Synthesis and Structure of New Carborane-Substituted Cyclotriphosphazenes

Domingo Abizanda,[a] Olga Crespo,[a] M. Concepcion Gimeno,[b] Josefina Jiménez,*[a] and Antonio Laguna*[b]

Abstract: The reactions of $[N_3P_3Cl_6]$ with one, two, or three equivalents of the difunctional 1,2-*closo*-carborane $C_2B_{10}H_{10}\{CH_2OH\}_2$ and K_2CO_3 in acetone have been investigated. These reactions led to the new *spiro-closo*-carboranylphosphazenes *gem*-$[N_3P_3Cl_{6-2n}\{(OCH_2)_2C_2B_{10}H_{10}\}_n]$ ($n=1$ (**1**), 2 (**2**)) and the first fully carborane-substituted phosphazene *gem*-$[N_3P_3\{(OCH_2)_2C_2B_{10}H_{10}\}_3]$ (**3**). A bridged product, *non-gem*-$[N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}]$ (**4**), was also detected. The reaction of the well-known *spiro* derivatives $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ and $[N_3P_3Cl_4(O_2C_{12}H_8)]$ with the same carborane-diol and K_2CO_3 in acetone gave the new compounds *gem*-$[N_3P_3(O_2C_{12}H_8)_{3-n}\{(OCH_2)_2C_2B_{10}H_{10}\}_n]$ ($n=1$ (**5**) or 2 (**6**), respectively), without signs of intra- or intermolecularly bridged species. Upon treatment with NEt_3 in acetone, compound **5** was converted into the corresponding *nido*-carboranylphosphazene. However, the reaction of *gem*-$[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_{10}H_{10}\}]$ (**5**) with NEt_3 in ethanol instead of acetone proceeded in a different manner to give the new compound $(NHEt_3)_2[N_3P_3(O_2C_{12}H_8)_2(O)\{OCH_2C_2B_9H_{10}CH_2OCH_2CH_3\}]$ (**7**). For compounds with two 2,2′-dioxybiphenyl units, *gem*-$[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_{10}H_{10}\}]$ (**5**), $(NHEt_3)[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_9H_{10}\}]$ (**8**), and $(NHEt_3)_2[N_3P_3(O_2C_{12}H_8)_2(O)\{OCH_2C_2B_9H_{10}CH_2OCH_2CH_3\}]$ (**7**), a mixture of different stereoisomers may be expected. However, for **5** and **7** only the *meso* compounds seem to be formed, with the same (*R*,*S*)-configuration as in the precursor $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$. The reaction of **5** to give **8** seems to proceed with a change of configuration at one phosphorus center, giving a racemic mixture. The crystal structures of the *nido*-carboranylphosphazenes **7** and **8** have been confirmed by X-ray diffraction methods.

Keywords: C-O coupling · carboranes · chirality · NMR spectroscopy · phosphazenes

Introduction

Phosphazenes, $[NPR_2]$, are an important class of inorganic compounds, the most striking characteristic of which is their ability to form high polymers, of which the properties can be tailored by the choice of appropriate R groups on phosphorus.[1] They are usually prepared by nucleophilic substitution reactions of alkoxides, aryloxides, or amines on halophosphazene cyclic trimer or high polymers as substrates.[1, 2]

To a more limited extent, inorganic, organometallic, or other organic side groups can be attached to the phosphazene skeleton to design materials with properties that are difficult to obtain with other more conventional polymers.[3] Thus, for example, *ortho*-carboranes $C_2B_{10}H_{10}R^-$ ($R=Me$ or Ph) have been connected to phosphazenes through C–P bonds by reaction of cyclic and high polymeric chlorophosphazenes with lithio derivatives of carboranes (Scheme 1), and these compounds have been reported to be of interest as high-temperature inmobilized-catalyst species or as materials with unusual electrical behavior.[4]

Skeletal cleavage reactions often accompany the concurrent halogen replacement in halophosphazenes when Grignard or organolithium reagents are employed. Thus, in the reactions with lithiocarboranes, high polymers have only been obtained when less than about 15% of halogen atoms were replaced by carborane groups.[4] These high polymers **V** and **VI** have also been obtained from cyclic carboranylphosphazenes of type **II** (see Scheme 1) by ring-opening polymerization, and these cyclic phosphazenes have also provided excellent models for structural and reactivity studies at the macromolecular level.[4]

Homopolymers with all the chloro substituents replaced by carboranes have likewise proved inaccessible by substitu-

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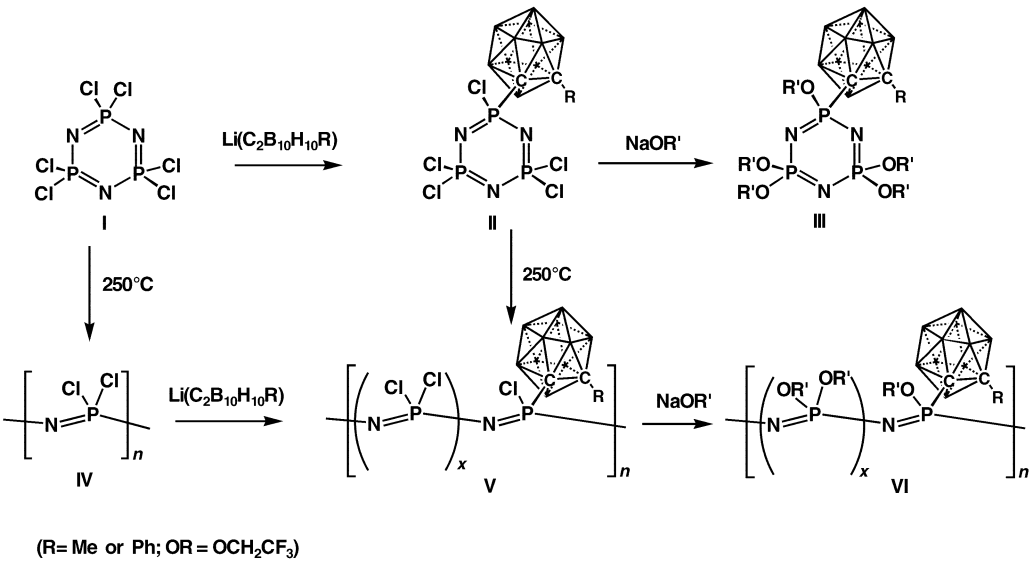


Scheme 1.

tion of the cyclic species and further ring-opening polymerization. Cyclophosphazenes that bear more than one organic group often resist polymerization, possibly for steric reasons.[4b, 5]

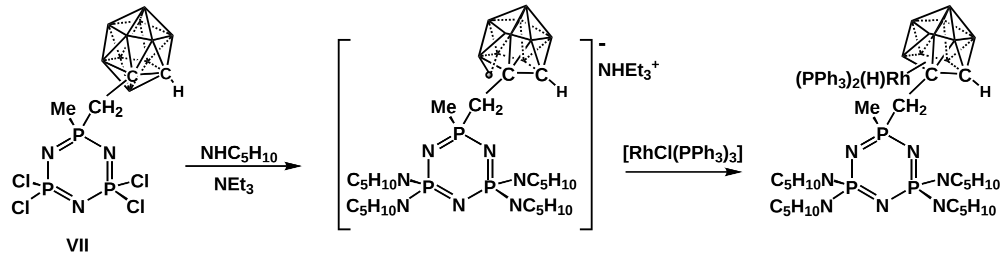
Abstract in Spanish: *En este trabajo se han investigado las reacciones de* $[N_3P_3Cl_6]$ *con 1, 2 ó 3 equivalentes del 1,2-closo-carborano difuncional,* $C_2B_{10}H_{10}\{CH_2OH\}_2$, *y* K_2CO_3 *en acetona. Estas reacciones dieron lugar a los nuevos spiro-closo-carboranilfosfazenos gem-*$[N_3P_3Cl_{6-2n}\{(OCH_2)_2C_2B_{10}H_{10}\}_n]$ *(n = 1 (**1**), 2 (**2**)) y al primer fosfazeno con carboranos como único grupo lateral gem-*$[N_3P_3\{(OCH_2)_2C_2B_{10}H_{10}\}_3]$ *(**3**). En estas reacciones se ha detectado también el compuesto no-gem-*$[N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}]$ *(**4**). La reacción de los conocidos spiro derivados* $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ *and* $[N_3P_3Cl_4(O_2C_{12}H_8)]$ *con el mismo carboranodiol dio los nuevos compuestos gem-*$[N_3P_3(O_2C_{12}H_8)_{3-n}\{(OCH_2)_2C_2B_{10}H_{10}\}_n]$ *(n = 1 (**5**) o 2 (**6**), respectivamente), sin signos de formación de especies en las que el carborano actúa de puente. El compuesto **5** reaccionó con* NEt_3 *en acetona con conversión al análogo nido-carboranilfosfazeno. Sin embargo, la reacción de ese mismo compuesto **5** con* NEt_3 *en etanol en lugar de acetona evolucionó de forma distinta, dando el compuesto nuevo* $(NHEt_3)_2[N_3P_3(O_2C_{12}H_8)_2(O)\{OCH_2C_2B_9H_{10}CH_2OCH_2CH_3\}]$ *(**7**). Para los derivados con dos unidades 2,2'-dioxibifenilo, gem-*$[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_{10}H_{10}\}]$ *(**5**),* $(NHEt_3)[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_9H_{10}\}]$ *(**8**), y* $(NHEt_3)_2[N_3P_3(O_2C_{12}H_8)_2(O)\{OCH_2C_2B_9H_{10}CH_2OCH_2CH_3\}]$ *(**7**), puede esperarse una mezcla de varios estereoisómeros. Sin embargo, para **5** y **7** sólo parecen formarse los compuestos meso, con la misma configuración (R,S) que en el producto de partida* $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$. *La reacción de **5** para dar **8** parece evolucionar, sin embargo, con un cambio en la configuración de un centro de fósforo, dando una mezcla racémica. Se han confirmado las estructuras cristalinas de los nido-carboranilfosfacenos **7** y **8** por difracción de Rayos X.*

The use of non-organometallic-carborane nucleophiles could be envisaged as leading to substitution of the chloro substituents in halopolyphosphazenes without skeletal cleavage. This prompted us to investigate the reactions with a functionalized *ortho*-carborane bearing alcohol groups, $C_2B_{10}H_{10}\{CH_2OH\}_2$, in the presence of K_2CO_3.

Since the use of difunctional reagents could lead to cross-linking in the first steps of the chlorine substitution process in $[NPCl_2]_n$, giving unstable insoluble materials,[6] we have first explored the reactions with hexachlorocyclotriphosphazene (**I**), and the results obtained are presented herein.

Notably, *nido*-carboranes can be obtained from *closo*-carboranes in the presence of a base,[7] and that these can function as π ligands for transition metals.[8] Thus, the use of a base, such as K_2CO_3, as a deprotonating reagent for the carborane-diol, $C_2B_{10}H_{10}\{CH_2OH\}_2$, could cause the reactions with chlorophosphazenes to proceed not only with substitution of the chloro substituents but also with conversion to *nido*-carboranylphosphazenes. Indeed, Allcock and co-workers have reported that cyclic or high polymeric *closo*-carboranylphosphazenes of the type **VII** (Scheme 2) are converted to *nido*-carboranylphosphazenes, and that the resulting anions are capable of ligand substitution reactions with metal complexes $[RhCl(PPh_3)_3]$ or $[M(CO)_6]$ (M = Mo or W).[9] Therefore, our objectives were: a) to ascertain whether intramolecularly or intermolecularly bridged species are formed in the reaction of $[N_3P_3Cl_6]$ with $C_2B_{10}H_{10}\{CH_2OH\}_2$, and if so, to try to avoid the formation of such bridged species by using other nucleophiles in the first steps of the chlorine substitution, b) to investigate the possibility of controlling the conversion to *nido*-carboranylphosphazenes in the presence of K_2CO_3, and c) to try to obtain cyclotriphosphazenes with all the chloro substituents replaced by carboranes.

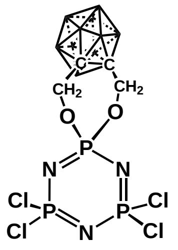
To the best of our knowledge, only a few carboranylcyclophosphazenes have been obtained to date, and only in cases wherein one chlorine atom is replaced by a carborane, as shown in Scheme 1 and Scheme 2.[4, 9]



Scheme 2.

Results and Discussion

Reactions of $[N_3P_3Cl_6]$ with $C_2B_{10}H_{10}\{CH_2OH\}_2$: The reaction of hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ with $C_2B_{10}H_{10}\{CH_2OH\}_2$, in a molar ratio of 1:1 or 1:2, in the presence of K_2CO_3 in acetone led to the new *closo*-carboranylphosphazenes *gem*-$[N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}]$ (**1**) and *gem*-$[N_3P_3Cl_2\{(OCH_2)_2C_2B_{10}H_{10}\}_2]$ (**2**), in which the dinucleophile replaced two chlorine atoms at the same phosphorus to form spirocyclic structures. However, these reactions were not clean, not even when the difunctional reagent was added very slowly and dropwise to minimize the formation of products with multiple substituents. With both stoichiometries, a mixture of **1** and **2** was observed, with a greater proportion of the derivative corresponding to the stoichiometric ratio used (see Experimental Section), and with a molar ratio of 1:2, *gem*-$[N_3P_3\{(OCH_2)_2C_2B_{10}H_{10}\}_3]$ (**3**) was also observed. Besides, in both of these reactions (1:1 and 1:2), *non-gem*-$[N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}]$ (**4**) with a transannularly bridged structure was also detected (about 30% or 8%, respectively), formed by the replacement of two chloro substituents on different phosphorus atoms.



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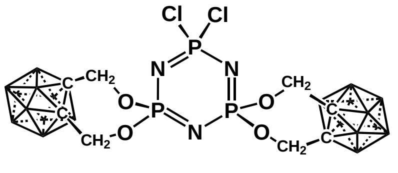

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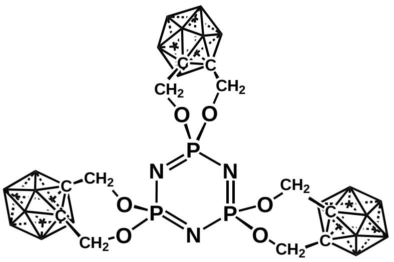

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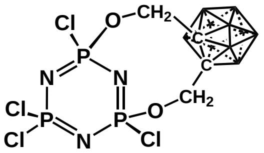

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The majority of compound **4** precipitated from the reaction mixture with a 1:1 molar ratio upon addition of CH_2Cl_2/hexane (1:15), and the tris-*spiro* derivative **3**, which is only sparingly soluble, was isolated in pure form by using a 1:3 ratio. From the reaction mixture with a 1:2 stoichiometry, it was possible to isolate compound **2** containing about 6% of **3** by virtue of its lower solubility in hexane (see Experimental Section). However, **1** could not be isolated, not even by chromatography techniques. Compounds **2**–**4** were identified by IR, ^1H and ^{31}P NMR spectroscopies, mass spectral and microanalytical data, and confirmation of the structure of **1** was obtained from IR, ^1H, and ^{31}P NMR, and mass spectral data. The IR spectra of all of these compounds feature peaks at around $1200\,cm^{-1}$ (br) (P=N)[10] and $2600\,cm^{-1}$ (br) (B–H)[11] (see Experimental Section), and the $^{31}P\{^1H\}$ NMR spectra consist of a singlet in the case of **3** and an AX_2 pattern in the cases of **1** and **2**, with signals at similar positions to those observed for tris-*spiro*-, mono-*spiro*-, and bis-*spiro*-biphenoxy derivatives, respectively (see Table 1).[2b, 12] For **4**, the $^{31}P\{^1H\}$ NMR spectrum shows an AB_2

Table 1. ^{31}P NMR data in $(CD_3)_2CO$ for **1**–**4**.

Compound	$\delta[NPCl_2]$[a]	$\delta[NPCl(O_2R)]$[a,b]	$\delta[NP(O_2R)]$[a,b]	$^2J(P,P)$[c]
gem-$[N_3P_3Cl_4(O_2C_{12}H_8)]$	25.8(d)	–	14.0(dd)	72.0
gem-$[N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}]$ (**1**)	25.34(d)	–	12.21(t)	72.8
gem-$[N_3P_3Cl_2(O_2C_{12}H_8)_2]$	29.8(dd)	–	20.7(d)	81.0
gem-$[N_3P_3Cl_2\{(OCH_2)_2C_2B_{10}H_{10}\}_2]$ (**2**)	28.95(t)	–	17.67(d)	77.8
gem-$[N_3P_3(O_2C_{12}H_8)_3]$	–	–	27.0(s)	–
gem-$[N_3P_3\{(OCH_2)_2C_2B_{10}H_{10}\}_3]$(**3**)	–	–	23.0(s)	–
Non-gem-$[N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}]$ (**4**)	24.36(dd)	21.62(d)	–	69.9

[a] Values in ppm. [b] R = $C_{12}H_8$ or $(CH_2)_2C_2B_{10}H_{10}$. [c] Values in Hz.

pattern with both chemical shifts in the region of $\delta = 20$ ppm, as has been observed for other cyclophosphazenes with a transannular bridge.[13] The ^{1}H and ^{13}C{^{1}H} NMR spectra of **4** show chemical equivalence of the two methylene groups, probably indicating a *cis* disposition, as has also been observed when 2,2′-dioxybiphenyl ($O_2C_{12}H_8$) acts as a transannular bridge.[13] The signals in the ^{13}C{^{1}H} NMR spectrum were assigned by comparison with those observed for other similar carboranes.[14] For the same sample, the phosphorus-decoupled ^{1}H NMR spectrum showed an AB pattern with $^2J(\mathrm{H,H}) = 14.7$ Hz ($\delta_A = 5.63$ ppm and $\delta_B = 5.13$ ppm in $(CD_3)_2CO$), indicating chemical inequivalence of the two protons of the same methylene group, as expected, while a simulation of the phosphorus-coupled ^{1}H NMR spectrum of the same sample (ABXX′ system) gave $^3J(\mathrm{H_A,P_x}) = {}^5J(\mathrm{H_A,P_{x'}}) = 8.6$ Hz and $^3J(\mathrm{H_B,P_x}) = {}^5J(\mathrm{H_B,P_{x'}}) = 7.4$ Hz. Its proton-coupled ^{31}P NMR spectrum showed split peaks for the resonance of the phosphorus atoms linked to the carborane substituent, as expected, with the same coupling constants.

The ^{1}H NMR spectrum of **1** showed a chemical equivalence of all the methylene protons, with $^3J(\mathrm{H,P}) = 19.2$ Hz, probably due to a fluxional process involving the carborane. (This signal became broader when the spectrum was acquired at −80 °C in acetone). Such a fluxional process was not observed in the case of compound **2**, the ^{13}C{^{1}H} NMR spectrum of which showed chemical equivalence of all the methylene groups, but its phosphorus-decoupled ^{1}H NMR spectrum consisted of an AB pattern with $^2J(\mathrm{H,H}) = 13.5$ Hz ($\delta_A = 4.94$ ppm and $\delta_B = 4.92$ ppm in $(CD_3)_2CO$).

The mass spectral and microanalytical data are summarized in the Experimental Section.

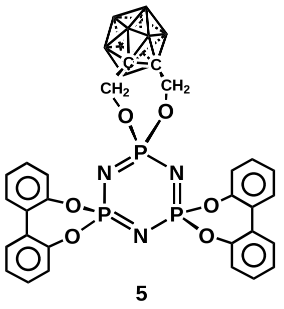
Reactions of *gem*-[$N_3P_3Cl_2(O_2C_{12}H_8)_2$] or *gem*-[$N_3P_3Cl_4(O_2C_{12}H_8)$] with $C_2B_{10}H_{10}\{CH_2OH\}_2$: In contrast to the above reactions, the well-known cyclotriphosphazenes *gem*-[$N_3P_3Cl_2(O_2C_{12}H_8)_2$] and *gem*-[$N_3P_3Cl_4(O_2C_{12}H_8)$][2b, 12] reacted with the same carborane-diol, $C_2B_{10}H_{10}\{CH_2OH\}_2$, in the presence of K_2CO_3 in acetone, to afford the new compounds *gem*-[$N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_{10}H_{10}\}$] (**5**) and *gem*-[$N_3P_3(O_2C_{12}H_8)\{(OCH_2)_2C_2B_{10}H_{10}\}_2$] (**6**). These were isolated in pure form and in high yield (>90%), without any signs of intra- or intermolecularly bridged species.

All the analytical and spectroscopic data were in accord with the formulae indicated for **5** and **6**. Thus, the IR spectra showed peaks at around 1200 cm^{-1} (br) (P=N)[10] and 2600 cm^{-1} (br) (B–H),[11] and the ^{31}P{^{1}H} NMR spectra consisted of an AB_2 pattern. The chemical shifts corresponding to the different phosphorus atoms were assigned by taking into account the proton-coupled ^{31}P NMR spectra. Thus, for example, for **5** the signals corresponding to the A portion of the spectrum are split by coupling to the carborane-methylene protons, with $^3J(\mathrm{P,H}) = 18.5$ Hz (in acetone).

As was observed for **2**, the ^{13}C{^{1}H} NMR spectrum of **6** showed chemical equivalence of all the methylene groups, and its phosphorus-decoupled ^{1}H NMR spectrum showed an AB system with $^2J(\mathrm{H,H}) = 12.1$ Hz ($\delta_A = 4.87$ ppm and $\delta_B = 4.82$ ppm in $(CD_3)_2CO$), indicating chemical inequivalence of the two protons of the same methylene group. An X-ray crystal analysis of compound **6** confirmed the proposed structure. Unfortunately, disorder problems precluded a good refinement and consequently data are not presented in full. The unit cell has the following dimensions: $a = 8.0635(5)$, $b = 13.2068(8)$, $c = 18.9681(12)$ Å, $\alpha = 95.790(1)$, $\beta = 92.743(1)$, $\gamma = 102.341(1)°$, triclinic $P\bar{1}$.

Compound **5** deserves special attention. Since the diol 2,2′-dioxybiphenyl exists in the form of rapidly interconverting *R* and *S* isomers,[15] different diastereomers may be formed when a racemic mixture of the diol is used and more than one diol unit is bonded to the cyclophosphazene ring. Thus, cyclophosphazenes made up of all-*R*- or all-*S*-configured phosphorus centers and/or having different *R*- or *S*-configured phosphorus centers within one N_3P_3 ring may be anticipated. In particular, in this case, the formation of three stereoisomers might have been expected, namely a pair of *R*,*R*- or *S*,*S*-configured enantiomers and the diastereotopic *meso* form. As has been observed for other similar cyclophosphazenes, such as *gem*-[$N_3P_3(O_2C_{12}H_8)_2(OR)_2$] and *gem*-[$N_3P_3(O_2C_{20}H_{12})_2(OR)_2$] (OR = *p*-$OC_6H_4OMe$[15]), these diastereoisomers may be distinguished by ^{31}P NMR spectroscopy. However, only one diastereoisomer seems to be formed here, as evidenced by the observation of a single set of resonances of an AB_2 spin system in the ^{31}P NMR spectrum of the crude reaction mixture. If we assume that the *R*,*S* configuration at the phosphorus centers of the well-known starting material *gem*-[$N_3P_3(O_2C_{12}H_8)_2Cl_2$][15] is retained in the course of the substitution reaction, then the two methylene groups (and the two carbon atoms of the carborane) become diastereotopic and should give rise to two resonance signals. On the other hand, if the configuration at one phosphorus center is changed under the reaction conditions from *R* to *S*—or vice versa—chiral cyclotriphosphazenes with *R*,*R*- and *S*,*S*-configured phosphorus centers will be obtained. In these, the two methylene groups (and the two carbon atoms of the carborane) are related by a C_2 axis of symmetry and only one resonance signal is to be expected.

In the ^{1}H and ^{13}C{^{1}H} NMR spectra of compound **5**, only one signal due to the methylene groups of the carborane is observed, but two signals due to the carbon atoms of $C_2B_{10}H_{10}$ are observed in the ^{13}C{^{1}H} NMR spectrum. The product therefore seems to be the *meso* diastereomer, containing one



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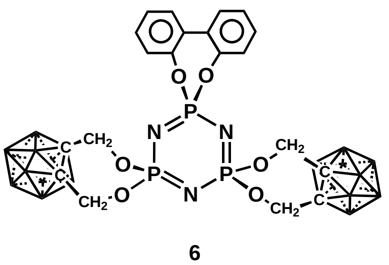

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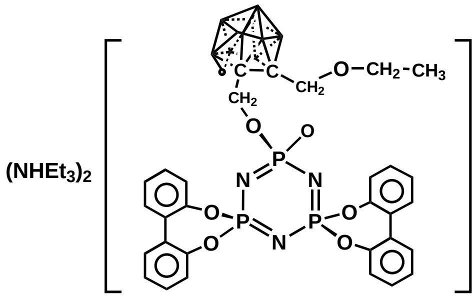
R- and one *S*-configured phosphorus center, as in the starting material. However, single crystals suitable for X-ray diffraction analysis could not be obtained.

In contrast to this, Grützmacher et al. have observed that when $[N_3P_3Cl_2\{(R,S)\text{-}(O_2C_{12}H_8)_2\}]$ reacts with hard nucleophiles such as 4-methoxyphenolate (or even with 2,2′-dioxybiphenolate), a change of configuration at one phosphorus center occurs to give a racemic mixture of chiral phosphazenes. Considering the findings of these authors, the sterically more demanding carborane should give rise to increased steric interactions, which, at first glance, may be smaller in the *meso* isomer.[15]

As observed for **1**, the ^{1}H NMR spectrum of **5** shows chemical equivalence of the two protons of the same methylene group. (This signal also became broader when the spectrum was recorded at −80 °C in acetone).

***nido*-Carborane formation**: It is noteworthy that in the reactions of $[N_3P_3Cl_6]$ with the carborane-diol, $C_2B_{10}H_{10}\{CH_2OH\}_2$, only *closo*-carboranylphosphazenes **1**–**4** were detected, without any signs of conversion to *nido*-carboranyl species, even when a great excess of K_2CO_3 (2.5 equivalents per alcohol) and conditions of refluxing for 4 h were used. However, in the reactions of *gem*-$[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ or *gem*-$[N_3P_3Cl_4(O_2C_{12}H_8)]$ with the carborane-diol, exclusively *closo*-carboranylphosphazenes **5** or **6** were only detected when a nearly stoichiometric amount of K_2CO_3 was employed to deprotonate the diol. The use of a larger amount of the base led to partial conversion to *nido*-carboranylphosphazenes. Evidence for the formation of *nido*-carboranyl species was clearly obtained from ^{1}H NMR spectra of the reaction mixture, which showed signals at $\delta \approx -2$, attributable to the bridging B-H-B proton of the open face of *nido*-carborane. However, complete conversion was not observed, even after prolonged reflux, and a mixture in which the *closo*-carboranylphosphazenes were still present was invariably obtained.

To obtain *nido*-carboranylphosphazenes, which might function as ligands for transition metals, *gem*-$[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_{10}H_{10}\}]$ (**5**) was treated with an excess of NEt_3 in ethanol, conditions often used for free carboranes. After 50 h at reflux, no *closo*-carboranyl species were detected, and the precipitate formed was identified as compound **7**.



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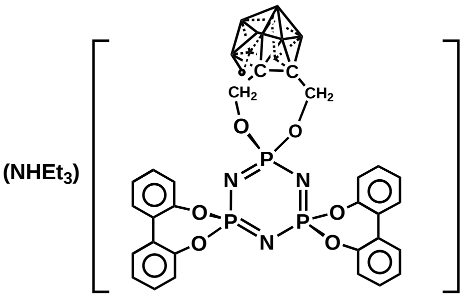
This unusual structure, which was confirmed by a single-crystal X-ray analysis, is likely to result not only from nucleophilic attack on the carborane cage leading to conversion to a *nido*-carboranylphosphazene,[7] but also from nucleophilic attack by ethoxide on the phosphorus atom linked to the carborane to give an intermediate with a pentacoordinate phosphorus, which could then undergo displacement of one OCH_2 unit of the carborane by ethoxide and further reorganization to give **7**.

Displacements of side groups in phosphazenes are well known during reactions with alkoxides,[13, 16] but, to the best of our knowledge, no further reorganization similar to that seen in this reaction has hitherto been observed. Further nucleophilic attack by ethoxide on the carborane-substituted phosphorus atom in compound **7** could lead to new functionalized *nido*-carboranes, reactions which are still under investigation.

To reduce the possibility of side reactions other than conversion to *nido*-carboranyl species, acetone was used as solvent instead of ethanol. Under these conditions, in the presence of NEt_3, compound **5** was quantitatively transformed to the *nido*-carboranylphosphazene species **8**, after stirring under reflux for 48 h.



8

All the spectroscopic and analytical data for **7** and **8** were in accord with the proposed formulae. Besides, both of these structures were confirmed by single-crystal X-ray analyses, as discussed in the following section. Thus, the IR and ^{1}H NMR spectra of compounds **7** and **8** confirmed the removal of the boron atom in the transformation. The former displays a ν(B−H) absorption at lower energies (at 2525 cm^{-1}) compared to the corresponding *closo*-carborane derivative (**5**), as has been observed for other *nido*-carboranes.[17] The IR spectra of both of these compounds also show absorptions attributable to ν(P=N) at around 1200 cm^{-1} and to ν(N−H) at around 3370 cm^{-1}.

In the ^{1}H NMR spectra, the signal centered at $\delta \approx -2.4$, assigned to the bridging B-H-B proton, is also consistent with *nido*-carborane formation.[17] The spectra of both of these compounds also show resonances corresponding to the other carborane protons, to the aromatic rings, and to $NHEt_3^+$ (see Experimental Section). For **7**, the ^{1}H NMR spectrum also features another two signals at $\delta = 3.48$ ppm (m, 2H) and $\delta = 1.05$ ppm (t, 3H), attributable to the ethoxide group. The signals in the ^{1}H NMR spectrum of **7**, on which the structural confirmation was based, were assigned by taking into account their multiplicities and the phosphorus-decoupled ^{1}H NMR spectrum of the same sample. In the latter spectrum, only the resonance at $\delta = 4.34$ ppm became more simple, showing an AB pattern ($\delta_A = 4.36$ ppm, $\delta_B = 4.31$ ppm, $^2J_{A,B} = 10.2$ Hz) instead of the ABX system observed in the phosphorus-coupled ^{1}H NMR spectrum, from which it can be concluded that this signal is due to the protons of the OCH_2 unit attached to the phosphorus atom. It should be pointed out that this ^{1}H NMR spectrum shows that the two protons of each of the methylene groups of the carborane are diastereotopic and that therefore rotation about the CH_2–C and CH_2–O bonds within the carborane cannot take place, which is not the case in the free carborane, $C_2B_{10}H_{10}\{CH_2OH\}_2$, in which all the methylenic protons are equivalent.

As for compound **5**, for **7** and **8** three stereoisomers might have been expected but again only one seems to be formed, as evidenced by the observation of a single set of resonances of an AX_2 or ABX spin system, respectively, in the $^{31}P\{^1H\}$ NMR spectra. However, unlike for compound **5**, for **7** and **8** neither the $^{13}C\{^1H\}$ NMR spectrum nor the ^{1}H NMR spectrum allows unequivocal assignment of the stereoisomer present, because of different reasons in each case. For (*R*,*S*)-**7**, the aforementioned probable lack of rotation about the $POCH_2$–$C_2B_9H_{10}$-$CH_2OCH_2CH_3$ bond renders the two hydrogen atoms of the OCH_2 unit directly linked to phosphazene (and the two $P(O_2C_{12}H_8)$ units) diastereotopic. In the chiral cyclotriphosphazenes (*R*,*R*)-**7** or (*S*,*S*)-**7**, these groups are not related by any symmetry element, even if there is rotation about such a bond. The ^{1}H NMR spectrum of **7** shows the two protons of each of the methylene groups to be non-equivalent, but the $^{31}P\{^1H\}$ NMR spectrum shows the two $P(O_2C_{12}H_8)$ units to be equivalent. X-ray analysis revealed an *R*,*S* configuration, presumably like that in the precursor **5**. For **8**, in the three possible stereoisomers, both the $P(O_2C_{12}H_8)$ units and the methylene groups are expected to be non-equivalent, due to the asymmetry imparted by the *nido*-carborane. Indeed, the $^{13}C\{^1H\}$ and ^{1}H NMR spectra show both groups to be nonequivalent, and the $^{31}P\{^1H\}$ NMR spectrum recorded in acetone consists of an ABX pattern, with A centered at $\delta = 27.53$ ppm $[P(O_2C_{12}H_8)]$, B at $\delta = 25.92$ ppm $[P(O_2C_{12}H_8)]$, and X at $\delta = 20.09$ ppm $[P\{(OCH_2)_2C_2B_9H_{10}\}]$. The chemical shifts of the respective phosphorus atoms were assigned by taking into account the proton-coupled ^{31}P NMR spectrum, in which the X portion of the spectrum is split by coupling to the carborane-methylene protons with $^3J(P,H) = 10.3$ Hz and $^3J(P,H) = 24.2$ Hz. X-ray analysis revealed an *S*,*S* and an *R*,*R* configuration at the two biphenoxy-substituted phosphorus centers and, therefore, the configuration at one phosphorus center must have changed in the course of the reaction if we assume an *R*,*S* configuration in the precursor **5**. This seems somewhat surprising in view of the observation by Grützmacher et al. that the presence of a PCl_2 group in the precursor seems to be necessary to observe a change in the configuration. Of course, the presence of the other stereoisomers in compound **5** would explain this change. However, this would mean that these diastereoisomers cannot be distinguished by NMR spectroscopy, which has not been observed by these authors.

On the other hand, we cannot offer a straightforward explanation as to why a change in the configuration is observed, especially as these same authors have observed that soft nucleophiles such as amines do not affect the configuration in $[N_3P_3Cl_2\{(R,S)\text{-}(O_2C_{12}H_8)_2\}]$.

It should also be pointed out that although compound **8** gives rise to an ABX $^{31}P\{^1H\}$ NMR spectrum in acetone solution, this pattern changes as the solvent is varied. Thus, the spectrum of the same sample in $CDCl_3$ showed an ABC spin system, with A centered at $\delta = 26.92$ ppm $[P(O_2C_{12}H_8)]$, B at $\delta = 22.80$ ppm $[P(O_2C_{12}H_8)]$, and C at $\delta = 20.30$ ppm $[P\{(OCH_2)_2C_2B_9H_{10}\}]$. Again, the signals were assigned by taking into account the proton-coupled ^{31}P NMR spectrum, in which the C portion of the spectrum is split by coupling to the carborane-methylene protons with $^3J(P,H) = 8.5$ Hz and $^3J(P,H) = 25.0$ Hz. The synthesis of the similar derivative $(NBu_4)[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_9H_{10}\}]$ (**9**) (see Experimental Section), with the NBu_4^+ counterion instead of $NHEt_3^+$, revealed that the different ^{31}P NMR pattern observed for **8** was due to the presence of the triethylammonium cation, suggesting that in $CDCl_3$ the proton of this ion occupies a fixed position acting as a bridge with one nitrogen atom of the cyclophosphazene unit. A similar situation has been observed for *gem*-$[N_3P_3(NC_5H_{10})_4(Me)\{CH_2C_2B_9H_{11}\}^-H^+]$,[9] in which the proton counterion occupies a fixed basic site on the phosphazene skeletal unit in $CDCl_3$ solution.

X-ray structure analyses of 7 and 8: X-ray structural analyses of **7** and **8** confirmed the proposed structures, as illustrated in Figure 1 and Figure 2, respectively (only the anions are shown); selected bond lengths and angles are listed in Table 2 for **7** and in Table 3 for **8**. Details of the data collections are given in Table 4.

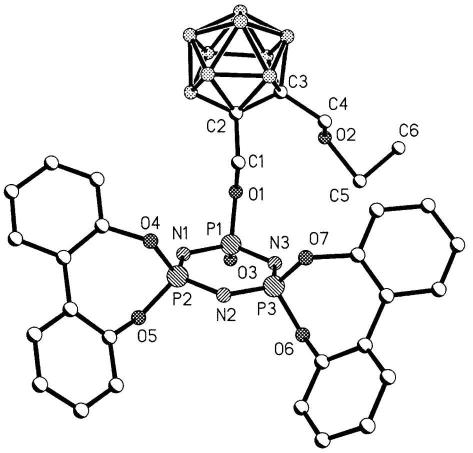


Figure 1. Structure of the anion of **7**. Hydrogen atoms have been omitted for clarity. Radii are arbitrary.

The structure of **7** shows the *nido*-carborane unit to be linked to the phosphazene ring through only one OCH_2 unit, and an *R*,*S* configuration at the two biphenoxy-substituted phosphorus centers. Although the poor precision (because of the low quality of the crystals and disordered solvent molecules) precludes detailed discussion of molecular dimensions, the phosphazene ring is seen to be almost planar (mean deviation from the best plane 0.0163 Å) and the P–O bonds that link the methoxy-carborane and biphenoxy units to the phosphazene skeleton are of normal length and are consistent

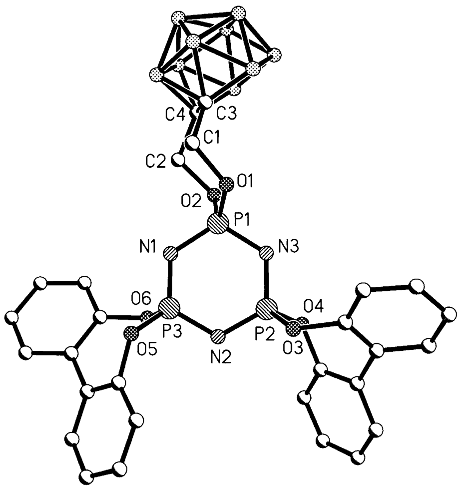


Figure 2. Structure of the anion of **8**. Hydrogen atoms have been omitted for clarity. Radii are arbitrary.

Table 2. Selected bond lengths [Å] and angles [°] for compound **7**

P1–O3	1.505(4)	P1–O1	1.584(4)	P1–N1	1.609(5)
P1–N3	1.611(5)	P2–N1	1.555(5)	P2–N2	1.582(5)
P2–O4	1.595(4)	P2–O5	1.595(4)	P3–N3	1.550(5)
P3–N2	1.576(5)	P3–O6	1.588(4)	P3–O7	1.596(4)
O1–C1	1.437(7)	O2–C4	1.346(9)	O2–C5	1.709(15)
C1–C2	1.492(9)	C2–C3	1.590(9)	C3–C4	1.585(10)
C5–C6	1.57(2)				
O3-P1-O1	102.4(2)	O3-P1-N1	112.6(3)	O1-P1-N1	106.9(3)
O3-P1-N3	113.1(3)	O1-P1-N3	108.2(3)	N1-P1-N3	112.8(3)
N1-P2-N2	119.5(3)	N1-P2-O4	112.3(3)	N2-P2-O4	104.5(3)
N1-P2-O5	106.0(3)	N2-P2-O5	111.7(3)	O4-P2-O5	101.4(2)
N3-P3-N2	119.7(3)	N3-P3-O6	105.2(3)	N2-P3-O6	111.4(3)
N3-P3-O7	113.3(3)	N2-P3-O7	103.9(2)	O6-P3-O7	102.2(2)
P2-N1-P1	124.2(3)	P3-N2-P2	119.2(3)	P3-N3-P1	124.4(3)
C1-O1-P1	118.2(4)	C4-O2-C5	105.5(8)	O1-C1-C2	111.2(5)
C1-C2-C3	117.2(6)				

Table 3. Selected bond lengths [Å] and angles [°] for compound **8**

P1–O1	1.561(2)	P1–O2	1.574(2)	P1–N1	1.590(2)
P1–N3	1.599(2)	P2–N2	1.565(2)	P2–N3	1.576(2)
P2–O4	1.583(2)	P2–O3	1.587(2)	P3–N1	1.563(2)
P3–O5	1.577(2)	P3–N2	1.581(2)	P3–O6	1.588(2)
O1–C1	1.461(3)	O2–C2	1.476(3)	C1–C3	1.504(3)
C2–C4	1.501(3)	C3–C4	1.569(3)		
O1-P1-O2	106.92(9)	O1-P1-N1	111.06(11)	O2-P1-N1	110.84(11)
O1-P1-N3	106.25(11)	O2-P1-N3	105.24(10)	N1-P1-N3	115.97(11)
N2-P2-N3	118.65(11)	N2-P2-O4	112.18(11)	N3-P2-O4	103.06(10)
N2-P2-O3	106.50(11)	N3-P2-O3	112.88(11)	O4-P2-O3	102.46(9)
N1-P3-O5	106.86(10)	N1-P3-N2	117.75(11)	O5-P3-N2	110.94(11)
N1-P3-O6	112.99(11)	O5-P3-O6	102.49(9)	N2-P3-O6	104.81(12)
P3-N1-P1	121.35(13)	P2-N2-P3	120.33(13)	P2-N3-P1	120.80(13)
C1-O1-P1	122.1(2)	C2-O2-P1	119.1(2)	O1-C1-C3	110.2(2)
O2-C2-C4	109.1(2)	C2-C4-C3	116.2(2)		

Table 4. Details of data collection and structure refinement for compounds **7** and **8**

Compound	**7**·2 CH_2Cl_2	**8**
chemical formula	$C_{44}H_{66}B_9Cl_4N_5O_7P_3$	$C_{37}H_{52}B_9N_4O_7P_3$
crystal habit	colorless prism	colorless prism
crystal size [mm]	0.20 × 0.15 × 0.10	0.40 × 0.20 × 0.18
crystal system	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/c$
a [Å]	15.9389(16)	9.7975(5)
b [Å]	21.501(2)	38.468(2)
c [Å]	17.2593(16)	12.7851(7)
α [°]	90	90
β [°]	110.394(2)	98.019(1)
γ [°]	90	90
U [Å^3]	5544.1(9)	4284.5(4)
Z	4	4
ρ_{calcd} [g^{-1}cm^{-3}]	1.329	1.326
M_r	1109.02	855.03
$F(000)$	2316	1792
T [°C]	− 100	− 100
$2\theta_{max}$ [°]	57	57
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.352	0.192
transmission	0.933, 0.965	0.355, 1.0
no. of reflections measured	36002	28350
no. of unique reflections	12951	10112
R_{int}	0.099	0.071
R[a] ($F > 4\sigma(F)$)	0.102	0.061
$wR2$[b] (F^2, all refl.)	0.317	0.143
no. of reflections used	12951	10109
no. of parameters	674	590
no. of restraints	491	0
S[c]	0.879	0.933
max. $\Delta\rho$ [e Å^{-3}]	0.568	0.516

[a] $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR(F^2)=[\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$, where $P=[F_o^2+2F_c^2]/3$ and a and b are constants adjusted by the program. [c] $S=[\Sigma\{w(F_o^2-F_c^2)^2\}/(n-p)]^{0.5}$, where n is the number of data and p the number of parameters.

with values reported for other related alkoxy- or aryloxycyclotriphosphazenes.[14, 18–20] As expected, the P1–O3 distance is shorter than the other P–O distances, which is a consequence of the greater bond order. Undoubtedly, the presence of this terminal oxygen atom will reduce the dπ–pπ character of the N1-P1-N3 segment, which is consistent with the longer distances observed for these bonds compared to the other P–N distances. Similar P–N and P–O distances have been observed in $[NBu_4][N_3P_3Cl_5O]$.[21] Furthermore, intermolecular hydrogen bonds are formed between O3 and the proton of one $NHEt_3^+$ group. The distances are O3–H5C# 1.797 Å and O3···H5C#–N5# 2.708 Å (# $x+1$, y, z).

The structure of **8** also shows the phosphazene ring to be almost planar (mean deviation from the best plane 0.0936 Å), with a slightly twisted conformation and an *S*,*S* configuration at the two biphenoxy-substituted phosphorus centers in the asymmetric unit. In the unit cell, both *S*,*S* and *R*,*R* configurations are present. The P–O bonds that bind the biphenoxy units to the phosphazene ring are also comparable in length (1.577(2) to 1.587(2) Å) to those reported for other biphenoxycyclotriphosphazenes,[14, 18–20] and the P–O bonds to the carborane unit are slighty shorter (1.574(2) Å and 1.561(2) Å) than the others. Within the carborane cage, the B–B bond lengths and internal acute angles are normal, which indicates no unusual interactions between this unit and the rest of the molecule. All P–N distances, P-N-P (average 120.82(13)°) and N-P-N (av 117.45(11)°) angles lie within the expected ranges.[22] The O1-P1-O2 angle (106.92(9)°) is slightly larger than the other O-P-O angles (102.46(9) and 102.49(9)°). An intermolecular hydrogen bond is formed between N3 and the proton H0 of the $NHEt_3^+$ counterion. The distances are N3–H0 2.023 and N3···H0–N5 2.898 Å. Thus, although this mode of interaction is unexpected, the X-ray results confirm the conclusions drawn from the ^{31}P NMR data.

Conclusion

The dinucleophile $C_2B_{10}H_{10}\{CH_2OH\}_2$ reacts with hexachlorocyclotriphosphazene in the presence of a base replacing the chloro substituents to give the new *spiro-closo*-carboranylphosphazenes *gem*-[$N_3P_3Cl_{6-2n}\{(OCH_2)_2C_2B_{10}H_{10}\}_n$] ($n=1$ (**1**), 2 (**2**), or 3 (**3**)), depending on the molar ratio used, and without signs of conversion to *nido*-carboranyl species. An intramolecularly bridged species, *non-gem*-[$N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}$], is also formed.

The use of another nucleophile, 2,2′-dihydroxybiphenyl, in the first steps of the substitution in $N_3P_3Cl_6$ avoided the formation of cross-linked species. Thus, the substitution of the chloro substituents in *gem*-[$N_3P_3Cl_2(O_2C_{12}H_8)_2$] and *gem*-[$N_3P_3Cl_4(O_2C_{12}H_8)$] by the same carborane-diol led to the new compounds *gem*-[$N_3P_3(O_2C_{12}H_8)_{3-n}\{(OCH_2)_2C_2B_{10}H_{10}\}_n$] ($n=1$ (**5**) or 2 (**6**)) in high yield.

Complete conversion of the *closo*-carboranylphosphazene **5** to the corresponding *nido*-carboranylphosphazene was only achieved by treatment with excess NEt_3 and prolonged reflux in acetone. However, the same reaction of **5** using ethanol as solvent led to a new cyclotriphosphazene $(NHEt_3)_2[N_3P_3(O_2C_{12}H_8)_2(O)\{OCH_2C_2B_9H_{10}CH_2OCH_2CH_3\}]$ (**7**).

For compounds with two 2,2′-dioxybiphenyl groups, **5**, **7**, and **8**, a mixture of different stereoisomers may be expected. However, in contrast to the findings of Grutzmacher et al.,[15] the reaction of *gem*-[$N_3P_3Cl_2(O_2C_{12}H_8)_2$] with $C_2B_{10}H_{10}\{CH_2OH\}_2$ to give **5** did not seem to affect the configuration at the phosphorus centers, leading to the *meso* compound, the configuration assumed for the precursor. Likewise, no change in the configuration of the phosphorus centers was apparent when **5** was treated with NEt_3 in ethanol to give the *nido*-carboranylphosphazene $(NHEt_3)_2[N_3P_3(O_2C_{12}H_8)_2(O)\{OCH_2C_2B_9H_{10}CH_2OCH_2CH_3\}]$ (**7**). However, the reaction of **5** to give $(NHEt_3)[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_9H_{10}\}]$ (**8**) seems to proceed with a change of configuration at one phosphorus center, giving a racemic mixture.

Experimental Section

Instrumentation: IR spectra were recorded in the range 4000–350 cm^{-1} on a Perkin-Elmer FT-IR Spectrum One spectrometer with samples as Nujol mulls between polyethylene sheets. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyser. Mass spectra were recorded on a VG Autospec by means of LSIMS techniques in a nitrobenzyl alcohol matrix. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Unity 300 spectrometer with samples in $CDCl_3$ or $(CD_3)_2CO$ solutions. Chemical shifts are quoted relative to $SiMe_4$ (^1H and ^{13}C, external) and H_3PO_4 (85 %) (^{31}P, external).

Solvents and reagents: K_2CO_3 was dried at 140 °C prior to use. The acetone used as solvent was distilled from anhydrous $CaSO_4$ under a dry nitrogen atmosphere. Hexachlorocyclotriphosphazene [$N_3P_3Cl_6$] (Strem Chemicals) was purified by recrystallization from hot hexane and dried in vacuo. NEt_3 and $NBu_4F\cdot 3H_2O$ were purchased from Aldrich. Carborane [$C_2B_{10}H_{10}(CH_2OH)_2$][23] and phosphazenes ([$N_3P_3Cl_2(O_2C_{12}H_8)_2$] and [$N_3P_3Cl_4(O_2C_{12}H_8)$]) were prepared by literature methods.[2b] The latter were purified by chromatography on a silica gel column eluting with dichloromethane/hexane (1:3). All the reactions were carried out under a dry nitrogen atmosphere.

Reaction of [$N_3P_3Cl_6$] with one equivalent of $C_2B_{10}H_{10}(CH_2OH)_2$: A solution of $C_2B_{10}H_{10}(CH_2OH)_2$ (0.102 g, 0.5 mmol) in acetone (10 mL) was added to a mixture of $N_3P_3Cl_6$ (0.174 g, 0.5 mmol) and K_2CO_3 (0.173 g, 1.25 mmol) in acetone (30 mL), and the resulting mixture was stirred for 1 h. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane (3 × 10 mL). Evaporation of the solvent in vacuo gave a white solid (0.232 g), which proved to be a mixture of *gem*-[$N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}$] (**1**) (ca. 51 %), *gem*-[$N_3P_3Cl_2\{(OCH_2)_2C_2B_{10}H_{10}\}_2$] (**2**) (19 %), and *non-gem*-[$N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}$] (**4**) (30 %).

The majority of compound **4** precipitated from the mixture upon addition of CH_2Cl_2/hexane (1:15). Yield: 0.046 g (20 %).

4: Elemental analysis calcd (%) for $C_4H_{14}B_{10}Cl_4N_3O_2P_3$ (479.0): C 10.02, H 2.95, N 8.77; found: C 10.52, H 3.12, N 8.26; IR (Nujol): $\tilde{\nu}=1187-1207$ (vs) (P=N); 2586 (s, br) and 2661 cm^{-1} (m) (B–H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=23.98$ ("t", 1P; PCl_2), 20.74 ppm ("d", 2P; $PCl\{OCH_2C_2B_{10}H_{10}CH_2O\}$) ($AB_2$ system, $^2J_{AB}=65.8$ Hz); $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): $\delta=24.36$ ("dd", 1P; PCl_2), 21.62 ppm ("d", 2P; $PCl\{OCH_2C_2B_{10}H_{10}CH_2O\}$) ($AB_2$ system, $^2J_{AB}=69.9$ Hz); ^1H NMR ($CDCl_3$): $\delta=5.06$ (m, $N=37.2$ Hz, 2H; OCH*H*), 4.65 (m, $N=34.2$ Hz, 2H; OC*H*H), 3.6–1 ppm (m, 10H; $B_{10}H_{10}$); ^1H NMR ($(CD_3)_2CO$): $\delta=5.63$ (m, $N=31.8$ Hz, 2H; OCH*H*), 5.13 (m, $N=30$ Hz, 2H; OC*H*H), 3.6–1 ppm (m, 10H; $B_{10}H_{10}$); $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): $\delta=79.84$ (s, 2C; OCH$_2$), 68.38 ppm (s, 2C; $C_2B_{10}H_{10}$); MS (LSIMS$^+$): m/z (%): 479 (100) [M^+] and peaks derived from the sequential loss of carborane and chloride.

1: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=24.83$ (d, 2P; PCl_2), 11.35 ppm (t, 1P; $P\{(OCH_2)_2C_2B_{10}H_{10}\}$) ($AX_2$ system, $^2J_{AX}=72.3$ Hz); $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): $\delta=25.34$ (d, 2P; PCl_2), 12.21 ppm (t, 1P; $P\{(OCH_2)_2C_2B_{10}H_{10}\}$) ($AX_2$ system, $^2J_{AX}=72.8$ Hz); ^1H NMR ($CDCl_3$): $\delta=4.71$ (d, $^3J(H,P)=19.2$ Hz, 4H; OCH_2), 3.4–1 ppm (m, 10H; $B_{10}H_{10}$); ^1H NMR ($(CD_3)_2CO$): $\delta=5.0$ (d, $^3J(H,P)=19.2$ Hz, 4H; OCH_2), 3.4–1 ppm (m, 10H; $B_{10}H_{10}$).

Reaction of [$N_3P_3Cl_6$] with two equivalents of $C_2B_{10}H_{10}(CH_2OH)_2$: A mixture of [$N_3P_3Cl_6$] (0.174 g, 0.5 mmol), $C_2B_{10}H_{10}(CH_2OH)_2$ (0.204 g, 1 mmol), and K_2CO_3 (0.346 g, 2.5 mmol) in acetone (40 mL) was stirred for 1 h at room temperature. The volatiles were evaporated in vacuo, and the residue was extracted with dichloromethane (3 × 10 mL). Evaporation of the solvent gave a white solid (0.276 g), which proved to be a mixture of *gem*-[$N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}$] (**1**) (ca. 11 %), *gem*-[$N_3P_3Cl_2\{(OCH_2)_2C_2B_{10}H_{10}\}_2$](**2**) (77 %), *gem*-[$N_3P_3\{(OCH_2)_2C_2B_{10}H_{10}\}_3$] (**3**) (3.3 %), and *non-gem*-[$N_3P_3Cl_4\{(OCH_2)_2C_2B_{10}H_{10}\}$] (**4**) (8.7 %). Addition of hexane (60 mL) led to the deposition of **2** as a white solid contaminated with about 6 % of **3** (0.119 g, 43 %).

The first solid obtained, which was insoluble in dichloromethane, was washed with water (60 mL), ethanol (3 × 5 mL), and hexane (3 × 5 mL). The resulting white solid (**3**) was dried in vacuo (0.023 g, 7.7 %).

2: Elemental analysis calcd (%) for $C_8H_{28}B_{20}Cl_2N_3O_4P_3$ (610.4): C 15.74, H 4.62, N 6.88; found: C 16.24, H 4.55, N 6.57; IR (Nujol): $\tilde{\nu}=1176$ (s), 1228–1280 (vs) (P=N); 2590 (s, br) and 2632 cm^{-1} (s) (B–H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=28.63$ (t, 1P; PCl_2), 16.75 ppm (d, 2P; $P\{(OCH_2)_2C_2B_{10}H_{10}\}$) ($AX_2$ system, $^2J_{AX}=76.8$ Hz); $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): $\delta=28.95$ (t, 1P; PCl_2), 17.67 ppm (d, 2P; $P\{(OCH_2)_2C_2B_{10}H_{10}\}$) ($AX_2$ system, $^2J_{AX}=77.8$ Hz); ^1H NMR ($CDCl_3$): $\delta=4.63$ (m, $N=49.8$ Hz, 8H; OCH_2), 3.6–1 ppm (m, 20H; $B_{10}H_{10}$); ^1H NMR ($(CD_3)_2CO$): $\delta=4.93$ (m, $N=49.8$ Hz, 8H; OCH_2), 3.6–1 ppm (m, 20H; $B_{10}H_{10}$); $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): $\delta=75.78$ (s, 4C; OCH$_2$), 67.33 ppm (s, 4C; $C_2B_{10}H_{10}$); MS (LSIMS$^+$): m/z (%): 611 (100) [$(M+H)^+$] and peaks derived from the sequential loss of carborane and chloride.

Synthesis of [$N_3P_3\{(OCH_2)_2C_2B_{10}H_{10}\}_3$] (3): A mixture of [$N_3P_3Cl_6$] (0.174 g, 0.5 mmol), $C_2B_{10}H_{10}(CH_2OH)_2$ (0.306 g, 1.5 mmol), and K_2CO_3 (0.52 g, 3.75 mmol) in acetone (40 mL) was stirred for 24 h at room temperature. The volatiles were evaporated in vacuo, and the residue was washed with water (60 mL), ethanol (3 × 5 mL), hexane (3 × 5 mL), and dichloromethane (20 mL). The resulting white solid of **3** was dried in vacuo. Yield: 0.30 g (81 %). Compounds **1**, **2**, and **3** were detected in the resulting dichloromethane solution.

Elemental analysis calcd (%) for $C_{12}H_{42}B_{30}N_3O_6P_3$ (741.7): C 19.43, H 5.71, N 5.67; found: C 19.40, H 5.55, N 5.61; IR (Nujol): $\tilde{\nu}=1177$ (s), 1256–1281 (vs) (P=N); 2586 (vs, br), 2638 (s), and 2651 cm^{-1} (s) (B–H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=21.92$ ppm (s, 3P; N_3P_3 ring); $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): $\delta=23.0$ ppm (s); ^1H NMR ($(CD_3)_2CO$): $\delta=4.91$ (br, 12H; OCH_2), 3.4–1 ppm (m, 30H; $B_{10}H_{10}$); MS (LSIMS$^+$): m/z (%): 743 (100) [$(M+H)^+$].

Synthesis of $\mathbf{[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_{10}H_{10}\}]}$ (5): $\mathrm{C_2B_{10}H_{10}(CH_2OH)_2}$ (0.102 g, 0.5 mmol) and $\mathrm{K_2CO_3}$ (0.173 g, 1.25 mmol) were added to a solution of *gem*-$\mathrm{[N_3P_3Cl_2(O_2C_{12}H_8)_2]}$ (0.287 g, 0.5 mmol) in acetone (40 mL), and the mixture was stirred under reflux for 2 h. The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane (3 × 10 mL). Concentration of the combined extracts to a volume of about 1 mL and addition of light petroleum (66–68 °C) led to the precipitation of **5** as a white solid. Yield: 0.335 g (95 %).

Elemental analysis calcd (%) for $\mathrm{C_{28}H_{30}B_{10}N_3O_6P_3}$ (705.6): C 47.66, H 4.28, N 5.95; found: C 48.08, H 4.58, N 5.63; IR (Nujol): $\tilde{\nu}=1170$ (vs, br), 1198–1273 (vs) (P=N); 2586 (s, br) and 2628 $\mathrm{cm^{-1}}$ (m) (B–H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta=25.37$ (2P; $\mathrm{P(O_2C_{12}H_8)}$), 23.61 ppm (1P; $\mathrm{P\{(OCH_2)_2C_2B_{10}H_{10}\}}$) ($\mathrm{AB_2}$ system, $^2J_{\mathrm{AB}}=101.3$ Hz); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): $\delta=26.35$ (2P; $\mathrm{P(O_2C_{12}H_8)}$), 24.56 ppm (1P; $\mathrm{P\{(OCH_2)_2C_2B_{10}H_{10}\}}$) ($\mathrm{AB_2}$ system, $^2J_{\mathrm{AB}}=101.5$ Hz); ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta=7.55-7.20$ (m, 16H; aromatic rings), 4.67 ppm (d, $^3J_{\mathrm{P,H}}=18.1$ Hz, 4H; $\mathrm{OC}H_2$), 3.4–1 (m, 10H; $\mathrm{B_{10}H_{10}}$); ^{1}H NMR ($\mathrm{(CD_3)_2CO}$): $\delta=7.77-7.41$ (m, 16H; aromatic rings), 4.91 (d, $^3J_{\mathrm{P,H}}=18.5$ Hz, 4H; $\mathrm{OC}H_2$), 3.4–1 ppm (m, 10H; $\mathrm{B_{10}H_{10}}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta=122.0$ (s), 126.55 (s), 128.92 (s), 130.07 (s), 130.24 (s), 148.22 (m, 24C; $\mathrm{C_{12}H_8}$), 74.22 (s, 2C; $\mathrm{O}C\mathrm{H_2}$), 66.11 (s, 1C; $C_2\mathrm{B_{10}H_{10}}$), 66.05 ppm (s, 1C; $C_2\mathrm{B_{10}H_{10}}$); MS (LSIMS$^+$): *m*/*z* (%): 706 (100) [M^+] and peaks derived from the sequential loss of carborane and biphenoxide.

Synthesis of $\mathbf{[N_3P_3(O_2C_{12}H_8)\{(OCH_2)_2C_2B_{10}H_{10}\}_2]}$ (6): A mixture of *gem*-$\mathrm{[N_3P_3Cl_4(O_2C_{12}H_8)]}$ (0.230 g, 0.5 mmol), $\mathrm{C_2B_{10}H_{10}(CH_2OH)_2}$ (0.204 g, 1 mmol), and $\mathrm{K_2CO_3}$ (0.35 g, 2.5 mmol) in acetone (40 mL) was refluxed for 2 h. The volatiles were evaporated in vacuo, and the residue was extracted with dichloromethane (3 × 10 mL). The solution was concentrated to a volume of about 1 mL, and subsequent addition of light petroleum or hexane led to the precipitation of **6** as a white solid. Yield: 0.337 g (93 %).

Elemental analysis calcd (%) for $\mathrm{C_{20}H_{36}B_{20}N_3O_6P_3}$ (723.7): C 33.19, H 5.01, N 5.81; found: C 33.60, H 5.32, N 5.70; IR (Nujol): $\tilde{\nu}=1190-1277$ (vs) (P=N); 2588 (vs, br) and 2628 $\mathrm{cm^{-1}}$ (s) (B–H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta=24.37$ (1P; $\mathrm{P(O_2C_{12}H_8)}$), 22.84 ppm (2P; $\mathrm{P\{(OCH_2)_2C_2B_{10}H_{10}\}}$) ($\mathrm{AB_2}$ system, $^2J_{\mathrm{AB}}=92$ Hz); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): $\delta=25.53$ (1P; $\mathrm{P(O_2C_{12}H_8)}$), 23.78 ppm (2P; $\mathrm{P\{(OCH_2)_2C_2B_{10}H_{10}\}}$) ($\mathrm{AB_2}$ system, $^2J_{\mathrm{AB}}=92.4$ Hz); ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta=7.58-7.19$ (m, 8H; aromatic rings), 4.61 (m, $N=47.7$ Hz, 8H; $\mathrm{OC}H_2$), 3.4–1 ppm (m, 20H; $\mathrm{B_{10}H_{10}}$); ^{1}H NMR ($\mathrm{(CD_3)_2CO}$): $\delta=7.73-7.29$ (m, 8H; aromatic rings), 4.84 (m, $N=53.2$ Hz, 8H; $\mathrm{OC}H_2$), 3.6–1 ppm (m, 20H; $\mathrm{B_{10}H_{10}}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta=121.65$ (s), 126.49 (s), 128.53 (s), 129.8 (s), 129.91 (s), 147.78 (m, 12C; $\mathrm{C_{12}H_8}$), 73.91 (s, 4C; $\mathrm{O}C\mathrm{H_2}$), 66.1 ppm (s, 4C; $\mathrm{C_2B_{10}H_{10}}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): $\delta=122.62$ (s), 127.58 (s), 129.39 (s), 130.8 (s), 131.12 (s), 148.79 (m, 12C; $\mathrm{C_{12}H_8}$), 75.94 (s, 4C; $\mathrm{O}C\mathrm{H_2}$), 66.84 ppm (s, 4C; $\mathrm{C_2B_{10}H_{10}}$); MS (LSIMS$^+$): *m*/*z* (%): 724 (100) [M^+] and peaks derived from the sequential loss of biphenoxide and carborane.

Synthesis of $\mathbf{(NHEt_3)_2[N_3P_3(O_2C_{12}H_8)_2(O)\{OCH_2C_2B_9H_{10}CH_2OCH_2CH_3\}]}$ (7): $\mathrm{NEt_3}$ (4.3 mL, 30.5 mmol) was added to a suspension of **5** (0.282 g, 0.4 mmol) in ethanol (30 mL) and the mixture was stirred under reflux for 50 h. The white precipitate of **7** formed was filtered off and washed with ethanol (3 × 5 mL) and hexane (3 × 5 mL). Yield: 0.256 g (68 %).

Elemental analysis calcd (%) for $\mathrm{C_{42}H_{67}B_9N_5O_7P_3}$ (944.2): C 53.43, H 7.15, N 7.42; found: C 53.0, H 6.82, N 7.22; IR (Nujol): $\tilde{\nu}=1177-1263$ (vs) (P=N); 2525 (s, br) and 2668 $\mathrm{cm^{-1}}$ (m, br) (B–H); 3368 $\mathrm{cm^{-1}}$ (br) (N–H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): $\delta=28.69$ (d, 2P; $\mathrm{P(O_2C_{12}H_8)}$), 8.59 (t, 1P; $\mathrm{P(O)\{OCH_2C_2B_9H_{10}CH_2OCH_2CH_3\}}$) ($\mathrm{AX_2}$ system, $^2J_{\mathrm{AX}}=69.6$ Hz); ^{1}H NMR ($\mathrm{(CD_3)_2CO}$): $\delta=10.65$ (br, 2H; $\mathrm{N}H\mathrm{Et_3^+}$), 7.94–7.38 (m, 16H; aromatic rings), 4.34 (m, $N=33.3$ Hz, 2H; $\mathrm{OC}H_2$), 3.83 (2H; $\mathrm{C_2B_9H_{10}C}H_2\mathrm{O}$, AB system, $\delta_{\mathrm{A}}=4.06$, $\delta_{\mathrm{B}}=3.6$, $^2J(\mathrm{H\text{-}H})=11.1$ Hz), 3.48 (2H; $\mathrm{OC}H_2\mathrm{CH_3}$, $\mathrm{ABX_3}$ system, $\delta_{\mathrm{A}}=3.55$, $\delta_{\mathrm{B}}=3.41$, $^2J_{\mathrm{AB}}(\mathrm{H\text{-}H})=9.4$ Hz, $^3J_{\mathrm{AX}}={}^3J_{\mathrm{BX}}(\mathrm{H,H})=6.9$ Hz), 3.12 (c, $^3J(\mathrm{H,H})=7.2$ Hz, 12H; $\mathrm{N\text{-}C}H_2$), 1.27 (t, $^3J(\mathrm{H,H})=7.2$ Hz, 18H; $\mathrm{N\text{-}CH_2C}H_3$), 1.05 (t, $^3J(\mathrm{H,H})=6.9$ Hz, 3H; $\mathrm{OCH_2C}H_3$), 3.1–0 (m, 9H; $\mathrm{B_9H_{10}}$), −2.43 ppm (br, 1H; $\mathrm{B_9H_{10}}$); MS (LSIMS$^-$): *m*/*z* (%): 741 (22) [$\{M-2(\mathrm{NHEt_3})\}^-$] and peaks derived from the loss of $\mathrm{OCH_2CH_3}$, $\mathrm{C_2B_9H_{10}}$, and biphenoxide.

Synthesis of $\mathbf{(NHEt_3)[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_9H_{10}\}]}$ (8): $\mathrm{NEt_3}$ (1 mL, 8.5 mmol) was added to a solution of **5** (0.141 g, 0.2 mmol) in acetone (30 mL) and the mixture was stirred under reflux for 48 h. The volatiles were then evaporated in vacuo and dichloromethane (1 mL) was added. Upon addition of light petroleum (20 mL), **8** precipitated as a white solid. Yield: 0.147 g (92 %).

Elemental analysis calcd (%) for $\mathrm{C_{34}H_{46}B_9N_4O_6P_3}$ (797.0): C 51.24, H 5.82, N 7.03; found: C 50.96, H 5.61, N 7.06; IR (Nujol): $\tilde{\nu}=1172$ (vs), 1190–1270 $\mathrm{cm^{-1}}$ (vs) (P=N); 2525 (s, br) (B–H); 3370 $\mathrm{cm^{-1}}$ (br) (N–H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta=26.92$ ("dd", 1$\mathrm{P_A}$; $\mathrm{P(O_2C_{12}H_8)}$), 22.80 ("dd", 1$\mathrm{P_B}$; $\mathrm{P(O_2C_{12}H_8)}$), 20.30 ppm ("dd", 1$\mathrm{P_C}$; $\mathrm{P\{(OCH_2)_2C_2B_9H_{10}\}}$) (ABC system, $^2J_{\mathrm{AB}}=92$ Hz, $^2J_{\mathrm{AC}}=86.3$ Hz, $^2J_{\mathrm{BC}}=81.7$ Hz); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): $\delta=27.53$ (1$\mathrm{P_A}$; $\mathrm{P(O_2C_{12}H_8)}$), 25.92 (1$\mathrm{P_B}$; $\mathrm{P(O_2C_{12}H_8)}$), 20.09 ppm ("dd", 1$\mathrm{P_X}$; $\mathrm{P\{(OCH_2)_2C_2B_9H_{10}\}}$) (ABX system, $^2J_{\mathrm{AB}}=93.7$ Hz, $^2J_{\mathrm{AX}}=97.3$ Hz, $^2J_{\mathrm{BX}}=82.7$ Hz); ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta=8.8$ (br, 1H; $\mathrm{N}H\mathrm{Et_3}$), 7.61–7.28 (m, 16H; aromatic rings), 4.70 ("dd", $^3J(\mathrm{P,H})=$ 8.5 Hz, $^2J(\mathrm{H,H})=12.6$ Hz, 2H; $\mathrm{OCH}H$), 4.22 ("dd", $^3J(\mathrm{P,H})=25$ Hz, $^2J(\mathrm{H,H})=12.6$ Hz, 2H; $\mathrm{OC}H\mathrm{H}$), 2.93 (q, $^3J(\mathrm{H,H})=7.2$ Hz, 6H; $\mathrm{NC}H_2\mathrm{CH_3}$), 1.22 (t, $^3J(\mathrm{H,H})=$ 7.2 Hz, 9H; $\mathrm{NCH_2C}H_3$), 3.4–1 (m, 9H; $\mathrm{B_9H_{10}}$), −2.64 ppm (m, 1H; $\mathrm{B_9H_{10}}$); ^{1}H NMR ($\mathrm{(CD_3)_2CO}$): $\delta=7.70-7.39$ (m, 16H; aromatic rings), 4.56 ("dd", $^3J(\mathrm{P,H})=$ 10.3 Hz, $^2J(\mathrm{H,H})=12.3$ Hz, 2H; $\mathrm{OCH}H$), 4.19 ("dd", $^3J(\mathrm{P,H})=24.2$ Hz, $^2J(\mathrm{H,H})=12.3$ Hz, 2H; $\mathrm{OC}H\mathrm{H}$), 3.43 (q, $^3J(\mathrm{H,H})=7.2$ Hz, 6H; $\mathrm{NC}H_2\mathrm{CH_3}$), 1.40 (t, $^3J(\mathrm{H,H})=7.2$ Hz, 9H; $\mathrm{NCH_2C}H_3$), 3.4–1 (m, 9H; $\mathrm{B_9H_{10}}$), −2.33 ppm (br, 1H; $\mathrm{B_9H_{10}}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta=121.92$ (m), 126.55 (m), 128.82 (m), 130.01 (m), 130.44 (m), 148.13 (m, 24C; $\mathrm{O_2C_{12}H_8}$), 72.34 (s, 1C; $\mathrm{O}C\mathrm{H_2}$), 72.27 (s, 1C; $\mathrm{O}C\mathrm{H_2}$), 58.3 (br, 2C; $\mathrm{C_2B_9H_{10}}$), 46.04 (s, 3C; $\mathrm{N}C\mathrm{H_2CH_3}$), 8.62 ppm (s, 3C; $\mathrm{NCH_2}C\mathrm{H_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): $\delta=122.93$ (m), 127.11 (m), 129.76 (m), 130.49 (m), 130.82 (m), 149.36 (m, 24C; $\mathrm{O_2C_{12}H_8}$), 72.20 (s, 1C; $\mathrm{O}C\mathrm{H_2}$), 72.12 (s, 1C; $\mathrm{O}C\mathrm{H_2}$), 58.0 (br, 2C; $\mathrm{C_2B_9H_{10}}$), 48.29 (s, 3C; $\mathrm{N}C\mathrm{H_2CH_3}$), 9.49 ppm (s, 3C; $\mathrm{NCH_2}C\mathrm{H_3}$); MS (LSIMS$^-$): *m*/*z* (%): 695 (100) [M^-] and peaks derived from the loss of $\mathrm{(CH_2)_2C_2B_9H_{10}}$ and $\mathrm{OC_{12}H_8}$.

Synthesis of $\mathbf{(NBu_4)[N_3P_3(O_2C_{12}H_8)_2\{(OCH_2)_2C_2B_9H_{10}\}]}$ (9): $\mathrm{NBu_4F\cdot 3\,H_2O}$ (0.15 g, 0.48 mmol) was added to a solution of **5** (0.282 g, 0.4 mmol) in acetone (40 mL) and the mixture was stirred under reflux for 16 h. The solution was concentrated to dryness and the residue was washed with isopropanol (3 × 10 mL) and hexane (3 × 5 mL). The white solid obtained was dried in vacuo. Yield: 0.349 g (93 %).

Elemental analysis calcd (%) for $\mathrm{C_{44}H_{66}O_6B_9N_4P_3}$ (937.3): C 56.39, H 7.10, N 5.98; found: C 55.93, H 7.40, N 5.71; IR (Nujol): $\tilde{\nu}=1172$ (vs), 1190–1270 (vs) (P=N); 2525 $\mathrm{cm^{-1}}$ (s, br) (B–H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta=26.52$ (1$\mathrm{P_A}$; $\mathrm{P(O_2C_{12}H_8)}$), 24.91 (1$\mathrm{P_B}$; $\mathrm{P(O_2C_{12}H_8)}$), 19.08 ppm ("dd", 1$\mathrm{P_X}$; $\mathrm{P\{(OCH_2)_2C_2B_9H_{10}\}}$) (ABX system, $^2J_{\mathrm{AB}}=93.7$ Hz, $^2J_{\mathrm{AX}}=97.3$ Hz, $^2J_{\mathrm{BX}}=82.7$ Hz); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{(CD_3)_2CO}$): $\delta=27.50$ (1$\mathrm{P_A}$; $\mathrm{P(O_2C_{12}H_8)}$), 26.18 (1$\mathrm{P_B}$; $\mathrm{P(O_2C_{12}H_8)}$), 19.9 ppm ("dd", 1$\mathrm{P_X}$; $\mathrm{P\{(OCH_2)_2C_2B_9H_{10}\}}$) (ABX system, $^2J_{\mathrm{AB}}=93.3$ Hz, $^2J_{\mathrm{AX}}=93.6$ Hz, $^2J_{\mathrm{BX}}=91.0$ Hz); ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta=7.54-7.26$ (m, 16H; aromatic rings), 4.56 ("dd", $^3J(\mathrm{P,H})=10.3$ Hz, $^2J(\mathrm{H,H})=12.3$ Hz, 2H; $\mathrm{OCH}H$), 4.16 ("dd", $^3J(\mathrm{P,H})=24.2$ Hz, $^2J(\mathrm{H,H})=$ 12.3 Hz, 2H; $\mathrm{OC}H\mathrm{H}$), 3.47 (m, 8H; $\mathrm{NBu_4^+}$), 1.86 (m, 8H; $\mathrm{NBu_4^+}$), 1.46 (m, 8H; $\mathrm{NBu_4^+}$), 1.10 (t, $^3J(\mathrm{H,H})=7.5$ Hz, 12H; $\mathrm{NBu_4^+}$), 3.4–1 (m, 9H; $\mathrm{B_9H_{10}}$), −2.30 (br, 1H; $\mathrm{B_9H_{10}}$); ^{1}H NMR ($\mathrm{(CD_3)_2CO}$): $\delta=7.70-7.39$ (m, 16H; aromatic rings), 4.55 ("dd", $^3J(\mathrm{P,H})=10.5$ Hz, $^2J(\mathrm{H,H})=12.3$ Hz, 2H; $\mathrm{OCH}H$), 4.18 ("dd", $^3J(\mathrm{P,H})=24.3$ Hz, $^2J(\mathrm{H,H})=12.3$ Hz, 2H; $\mathrm{OC}H\mathrm{H}$), 3.48 (m, 8H; $\mathrm{NBu_4^+}$), 1.86 (m, 8H; $\mathrm{NBu_4^+}$), 1.46 (m, 8H; $\mathrm{NBu_4^+}$), 1.01 (t, $^3J(\mathrm{H,H})=7.2$ Hz, 12H; $\mathrm{NBu_4^+}$), 3.4–1 (m, 9H; $\mathrm{B_9H_{10}}$), −2.30 ppm (br, 1H; $\mathrm{B_9H_{10}}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta=122.19$ (m), 126.22 (m), 129.1 (m), 129.76 (m), 129.99 (m), 148.56 (m, 24C; $\mathrm{O_2C_{12}H_8}$), 71.37 (br, 2C; $\mathrm{O}C\mathrm{H_2}$), 58.0 (br, 2C; $\mathrm{C_2B_9H_{10}}$), 58.9 (s, 4C; $\mathrm{NBu_4^+}$), 23.9 (s, 4C; $\mathrm{NBu_4^+}$), 19.64 (s, 4C; $\mathrm{NBu_4^+}$), 13.63 ppm (s, 4C; $\mathrm{NBu_4^+}$); MS (LSIMS$^-$) *m*/*z* (%): 695 (100) [M^-] and peaks derived from the loss of $\mathrm{(CH_2)_2C_2B_9H_{10}}$ and $\mathrm{OC_{12}H_8}$.

Crystal structure determinations: The crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of a Bruker SMART diffractometer. Data were collected by using monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\alpha=0.71073$ Å) in ω-scan mode. An absorption correction was applied with the program SADABS, based on multiple scans. The structures were solved by direct methods and refined against F^2 using the program SHELXL-97.[24] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further crystal data are given in Table 4. The structure of **7** contains two dichloromethane molecules, one of which is disordered.

CCDC-200259 and CCDC-200260 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; or deposit@ccdc.cam.ac.uk).

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