesis of the 1,3,2-dioxaphospholanes **15** and **16**.



Scheme 6. Slow dimerization of the *P*-diethylamino- and *P*-ethoxy derivatives **15** and **16**.

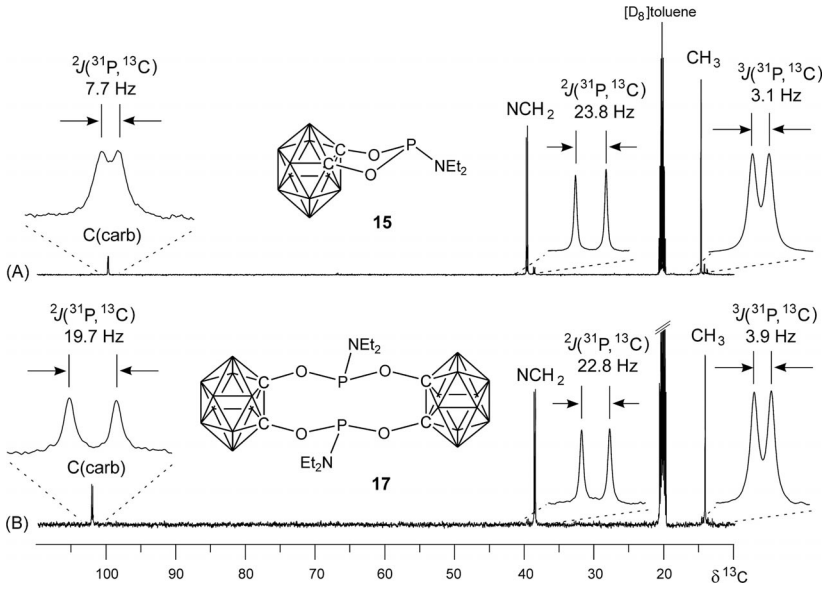
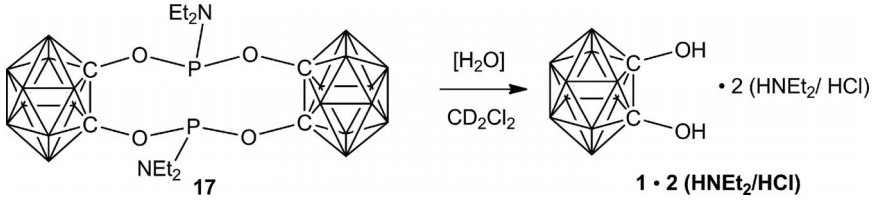
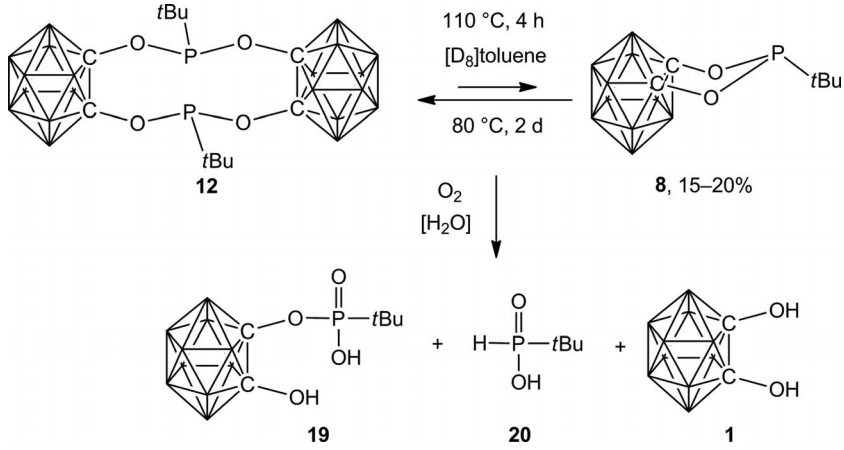


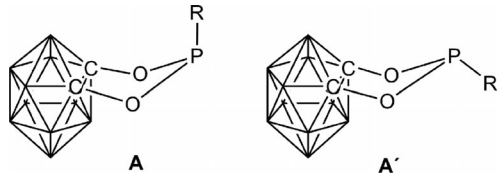
Figure 3. (A) 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of 2-diethylamino-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (**15**) (in [D_8]toluene, at 23 °C) (from the reaction of **2** with Et_2NPCl_2). (B) 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of 2,7-diethylamino-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (**17**) (in [D_8]toluene, at 23 °C) [from the reaction of **2**(nEt$_2$O) with Et_2NPCl_2].



Scheme 7. Hydrolysis of dimer **17** to 1,2 dihydroxy-1,2-dicarba-*closo*-dodecaborane(12) (**1**).



Scheme 8. Reversibility of dimerization accompanied by hydrolysis/oxidation.



Scheme 9. Conceivable conformations of 1,3,2-dioxaphospholanes with an annelated carborane unit.

The linear correlation between calculated (keeping in mind the shortcomings of the theoretical approach[21]) and experimental δ^{31}P values (Figure S2 and Table S2 in the Supporting Information) support the structural assignment for the solution state of monomers and dimers.

X-ray Analyses

The molecular structure of dimer **13** and the hydrolysis/oxidation products **1**·2(HNEt$_2$/HCl) and **19** are shown in Figures 4, 5, and 6. The repulsion between the oxygen atoms linked in vicinal positions to the rigid carborane framework is evident by the fairly long C–C distances between the carborane carbon atoms. Indeed, the structures determined here (see Table 3 for distances and angles) are the first examples of this type of molecule. Data for comparison are listed in Table 4. For neutral *ortho*-carborane derivatives with second-row substituents, the examples described here possess the longest C–C bonds, and this can be traced both to electronic and steric effects. The long C–C distances were predicted by calculations for **1**[4] and confirmed also by the results from calculations for **13** and **19**, which were carried out in this work. In the ten-membered ring in **13**, the four oxygen atoms are in a plane (mean deviation 1.9 pm), and both phosphorus atoms are shifted out of this plane (88.8, 88.5 pm). The substituents at the phosphorus atoms are symmetrically oriented in a way to minimize contacts with the carborane units. Except for the C–C distances, all other distances in the carborane moieties are found in the usual range.[1,2] This is also true for **19** and **1**·2(HNEt$_2$/HCl).

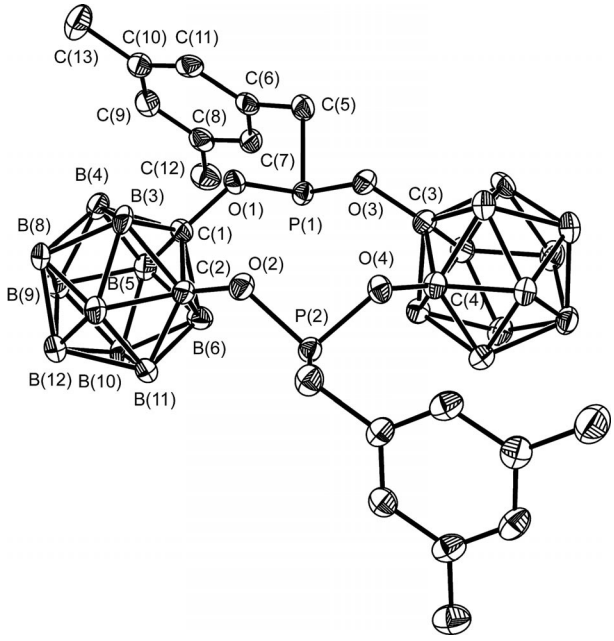


Figure 4. ORTEP plot (50% probability; hydrogen atoms are omitted for clarity) of the molecular structure of dimers **13**. For selected distances and angles, see Table 3.

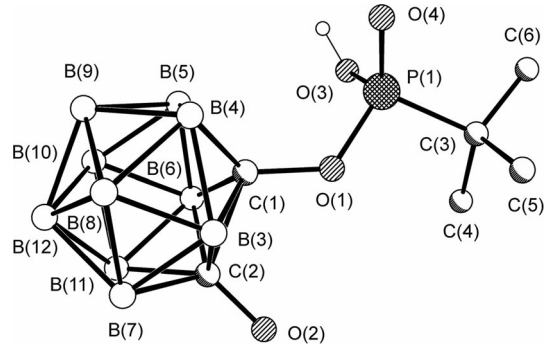


Figure 5. Molecular structures of **19** (ball-and-stick model). The structure determination was carried out using a dataset from an apparently slightly imperfect and rather small crystal [poor I/σ ratio overall = 1.7; the position of the hydrogen atom at the terminal C–O(2)H group of the carborane cage could not be determined]. For selected distances and angles, see Table 3.

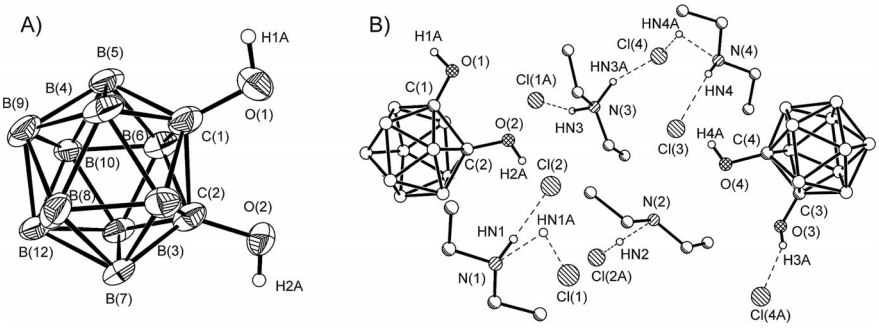


Figure 6. Molecular structures of **1** together with 2 HNEt$_2$/HCl. (A) ORTEP plot of the molecular structure of **1** [50% probability; hydrogen atoms (except of OH) and HNEt$_2$/HCl are omitted for clarity]. For selected distances and angles, see Table 3. (**B**) One view of the arrangement of molecules of **1**·2(HNEt$_2$/HCl) in the crystal lattice (ball-and-stick model) showing close intermolecular contacts: N(1)–HN1···Cl(2) 215 pm, N(3)–HN3···Cl(1A) 190 pm, N(3)–HN3A···Cl(4) 195 pm, N(4)–HN4···Cl(3) 236 pm, O(3)–H(3A)···Cl(4A) 219 pm. The direction of the O(3)–H3A bond is influenced by a hydrogen-bridge bonding to the neighboring Cl(4A) atom.

Table 3. Selected bond lengths [pm] and angles [°] of the *ortho*-carborane derivatives **13**, **13**(calcd.), **19**, **19**(calcd.), **1**·**2**($HNEt_2$/HCl), and **1**(calcd.).

	13	**13**(calcd.)	**19**	**19**(calcd.)	**1**·2($HNEt_2$/HCl)	$B_{10}H_{10}C_2(OH)_2$ **1** (calcd.)
C(1)–O(1)	136.9(5)	136.2	139.2(12)	136.9	133.4(11)	136.3
C(2)–O(2)	136.9(4)	136.6	131.6(13)	136.4	136.6(10)	136.3
C(3)–O(3)	136.6(4)	136.6			132.4(10)	
C(4)–O(4)	138.0(4)	136.2			138.0(9)	
C(1)–C(2)	171.7(5)	174.4	173.9(14)	173.7	178.5(11)	177.2
C(3)–C(4)	169.7(5)	174.4			178.7(10)	
O(1)–P(1)	167.0(2)	171.8	160.3(8)	166.5		
O(2)–P(2)	168.2(3)	169.8				
O(3)–P(1)	167.5(3)	169.8	158.2(14)	162.3		
O(4)–P	167.3(3)	171.8	147.7(7)	147.9		
P(1)–C	180.9(4)	185.1	178.2(12)	183.5		
P(2)–C	181.4(4)	185.1				
P(1)–O(1)–C(1)	121.9(2)	124.49	126.7(6)	128.0		
P(1)–O(3)–C(3)	121.4(2)	126.06				
P(2)–O(2)–C(2)	120.8(2)	126.06				
P(2)–O(4)–C(4)	123.2(2)	124.49				
O(1)–C(1)–C(2)	116.4(3)	115.50	111.6(8)	113.7	116.6(7)	115.70
O(2)–C(2)–C(1)	115.8(3)	116.88	115.7(9)	116.0	112.5(7)	115.68
O(3)–C(3)–C(4)	116.3(3)	116.87			116.6(7)	
O(4)–C(4)–C(3)	115.8(3)	115.50			113.3(7)	
O(1)–P(1)–O(3)	95.24(12)	95.90	109.4(7)	103.0		
O(2)–P(2)–O(4)	96.07(14)	95.91				
O(1)–P(1)–O(4)			111.2(4)	114.7		
O(3)–P(1)–O(4)			112.6(7)	114.1		
O(1)–P(1)–C(3)			103.0(5)	100.1		
O(3)–P(1)–C(3)			103.0(7)	104.2		
O(4)–P(1)–C(3)			116.8(5)	118.7		
Plane O(1)–C(1)–C(2)–O(2)	0.46		0.4		1.7	
Plane O(3)–C(3)–C(4)–O(4)	0.41				1.6	
Plane O(1)–O(2)–O(3)–O(4)	1.9					
Distance [pm] of P(1) from the plane O(1)–O(2)–O(3)–O(4)	88.8					
Distance [pm] of P(2) from the plane O(1)–O(2)–O(3)–O(4)	88.5					

Conclusion

For steric reasons, the annelated carborane skeleton in 1,3,2-dioxaphospholanes enhances the inherent strain in the five-membered rings. In the case of halogen substituents at phosphorus, disproportionation towards phosphite derivatives takes place, whereas with all organo substituents at phosphorus, dimers that contain ten-membered rings are the preferred products. One example of the latter was characterized by X-ray analysis. The sensitivity of all products towards hydrolysis/oxidation allowed us to isolate 1,2-dihydroxy-1,2-dicarba-*closo*-dodecaborane(12) (**1**) for the first time in a crystalline matrix that was suitable for X-ray diffraction studies.

Experimental Section

General: All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. CD_2Cl_2 was distilled from CaH_2 in an atmosphere of argon. All other solvents were distilled from Na metal in an atmosphere of argon. The starting carborane **1** was prepared as described.[3] Other starting materials were purchased from Katchem. (*ortho*-carborane), MCAT GmbH (3,5-dimethyl-benzylphosphane dibromide), and Aldrich [butyllithium (1.6 M in hexane), PCl_3 (99.999%), PBr_3 (>99.99%), PI_3 (99%), *i*$PrPCl_2$ (97%), *t*$BuPCl_2$ (97%), $PhPCl_2$ (97%), $EtOPCl_2$ (98%), Et_2NPCl_2 (97%)]. Most syntheses were carried out on a small scale sufficient for NMR spectroscopic studies. Because of the small scale, the sensitivity to hydrolysis, and the multiple reaction pathways, it proved difficult to obtain analytically pure materials. NMR spectroscopic measurements: Bruker DRX 500: ^1H, ^{11}B, ^{13}C, and ^{31}P; chemical shifts are given relative to Me_4Si [δ^1H ($CHDCl_2$) = 5.33 ppm, ($C_6D_5CD_2H$) = (2.08 ± 0.01) ppm ; $\delta^{13}C$ (CD_2Cl_2) = 53.8 ppm, ($C_6D_5CD_3$) = 20.4 ppm, (C_4D_8O) = (25.4 ± 0.1) ppm]; external BF_3·OEt_2 [$\delta^{11}B$ = (0 ± 0.3) ppm for $\Xi(^{11}B)$ = 32.083971 MHz], external LiCl, D_2O ≈ 9.7 M [δ^7Li = (0 ± 0.1) ppm for $\Xi(^7Li)$ = 38.863790 MHz], and external aqueous H_3PO_4 (85%) [$\delta^{31}P$ = 0 ppm for $\Xi(^{31}P)$ = 40.480747 MHz]. Assignments of ^1H and ^{11}B NMR spectroscopic signals are based on $^1H\{^{11}B\}$ selective heteronuclear decoupling experiments. Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for ^{12}C, ^1H, ^{11}B, ^{16}O, ^{31}P).

Table 4. C_{carb}–C_{carb} and C_{carb}–O distances [pm] for selected C_{cage}-substituted *ortho*-carborane derivatives.

	C_{carb}–C_{carb}	C_{carb}–O	References
1,2-$C_2B_{10}H_{12}$	162.9		[22]
1-OC(O)CH_2R–$C_2B_{10}H_{11}$	162.7	139.6	[7c]
1-OH–2-COOH–$C_2B_{10}H_{10}$	166.0	137.4	[7b]
1-OC(O)CH_3–2-COOH–$C_2B_{10}H_{10}$	169.4	137.8	[7d]
1-OH–2-Ph–$C_2B_{10}H_{10}$·0.5H_2O	172.3	136.6	[7e]
[1-O–2-Ph–$C_2B_{10}H_{10}$]$^-$[$C_{10}H_6(NMe_2)_2H$]$^+$	200.1(3)	124.5(3)	[7f]
[1-O–2-Ph–$C_2B_{10}H_{10}$]$^-$[Ph_3PMe]$^+$	206.5(7)	122.8(7)	[7e]
[$B_{10}H_{10}C_2O_2PCH_2$(3,5-Me_2–C_6H_3)]$_2$ (**13**)	171.7(5) 169.7(5)	136.6(4)–138.0(4)	this work
1-OH–2-[OPO(OH)(*t*Bu)]–$C_2B_{10}H_{10}$ (**19**)	173.9(14)	131.6(13) (OH) 139.2(12) (OP)	this work
1,2-$(OH)_2$–$C_2B_{10}H_{10}$·2($HNEt_2$/HCl)	178.5(11) 178.7(10)	133.4(11) 136.6(10) 132.4(10) 138.0(9)	this work
1,2-$(COOH)_2$–$C_2B_{10}H_{10}$·0.5C_2H_5OH	165.1(2)–166.0(2)		[23a]
1,2-[CH(OH)(Ar)]$_2$–$C_2B_{10}H_{10}$·*n*ROH	166.7–171.2		[23b]
1,2-$(SiMe_3)_2$–$C_2B_{10}H_{10}$	171.4(4)		[23c]
1,2-$(PPh_2)_2$–$C_2B_{10}H_{10}$	172.2(4) 169.7 (4)		[23d] [23e]
1,2-$(Ph)_2$–$C_2B_{10}H_{10}$	173.3(4)/172.0(4)		[23f]
1,2-$(SeMe)_2$–$C_2B_{10}H_{10}$	175.1(6)		[23g]
1,2-$(SPh)_2$–$C_2B_{10}H_{10}$	179.9(3)		[23h]
1,2-$(SMe)_2$–$C_2B_{10}H_{10}$	180.33(18)		[23i]

Melting points (uncorrected) were determined with a Büchi 510 melting-point apparatus.

All quantum chemical calculations were carried out using the Gaussian 09 program package.[24] Optimised geometries at the B3LYP/6-311+G(d,p) level of theory[19] were found to be minima by the absence of imaginary frequencies. NMR spectroscopic parameters were calculated[25,26] at the same level of theory. Calculated chemical shifts δ^{13}C and δ^{31}P were converted by δ^{13}C (calcd.) = $\sigma(^{13}C, TMS) - \sigma(^{13}C)$, with $\sigma(^{13}C, TMS)$ = +181 ppm and δ^{13}C (TMS) = 0 ppm, ^{31}P(calcd.) = $\sigma[^{31}P, P(OMe)_3] - \sigma(^{31}P)$ + 138 ppm; with $\sigma[^{31}P, P(OMe)_3]$ = 159.8 ppm [δ^{31}P = 138 ppm and δ^{31}P(aqueous H_3PO_4 (85%) = 0 ppm].

1,2-Dihydroxy-1,2-dicarba-*closo*-dodecaborane(12) (1): $^1H\{^{11}B\}$ NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 1.94 [br. s, 2 H, HB for $\delta(^{11}B)$ = –10.9 ppm], 2.11 [br. s, 2 H, HB for $\delta(^{11}B)$ = –16.5 ppm], 2.38 [br. s, 2 H, HB for $\delta(^{11}B)$ = –11.6 ppm], 2.45 [br. s, 4 H, HB for $\delta(^{11}B)$ = –12.8 ppm], 3.13 (s, 2 H, OH) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –16.5 (2 B), –12.8 (4 B), –11.6 (2 B), –10.9 (2 B) ppm. ^{11}B NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –16.5 [d, $^1J(^{11}B,^1H)$ = 154 Hz, 2B], –12.8 [d, $^1J(^{11}B,^1H)$ = 175 Hz, 4B], –11.6 [d, $^1J(^{11}B,^1H)$ = 172 Hz, 2B], –10.9 [d, $^1J(^{11}B,^1H)$ = 160 Hz, 2B] ppm.

Dilithium 1,2-Dicarba-*closo*-dodecaborane-1,2-diolate [(1,2-$C_2B_{10}H_{10}$)O_2Li_2] (2): Butyllithium (0.40 mL of a 1.6 M solution in hexane, 0.64 mmol) was added to a solution of carborane **1** (55.8 mg, 0.32 mmol) in [D_8]toluene (0.1 mL) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. The white precipitate was separated using a centrifuge and by decanting the supernatant liquid. The residue as a white solid was dried in a vacuum (2 h, 8×10^{-3} Torr) to give 47.9 mg (80%) of **2** as a white powder. $^1H\{^{11}B\}$ NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 2.00 (br. s, 2 H), 2.21 (br. s, 2 H), 2.27 (br. s, 4 H), 2.42 (br. s, 2 H) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –17.7 (6 B), –14.2 (2 B), –9.6 (2 B) ppm.

Dilithium 1,2-Dicarba-*closo*-dodecaborane-1,2-diolate [(1,2-$C_2B_{10}H_{10}$)O_2Li_2](nEt$_2$O) [2(nEt$_2$O)]: Butyllithium (0.28 mL of a 1.6 M solution in hexane, 0.45 mmol) was added to a solution of carborane **1** (39.6 mg, 0.225 mmol) in [D_8]toluene (0.1 mL) and Et_2O (0.05 mL) at 0 °C. The reaction mixture was stirred for 1 h at room temp., during which a layer of oil from **2**(nEt$_2$O) formed at the bottom. The top layer was decanted after centrifugation, and the oily residue was dried in a vacuum (2 h, 8×10^{-3} Torr) to give 21.6 mg of **2**(Et_2O). The remaining oily solid was dissolved in [D_8]toluene. Compound **2**(Et_2O) (n = 1): $^1H\{^{11}B\}$ NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 1.07, 3.30 (t, q, ≈10 H, OEt_2), 2.35 (br. s, 4 H), 2.60 (br. s, 6 H) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –18.2 (6 B), –14.3 (2 B), –8.5 (2 B) ppm.

Then the excess amount of Et_2O (0.05 mL) was added in portions to a suspension of **2**(Et_2O) in [D_8]toluene. Compound **2**(nEt$_2$O) (n = 40): $^1H\{^{11}B\}$ NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 1.05, 3.30 (t, q, ≈400 H, OEt_2), 2.00 (br. s, 4 H), 2.43 (br. s, 6 H) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz; [D_8]toluene; 25 °C): δ = –18.9 (6 B), –14.3 (2 B), –8.3 (2 B) ppm.

Reaction of 2 with PCl_3

2-Chloro-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (3a), 1,2-Bis{4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholan-2-yl}oxy-1,2-dicarba-*closo*-dodecaborane(12) (4), and 1-{4,5-[1,2-Dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholan-2-yl}oxy-2-hydroxy-1,2-dicarba-*closo*-dodecaborane-(12) (5): Freshly prepared [(1,2-$C_2B_{10}H_{10}$)O_2Li_2] (**2**) (48.7 mg, 0.26 mmol) was dissolved in [D_8]toluene (0.5 mL); the solution was cooled to –30 °C, and PCl_3 (0.023 mL, 0.26 mmol) was injected through a microsyringe. After stirring the reaction mixture for 2 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **3a** (65%), **4** (25%), and **5** (10%), together with PCl_3 (^{31}P NMR spectroscopy). Volatile materials were removed in a vacuum to give a

mixture that contained **3a** (15%), **4** (70%), and **5** (15%). After 3 d at room temp., the mixture contained only **4** and **5**. A white powder that consisted of products **4** and **5** was formed that showed rather low solubility in [D$_8$]toluene. Compound **5**: ^{1}H NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 3.88 (br. s, 1 H, OH) ppm. EI-MS (70 eV) for $C_4H_{21}O_4B_{20}P$ (380.40): *m*/*z* (%) = 380 (5) [M$^+$], 222 (100) [$C_2H_{10}B_{10}O_2POH$], 176 (80) [$C_2H_{12}B_{10}O_2$].

Reaction of 2 with PBr_3

2-Bromo-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (3b), (4), and (5): The same procedure as for **3a** was applied, and after addition of PBr_3 (0.014 mL, 0.148 mmol) a mixture that contained **3b** (75%), **4** (10%), and **5** (15%), together with PBr_3 and small amount of unidentified side products (^{31}P NMR spectroscopy) was obtained. Volatile materials were removed in a vacuum to give the final mixture that contained **3b** (70%), **4** (15%), and **5** (15%). Compound **3b**: ^{1}H{^{11}B} NMR (500.13 MHz, [D$_8$]-toluene, 25 °C): δ = 1.92 [br. s, 1 H, HB for δ(^{11}B) = –4.2 ppm], 2.14 [br. s, 1 H, HB for δ(^{11}B) = –14.1 ppm], 2.22 [br. s, 3 H, HB for δ(^{11}B) = –12.3, –13.5 ppm], 2.49 [br. s, 2 H, HB for δ(^{11}B) = –15.3 ppm], 2.54 [br. s, 2 H, HB for δ(^{11}B) = –14.6 ppm], 2.33 [br. s, 1 H, HB for δ(^{11}B) = –8.8 ppm] ppm. ^{11}B{^{1}H} NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –15.3 (2 B), –14.6 (2 B), –14.1 (1 B), –13.5 (1 B), –12.3 (2 B), –8.8 (1 B), –4.2 (1 B) ppm. ^{11}B NMR (160.5 MHz; [D$_8$]toluene; 25 °C): δ = –15.3 (d, 2 B), –14.6 (d, 2 B), –14.1 (1 B), –13.5 (1 B), –12.3 [d, ^1J(^{11}B,^{1}H) = 165 Hz, 2B], –8.8 [d, ^1J(^{11}B,^{1}H) = 179 Hz, 1B], –4.2 [d, ^1J(^{11}B,^{1}H) = 181 Hz, 1B] ppm.

Reaction of 2 with PI_3

2-Iodo-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (3c), (4), (5), and 1,2-Bis(diiodophosphanyl)oxy-1,2-dicarba-*closo*-dodecaborane(12) (6): Again the procedure described for **3a** was applied, and PI_3 (90 mg, 0.22 mmol) was added. Insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **3c** (25%) and **6** (75%) together with PI_3 (^{31}P NMR spectroscopy). After 2 h at 100 °C, the mixture contained **5** and **1** together with PI_3. Compound **6:** ^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]toluene, 25 °C): δ = 93.3 [^2J(^{31}P,$^{13}C_{carb}$) = 14.5 Hz] ppm. ^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]toluene, 25 °C): δ = 102.1 ppm.

Reactions of 2 with RPX_2

2-(1-Methylethyl)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (7) and 2,7-Di(1-methylethyl)-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (11): Freshly prepared [(1,2-$C_2B_{10}H_{10}$)O_2Li_2] (**2**) (25.4 mg, 0.135 mmol) was dissolved in [D$_8$]toluene (0.5 mL); the solution was cooled to –30 °C, and *i*PrPCl$_2$ (19.6 mg, 0.017 mL, 0.135 mmol) was injected through a microsyringe. After stirring the reaction mixture for 2 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **7** (80%), **11** (10%), $B_{10}H_{10}C_2$[OPCl(*i*Pr)]$_2$ (10%), and a small amount of unidentified intermediate products (from ^{31}P NMR spectroscopy). After 24 h at room temp., the mixture contained **7** (5%), **11** (85%), and $B_{10}H_{10}C_2$[OPCl(*i*Pr)]$_2$ (10%). Volatile materials were removed in a vacuum to give **11** as a white solid that showed rather low solubility in [D$_8$]toluene. The remaining solid of **11** was washed with [D$_8$]toluene and dried in a vacuum. Compound **7**: ^{1}H NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.51 [dd, ^3J(^{31}P,^{1}H) = 17.7, ^3J(^{1}H,^{1}H) = 7.1 Hz, 6 H, CH$_3$], 1.23 [dsept ^2J(^{31}P,^{1}H) = 3.5, ^3J(^{1}H,^{1}H) = 7.1 Hz, 1 H, PCH] ppm. **$B_{10}H_{10}C_2$[OPCl(*i*Pr)]$_2$**: ^{1}H NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.83 (m, 12 H, CH$_3$), 1.54, 1.61 (dsept, dsept, 1 H, 1 H, PCH) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]toluene, 25 °C): δ = 14.7 [d, ^2J(^{31}P,^{13}C) = 17.6 Hz, CH$_3$], 14.8 [d, ^2J(^{31}P,^{13}C) = 17.6 Hz, CH$_3$], 36.1 [d, ^1J(^{31}P,^{13}C) = 29.4 Hz, CH], 36.2 [d, ^1J(^{31}P,^{13}C) = 29.4 Hz, CH], 102.5 [d, ^2J(^{31}P,^{13}C) = 14.0 Hz, C(carb)], 102.6 [d, ^2J(^{31}P,^{13}C) = 14.0 Hz, C(carb)] ppm. ^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]toluene, 25 °C): δ = 213.4, 213.5 ppm.

2-(1,1-Dimethylethyl)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (8) and 2,7-Bis(1,1-dimethylethyl)-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (12): Freshly prepared [(1,2-$C_2B_{10}H_{10}$)O_2Li_2] **2** (24.9 mg, 0.132 mmol) was dissolved in [D$_8$]toluene (0.4 mL); the solution was cooled to –30 °C, and a solution of *t*BuPCl$_2$ (0.021 mg, 0.132 mmol) in [D$_8$]toluene (0.2 mL) was added. After 1 h at room temp., no reaction had taken place. After stirring the reaction solution for 24 h at room temp., the mixture contained **8** (60%), **12** (30%), and **12′** (10%, possibly a trimer), together with *t*BuPCl$_2$ (^{31}P NMR spectroscopy). Insoluble materials were separated by centrifugation, the clear liquid was collected, and volatile materials were removed in a vacuum to give a mixture that contained **8** (55%), **12** (35%), and **12′** (trimer) (10%). After 2–3 d at room temp., the mixture contained **12** (70%) and **12′** (trimer) (30%). A white powder that consisted of products **12/12′** was formed that showed rather low solubility in [D$_8$]toluene and a somewhat better solubility in CD_2Cl_2. Compound **8**: ^{1}H NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.58 [d, ^3J(^{31}P,^{1}H) = 13.9 Hz, 9 H, CH$_3$] ppm. Compound **12′** (trimer): ^{1}H NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.76 [d, ^3J(^{31}P,^{1}H) = 15.0 Hz, 27 H, CH$_3$] ppm.

2-(3,5-Dimethylphenylmethyl)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (9) and 2,7-Bis(3,5-dimethylphenylmethyl)-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (13): Freshly prepared [(1,2-$C_2B_{10}H_{10}$)O_2Li_2] (**2**) (33.3 mg, 0.177 mmol) was dissolved in [D$_8$]toluene (0.5 mL); the solution was cooled to –30 °C, and (3,5-Me$_2$–C$_6$H$_3$)CH_2PBr_2 (54.9 mg, 0.177 mmol) was injected through a microsyringe. After 30 min at room temp., the mixture contained **9** (20%), **13** (10%), and unidentified intermediate products (70%), together with (3,5-Me$_2$–C$_6$H$_3$)CH_2PBr_2 (from ^{31}P NMR spectroscopy). After stirring the reaction mixture for 24 h at room temp., the mixture contained **13** (60%) and intermediate products (40%), together with (3,5-Me$_2$–C$_6$H$_3$)CH_2PBr_2 (from ^{31}P NMR spectroscopy). Insoluble materials were separated by centrifugation, the clear liquid was collected, and volatile materials were removed in a vacuum. The remaining white solid was dissolved in [D$_8$]toluene and the mixture was heated by 65 °C for 4 h. A white powder that consisted of products **13** was formed that showed rather low solubility in [D$_8$]toluene and CD_2Cl_2. Insoluble materials were separated by centrifugation and washed with [D$_8$]toluene. The residue was dissolved in CD_2Cl_2, the solid on the surface of the solution was collected and dried in a vacuum to give **13** as a white solid.

2-Phenyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (10) and 2,7-Diphenyl-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (14): Freshly prepared [(1,2-$C_2B_{10}H_{10}$)O_2Li_2] (**2**) (27.7 mg, 0.147 mmol) was dissolved in [D$_8$]toluene (0.5 mL); the solution was cooled to –30 °C, and PhPCl$_2$ (26.3 mg, 0.020 mL, 0.147 mmol) was injected through a microsyringe. After stirring the reaction mixture for 2 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **10** (50%), $B_{10}H_{10}C_2$[OPCl(Ph)]$_2$ (25%), and unidentified intermediate products (25%) (from ^{31}P NMR spectroscopy). After 24 h at room

temp., the mixture contained **10** (5%), **14** (<5%), $B_{10}H_{10}C_2$[OPCl(Ph)]$_2$ (35%), and intermediate products (55%). Volatile materials were removed in a vacuum, and the residue was dissolved in CD_2Cl_2. The remaining mixture contained **10** (<5%), **14** (<35%), $B_{10}H_{10}C_2$[OPCl(Ph)]$_2$ (25%), and intermediate products (35%). After 24 h at room temp., the mixture contained **14** (80%), $B_{10}H_{10}C_2$[OPCl(Ph)]$_2$ (15%), and $PhPCl_2$ (Figure 1).

2-Diethylamino-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (15): Freshly prepared [(1,2-$C_2B_{10}H_{10}$)O_2Li_2] (**2**) (47.9 mg, 0.255 mmol) was dissolved in [D_8]toluene (0.5 mL); the solution was cooled to –30 °C, and Et_2NPCl_2 (44.3 mg, 0.037 mL, 0.255 mmol) was injected through a microsyringe. After stirring the reaction mixture for 1 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **15** (95%) and **17** (<5%) as a white oil. After two weeks in [D_8]toluene at room temp., the mixture contained **15** (80%) and **17** (20%). Compound **15**: $^1H\{^{11}B\}$ NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 0.64 [t, $^3J(^1H,^1H)$ = 7.1 Hz, 6 H, CH_3], 2.25 [br. s, 1 H, HB for $\delta(^{11}B)$ = –15.8 ppm], 2.37 [br. s, 1 H, HB for $\delta(^{11}B)$ = –13.5 ppm], 2.45 [br. s, 2 H, HB for $\delta(^{11}B)$ = –11.5 ppm], 2.62 [dq, $^3J(^1H,^1H)$ = 7.1, $^3J(^{31}P,^1H)$ = 10.9 Hz, 4 H, $PNCH_2$], 2.70 [br. s, 3 H, HB for $\delta(^{11}B)$ = –15.3, –3.3 ppm], 2.80 [br. s, 2 H, HB for $\delta(^{11}B)$ = –13.5 ppm], 2.97 [br. s, 1 H, HB for $\delta(^{11}B)$ = –8.1 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –15.8 (1 B), –15.3 (2 B), –13.5 (3 B), –11.5 (2 B), –8.1 (1 B), –3.3 (1 B) ppm. ^{11}B NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –15.8 [d, $^1J(^{11}B,^1H)$ = 156 Hz, 1B], –15.3 [d, $^1J(^{11}B,^1H)$ = 168 Hz, 2B], –13.5 [d, $^1J(^{11}B,^1H)$ = 153 Hz, 3B], –11.5 [d, $^1J(^{11}B,^1H)$ = 153 Hz, 2B], –8.1 [d, $^1J(^{11}B,^1H)$ = 174 Hz, 1B], –3.3 [d, $^1J(^{11}B,^1H)$ = 182 Hz, 1B] ppm.

Volatile materials were removed in a vacuum and the residue was dissolved in CD_2Cl_2. This solution was left at room temperature for two weeks, after which transparent colorless crystals of **1**·2($HNEt_2$/HCl) (m.p. 260–270 °C) suitable for X-ray analysis could be collected. ^1H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 1.37 [t, 6 H, CH_3, $^3J(^1H,^1H)$ = 7.4 Hz], 3.04 (q, 4 H, NCH_2), 8.48 (s, 2 H, COH) ppm.

2-Ethoxy-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-dioxaphospholane (16): Freshly prepared [(1,2-$C_2B_{10}H_{10}$)O_2Li_2] (**2**) (33.2 mg, 0.177 mmol) was dissolved in [D_8]toluene (0.5 mL); the solution was cooled to –30 °C, and $EtOPCl_2$ (26.0 mg, 0.02 mL, 0.177 mmol) was injected through a microsyringe. After stirring the reaction mixture for 1 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **16** (80%) and a small amount of unidentified products. Volatile materials were removed in a vacuum to give the mixture contained **16** (95%) and **18** (<5%) as a white oil. Compound **16**: $^1H\{^{11}B\}$ NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 0.68 [t, $^3J(^1H,^1H)$ = 7.0 Hz, 3 H, CH_3], 2.25 [br. s, 1 H, HB for $\delta(^{11}B)$ = –14.5 ppm], 2.31 [br. s, 1 H, HB for $\delta(^{11}B)$ = –4.8 ppm], 2.35 [br. s, 1 H, HB for $\delta(^{11}B)$ = –13.5 ppm], 2.37 [br. s, 2 H, HB for $\delta(^{11}B)$ = –12.4 ppm], 2.67 [br. s, 2 H, HB for $\delta(^{11}B)$ = –15.3 ppm], 2.76 [br. s, 2 H, HB for $\delta(^{11}B)$ = –14.5 ppm], 2.85 [br. s, 1 H, HB for $\delta(^{11}B)$ = –5.5 ppm], 3.27 [dq, $^3J(^1H,^1H)$ = 7.0 Hz, $^3J(^{31}P,^1H)$ = 9.9 Hz, 2 H, $POCH_2$] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –15.3 (2 B), –14.5 (3 B), –13.5 (1 B), –12.4 (2 B), –5.5 (1 B), –4.8 (1 B) ppm. ^{11}B NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –15.3 [d, $^1J(^{11}B,^1H)$ = 162 Hz, 2B], –14.5 [d, $^1J(^{11}B,^1H)$ = 142 Hz, 3B], –13.5 [d, $^1J(^{11}B,^1H)$ = 160 Hz, 1B], –12.4 [d, $^1J(^{11}B,^1H)$ = 164 Hz, 2B], –5.5 [d, $^1J(^{11}B,^1H)$ = 190 Hz, 1B], –4.8 [d, $^1J(^{11}B,^1H)$ = 180 Hz, 1B] ppm. EI-MS (70 eV) for $C_4H_{15}O_3B_{10}P$ (250.2): *m*/*z* (%) = 250 (55) [M^+], 222 (65) [$M^+ - C_2H_4$], 175 (100) [$C_2H_{11}B_{10}O_2$].

Reactions of 2(nEt$_2$O) with RPX_2

2,7-Di(1-methylethyl)-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano-(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (11): A suspension of **2**(nEt$_2$O) (0.136 mmol) in [D_8]toluene was cooled to –30 °C, and iPrPCl$_2$ (19.7 mg, 0.017 mL, 0.136 mmol) was injected through a microsyringe. After stirring the reaction mixture for 2 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. Volatile materials were removed in a vacuum to give **11** as a white solid together with side products $B_{10}H_{10}C_2$[OPCl(iPr)]$_2$ (ca. 5%). The remaining solid of **11** was washed with [D_8]toluene and dried in a vacuum; m.p. 160–170 °C. Compound **11**: $^1H\{^{11}B\}$ NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 0.75 [dd, $^3J(^{31}P,^1H)$ = 16.7, $^3J(^1H,^1H)$ = 7.3 Hz, 12 H, CH_3], 1.39 [dsept $^2J(^{31}P,^1H)$ = 3.8, $^3J(^1H,^1H)$ = 7.3 Hz, 2 H, PCH], 2.23, 2.26 [br. s, br. s, 2 H, 2 H, HB for $\delta(^{11}B)$ = –16.0 ppm], 2.50 [br. s, 8 H, HB for $\delta(^{11}B)$ = –10.6, –13.0 ppm], 2.54 [br. s, 4 H, HB for $\delta(^{11}B)$ = –13.0 ppm], 2.65 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.5 ppm], 3.25 [br. s, 2 H, HB for $\delta(^{11}B)$ = –13.0 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –16.0 (4 B), –13.0 (10 B), –10.6 (4 B), –9.5 (2 B) ppm. ^{11}B NMR (160.5 MHz, [D_8]toluene, 25 °C): δ = –16.0 [d, $^1J(^{11}B,^1H)$ = 144 Hz, 4B], –13.0 (d, 10B), –10.6 [d, $^1J(^{11}B,^1H)$ = 160 Hz, 4B], –9.5 (d, 2 B) ppm. EI-MS (70 eV) for $C_{10}H_{34}O_4B_{20}P_2$ (496.5): *m*/*z* (%) = 496 (15) [M^+], 453 (40) [$M^+ - C_3H_7$], 264 (10) [(M/2 + O)$^+$], 248 (5) [M/2$^+$], 238 (15), 232 (10) [(M/2 – O)$^+$], 205 (50) [M/2$^+ - C_3H_7$], 176 (10) [$C_2H_{12}B_{10}O_2$], 146 (10), 44 (100) [C_3H_8].

2,7-Bis(1,1-dimethylethyl)-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (12): A suspension of **2**(nEt$_2$O) (0.195 mmol) in [D_8]toluene was cooled to –30 °C, and a solution of tBuPCl$_2$ (0.031 mg, 0.195 mmol) in [D_8]toluene (0.2 mL) was added. After stirring the reaction mixture for 2 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **12** (70%), **12′** (possibly a trimer) (20%), a small amount of unidentified products (10%) together with tBuPCl$_2$ (^{31}P NMR spectroscopy). The solution was heated by 80 °C for 5 d. A white powder that consisted of products **12** was formed that showed rather low solubility in [D_8]toluene. Insoluble solids were separated by centrifugation, washed with [D_8]toluene and dried in a vacuum to give **12** as a white solid; m.p. 185–195 °C. Compound **12**: ^1H NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 0.86 [d, $^3J(^{31}P,^1H)$ = 15.1 Hz, 18 H, CH_3] ppm. EI-MS (70 eV) for $C_{12}H_{38}O_4B_{20}P_2$ (524.6): *m*/*z* (%) = 524 (3) [M^+], 467 (100) [$M^+ - C_4H_9$], 412 (10) [$M^+ - C_4H_9 - C_4H_8$], 351 (3), 205 (5), 57 (100) [$C_4H_9^+$].

2,7-Bis(3,5-dimethylphenylmethyl)-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (13): A suspension of **2**(nEt$_2$O) (0.21 mmol) in [D_8]toluene was cooled to –30 °C, and (3,5-Me_2–C_6H_3)CH_2PBr_2 (65.0 mg, 0.21 mmol) was injected through a microsyringe. After stirring the reaction mixture for 2 h at room temperature, insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **13** (30%) and unidentified intermediate products (70%), together with (3,5-Me_2–C_6H_3)CH_2PBr_2 (from ^{31}P NMR spectroscopy). Volatile materials were removed in a vacuum. The residue was dissolved in CD_2Cl_2, and the solid swimming on top of the solution was collected and dried in a vacuum to give **13** (30.5 mg, 45%) as a white solid; m.p. 240–245 °C. Transparent colorless crystals of **13** for X-ray analysis were grown from the CD_2Cl_2 solution after one week at –30 °C. $^1H\{^{11}B\}$ NMR (500.13 MHz, [D_8]toluene, 25 °C): δ = 2.05 (s, 12 H, CH_3), 2.23, 2.30 [br. s, br. s, 4 H, 2 H, HB for $\delta(^{11}B)$ = –15.9 ppm], 2.42 [br. s, 10 H, HB for $\delta(^{11}B)$ = –11.0, –13.1 ppm], 2.71 [br. s, 2 H, HB for $\delta(^{11}B)$ =

–13.1 ppm], 2.74 [d, $^2J(^{31}P,^1H)$ = 9.7 Hz, 4 H, PCH_2], 3.24 [br. s, 2 H, HB for $\delta(^{11}B)$ = –13.1 ppm], 6.58 (s, 4 H, CH, Ph), 6.66 (s, 2 H, CH, Ph) ppm. ^1H NMR (500.13 MHz, [D$_8$]thf, 25 °C): δ = 2.30 (s, 12 H, CH_3), 3.22 [d, $^2J(^{31}P,^1H)$ = 9.1 Hz, 4 H, PCH_2], 6.88 (s, 4 H, CH), 6.95 (s, 2 H, CH) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]-toluene, 25 °C): δ = –15.9 (6 B), –13.1 (10 B), –11.0 (4 B) ppm. EI-MS (70 eV) for $C_{22}H_{42}O_4B_{20}P_2$ (648.7): *m/z* (%) = 649 (3) [M$^+$], 530 (70) [M$^+$ – C_9H_{11}], 341 (5) [(M/2 + O)$^+$], 325 (10) [M/2$^+$], 361 (4), 206 (25) [M/2$^+$ – C_9H_{11}], 176 (4) [$C_2H_{12}O_2B_{10}$], 147 (10), 119 (100) [C_9H_{11}].

2,7-Diphenyl-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (14): A suspension of **2**(*n*Et$_2$O) (0.145 mmol) in [D$_8$]toluene was cooled to –30 °C, and $PhPCl_2$ (0.026 mg, 19.7 mL, 0.145 mmol) in [D$_8$]toluene (0.2 mL) was injected through a microsyringe. After stirring the reaction mixture for 2 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **14** (85%) and **14′** (possibly a trimer) (15%), together with $PhPCl_2$ (from ^{31}P NMR spectroscopy). Volatile materials were removed in a vacuum, washed with [D$_8$]toluene and dried in a vacuum to give a mixture that contained **14** (90%) and **14′** (trimer) (10%) as a white solid. $^1H\{^{11}B\}$ NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 1.85, 1.89 [br. s, br. s, 2 H, 2 H, HB for $\delta(^{11}B)$ = –16.1 ppm], 2.00 [br. s, 4 H, HB for $\delta(^{11}B)$ = –10.9 ppm], 2.29 [br. s, 4 H, HB for $\delta(^{11}B)$ = –13.4 ppm], 2.55 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.6 ppm], 2.60 [br. s, 4 H, HB for $\delta(^{11}B)$ = –13.4 ppm], 3.45 [br. s, 2 H, HB for $\delta(^{11}B)$ = –13.4 ppm], 7.52 (m, 4 H, Ph), 7.63 (m, 2 H, Ph), 7.69 (m, 4 H, Ph) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, CD_2Cl_2, 25 °C): δ = –16.1 (4 B), –13.4 (10 B), –10.9 (4 B), –9.6 (2 B) ppm. ^{11}B NMR (160.5 MHz, CD_2Cl_2, 25 °C): δ = –16.1 [d, $^1J(^{11}B,^1H)$ = 162 Hz, 4B], –13.4 [d, $^1J(^{11}B,^1H)$ = 150 Hz, 10B], –10.9 [d, $^1J(^{11}B,^1H)$ = 164 Hz, 4B], –9.6 (2B) ppm.

2,7-Diethylamino-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano-(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (17): A suspension of **2**(*n*Et$_2$O) (0.12 mmol) in [D$_8$]toluene was cooled to –30 °C, and Et_2NPCl_2 (20.9 mg, 0.017 mL, 0.12 mmol) was injected through a microsyringe. After stirring the reaction mixture for 1 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **15** (70%) and dimer **17** (30%), together with Et_2NPCl_2 (^{31}P NMR spectroscopy). Volatile materials were removed in a vacuum to give the dimer **17** as a white solid together with **15** (<5%); m.p. 120–125 °C (decomposition). Compound **17**: $^1H\{^{11}B\}$ NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.79 [t, $^3J(^1H,^1H)$ = 7.1 Hz, 12 H, CH_3], 2.29 [br. s, 6 H, HB for $\delta(^{11}B)$ = –16.2 ppm], 2.51 [br. s, 10 H, HB for $\delta(^{11}B)$ = –11.0, –13.4 ppm], 2.71 [br. s, 2 H, HB for $\delta(^{11}B)$ = –13.4 ppm], 2.75 [dq, $^3J(^1H,^1H)$ = 7.1 Hz, $^3J(^{31}P,^1H)$ = 11.2 Hz, 8 H, $PNCH_2$], 3.22 [br. s, 2 H, HB for $\delta(^{11}B)$ = –13.4 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –16.2 (6 B), –13.4 (8 B), –11.0 (6 B) ppm. ^{11}B NMR (160.5 MHz, [D$_8$]toluene, 25 °C): δ = –16.2 [d, $^1J(^{11}B,^1H)$ = 140 Hz, 6B], –13.4 [d, $^1J(^{11}B,^1H)$ = 157 Hz, 8B], –11.0 [d, $^1J(^{11}B,^1H)$ = 155 Hz, 6B] ppm. EI-MS (70 eV) for $C_{12}H_{40}N_2O_4B_{20}P_2$ (554.6): *m/z* (%) = 554 (5) [M$^+$], 482 (25) [M$^+$ – NEt_2], 277 (40) [M/2$^+$], 262 (100) [(M/2 – CH_3)$^+$], 248 (10) [(M/2 – C_2H_5)$^+$], 233 (3) [(M/2 – C_2H_5 – CH_3)$^+$], 222 (5) [$C_2H_{11}B_{10}O_3P$], 205 (30) [(M/2 – NEt_2)$^+$], 175 (25) [$C_2H_{11}B_{10}O_2$].

2-Ethoxy-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-dioxa-2-phospholane (16) and 2,7-Diethoxy-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraoxacyclodecane (18): A suspension of **2**(*n*Et$_2$O) (0.175 mmol) in [D$_8$]toluene was cooled to –30 °C, and $EtOPCl_2$ (25.7 mg, 0.02 mL, 0.175 mmol) was injected through a microsyringe. After stirring the reaction mixture for 1 h at room temp., insoluble materials were separated by centrifugation, and the clear liquid was collected. The mixture contained **16** (90%), **18** (<5%), and a small amount of unidentified products (5%), together with $EtOPCl_2$ (from ^{31}P NMR spectroscopy). After 24 h at room temp., the mixture contained **16** (80%), **18** (15%), and a small amount of unidentified products (5%), together with $EtOPCl_2$. The products **16** and **18** decomposes slowly in [D$_8$]toluene under Ar at room temp. Compound **18**: ^1H NMR (500.13 MHz, [D$_8$]toluene, 25 °C): δ = 0.84 [t, $^3J(^1H,^1H)$ = 7.0 Hz, 6 H, CH_3], 3.27 [dq, $^3J(^1H,^1H)$ = 7.0, $^3J(^{31}P,^1H)$ = 7.0 Hz, 4 H,

Table 5. Crystallographic data of the *ortho*-carborane derivatives **13**, **19**, and **1**·2($HNEt_2$/HCl).[a]

	13	**19**	**1**·2($HNEt_2$/HCl)
Formula	$C_{22}H_{42}B_{20}O_4P_2$	$C_6H_{19}B_{10}O_4P$	$C_{10}H_{36}B_{10}Cl_2N_2O_2$
Crystal	colorless prism	colorless prism	colorless needle
Dimensions [mm^3]	0.20 × 0.18 × 0.16	0.16 × 0.12 × 0.10	0.20 × 0.12 × 0.10
T [K]	133(2) K	133(2) K	133(2) K
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [pm]	1101.2(2)	1111.8(2)	719.31(14)
b [pm]	1349.9(3)	1077.7(2)	1110.5(2)
c [pm]	1386.9(3)	1350.8(3)	3127.1(6)
α [°]	107.51(3)		84.66(3)
β [°]	107.54(3)	98.27(3)	87.64(3)
γ [°]	103.92(3)		75.46(3)
Z	2	4	4
Absorption coefficient (μ) [mm^{-1}]	0.156	0.172	0.276
Measuring range (ϑ) [°]	1.68–25.71	1.85–25.77	1.90–25.66
Reflections collected	11761	9022	8372
Independent reflections [$I \geq 2\sigma(I)$]	3855	1028	2892
Absorption correction	none[b]	none[b]	none[b]
Refined parameters	433	190	470
wR2/*R1* [$I \geq 2\sigma(I)$]	0.139/0.065	0.249/0.134	0.308/0.118
Max./min. residual electron density, [e pm^{-3} 10^{-6}]	0.470/–0.352	0.515/–0.595	0.493/–0.621

[a] A STOE IPDS II diffractometer was used in all cases with graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). [b] Absorption corrections did not improve the parameter set.

$POCH_2$] ppm. EI-MS (70 eV) for $C_8H_{30}O_6B_{20}P_2$ (500.4): *m*/*z* (%) = 500 [M^+].

1-[(1,1-Dimethylethyl)hydroxyphosphinyl]oxy-2-hydroxy-1,2-dicarba-*closo*-dodecaborane(12) (19) and *t*Butylphosphinic Acid (20): The mixture of **14/14′** (9:1) was dissolved in [D_8]toluene, placed into an NMR spectroscopy tube, and heated at 110 °C (oil bath) for 4 h. The mixture contained **14** (50%), **14′** (trimer) (15%), **8** (20%), **19** (10%), and **20** (5%), together with **1** (from ^{31}P and ^{1}H NMR spectroscopy). After 2 d at 80 °C, the mixture contained **14** (60%), **14′** (trimer) (10%), **8** (<5%), **19** (10%), and **20** (15%), together with **1**. The [D_8]toluene solution was cooled to –30 °C to give **20** as a white powder. Volatile materials were removed in a vacuum, and the residue was dissolved in CD_2Cl_2. This solution was left at room temp. for one week, after which transparent crystals of **19** (m.p. 160–165 °C) suitable for X-ray analysis could be collected. Compound **19**: $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2, 25 °C): δ = 72.6 ppm. Compound **20**: ^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = 1.13 [d, $^{3}J(^{31}P,^{1}H)$ = 18.1 Hz, 9 H, CH_3], 6.74 [d, $^{1}J(^{31}P,^{1}H)$ = 540.2 Hz, 1 H, PH] ppm. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 25 °C): δ = 22.2 [d, $^{2}J(^{31}P,^{13}C)$ = 1.8 Hz, CH_3], 31.0 [d, $^{2}J(^{31}P,^{13}C)$ = 94.7 Hz, PC] ppm. $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2, 25 °C): δ = 51.7 ppm. ^{31}P NMR (202.5 MHz, CD_2Cl_2, 25 °C): δ = 51.7 [dm, $^{1}J(^{31}P,^{1}H)$ = 540.5 Hz] ppm.

Crystal Structure Determination of 13, 19, and 1·2($HNEt_2$/HCl): Structure solutions and refinements were carried out with the program package SHELXTL-PLUS V.5.1.[27] Details pertinent to the crystal structure determination are listed in Table 5. Crystals of appropriate size were sealed under argon in Lindemann capillaries, and the data collections were carried out at 133 K.

CCDC-961687 (**13** at 133 K), -961685 (for **19** at 133 K), and -961686 [for $B_{10}H_{10}C_2(OH)_2$·2($HNEt_2$/HCl) at 133 K] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Alternative synthetic pathway, NMR data of **2** and **2**($n$$Et_2O$), calculated and experimental $\delta^{31}P$ data.

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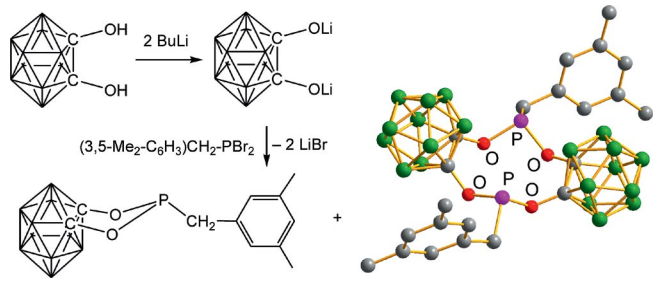

Most of the title compounds were found to be unstable as monomers and tend to dimerize, even faster than comparable derivatives without the annelated carborane unit.

