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New macrobicyclic triphosphazides and triphosphazenes formed by self-assembly of tripodal triazides with triphosphanes

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Abstract—The self-assembly of tris(3-azidobenzyl)amines with 1,1,1-tris[(diphenylphosphino)methyl]ethane via tripod–tripod coupling proceeds successfully to give chiral macrobicyclic triphosphazides. The heating of these macrobicyclic cages induces a remarkable stepwise triple extrusion of molecular nitrogen to afford tri-λ^5-phosphazenes, which preserved the chiral, propeller-like topology of their precursors. The replacement of one benzylic arm by an *ortho*-phenethylic or propylenic one still allows the success of the self-assembly. However, the quaternization of the pivotal nitrogen atom of the triamine in the form of *N*-oxide prevented its coupling with the triphosphane.

1. Introduction

The synthesis, structure, and properties of numerous macrobicyclic cages have been intensively studied during the past few decades. In fact, several synthetic strategies may be devised for the construction of such molecular architectures. The more direct one is the tripod–tripod coupling, a molecular self-assembly process that implies the formation of three bonds in a single step.[1] A reaction of this type requires first complementary components containing two or more interaction sites capable of establishing multiple connections, and second the reversibility of the connecting events in order to allow the full exploration of the energy hypersurface of the system.[2] A major drawback of tripod–tripod coupling is the occurrence of extensive side reactions, which minimize the yield of the expected bicyclic product. Only in limited cases,[3] such processes have been carried out in synthetically useful yields, provided that fine tuning of reagents, reactions, and conditions could be achieved.

The imination reaction of tervalent phosphorus compounds with organic azides is known as Staudinger reaction,[4] a two-step process involving the initial nucleophilic attack of a P^{III} center, usually a tertiary phosphane $(R^1)_3P$, to the terminal nitrogen atom of an azide R^2N_3 followed by dinitrogen extrusion from the intermediate phosphazide $(R^1)_3PN_3R^2$ giving the λ^5-phosphazene $(R^1)_3P{=}NR^2$ (also known as phosphine imine or iminophosphorane). Only in a few instances, the primary imination products, phosphazides, have been isolated.[5]

In previous communications,[6] we reported the preparation of the first examples of chiral C_3-symmetric, macrobicyclic triphosphazides formed by two tripodal subunits by means of triple P–N bond formation in Staudinger reaction, and without recourse to high-dilution conditions.

Here we present the results of a detailed study on the preparation, characterization, and properties of a variety of macrobicyclic triphosphazides and tri-λ^5-phosphazenes formed by self-assembly of pivotal triazides bearing a tribenzylamine skeleton with 1,1,1-tris[(diphenylphosphino)methyl]ethane. The validity of this method has been extended to other triazides where one benzylic arm is replaced by an *ortho*-phenethylic or propylenic one.

2. Results and discussion

2.1. Preparation of tris(3-azidobenzyl)amines (1)

A wide range of new tris(3-azidobenzyl)amines **1** of C_3, C_s, and C_1 local symmetries (Fig. 1 and Table 1) were prepared by standard procedures.

As a representative example, the synthesis of the asymmetric triazides **1c** and **1d** is outlined in Scheme 1, which is based on the sequential reduction of 2-chloro-5-nitrobenzaldehyde to 5-amino-2-chlorobenzyl alcohol, which is further converted into the corresponding azidobenzyl alcohol in the usual way (diazotization/azidation). This alcohol reacted

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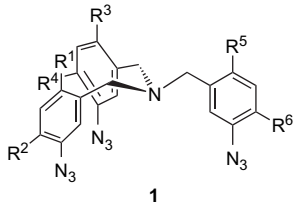


Figure 1. Tripodal triazides **1**.

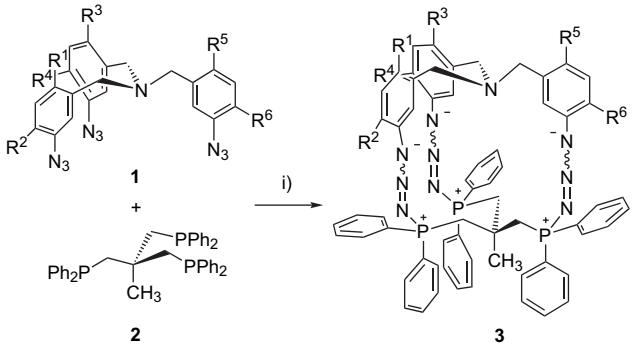
Table 1. Tris(3-azidobenzyl)amines **1**

Compound	R^1	R^2	R^3	R^4	R^5	R^6
1a	H	H	H	H	H	H
1b	Br	H	Br	H	Br	H
1c	Br	H	Br	H	Cl	H
1d	Br	H	Cl	H	H	H
1e	H	CH_3	H	CH_3	H	CH_3
1f	H	CH_3	H	CH_3	H	H
1g	H	CH_3	H	H	H	H

with thionyl chloride to yield 5-azido-2-chlorobenzyl chloride that was converted into the corresponding primary benzylamine by Gabriel reaction. Further alkylation with 5-azido-2-bromobenzyl bromide afforded **1c** and the expected secondary amine, which is alkylated by 3-azidobenzyl iodide finally yielding **1d**. A detailed description for the synthesis of the rest of compounds **1** prepared, as well as their spectroscopic data, can be found in Supplementary data.

2.2. Tripod–tripod coupling of triazides 1 with 1,1,1-tris[(diphenylphosphino)methyl]ethane (2)

The tripod–tripod coupling of triazides **1** with 1,1,1-tris[(diphenylphosphino)methyl]ethane (**2**) was carried out in diethyl ether solution at room temperature. The resulting macrobicyclic triphosphazides **3** (Scheme 2) precipitated from the reaction medium as yellow solids and were obtained in good yields, with the only exception of **3e** that could not be prepared (Table 2). In this last case (Table 2, entry 5), the material isolated from the reaction was a complex mixture, which seems to contain compounds combining both phosphazide and phosphazene units, as indicated by its ^{1}H,

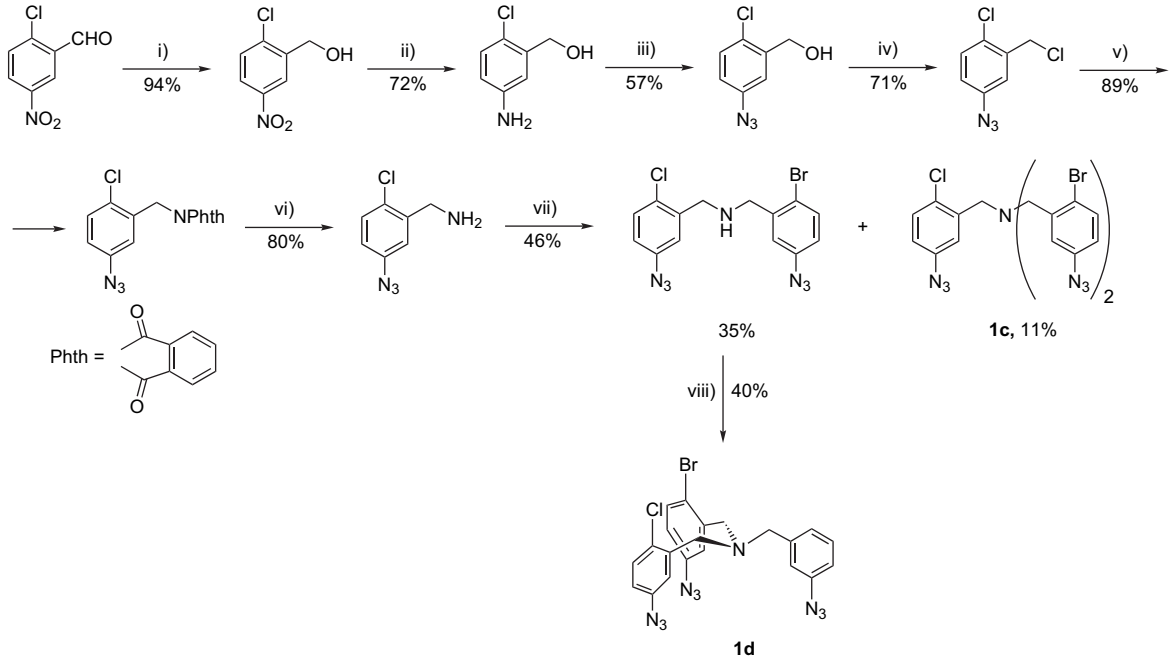


Scheme 2. Synthesis of triphosphazides **3**. Conditions: (i) Et_2O, 25 °C, 3 h.

Table 2. Triphosphazides **3**

Entry	Compound	R^1	R^2	R^3	R^4	R^5	R^6	Yield (%)
1	**3a**	H	H	H	H	H	H	79
2	**3b**	Br	H	Br	H	Br	H	63
3	**3c**	Br	H	Br	H	Cl	H	80
4	**3d+3d′**	Br	H	Cl	H	H	H	66
5	**3e**	H	CH_3	H	CH_3	H	CH_3	—[a]
6	**3f**	H	CH_3	H	CH_3	H	H	77
7	**3g**	H	CH_3	H	H	H	H	79

[a] Complex mixture.



Scheme 1. Synthesis of triazides **1c** and **1d**. Reagents and conditions: (i) $NaBH_4$, MeOH, 0→25 °C, 24 h; (ii) Fe–AcOH, EtOH, reflux, 4 h; (iii) $NaNO_2$, dil H_2SO_4, 0 °C, 30 min, then NaN_3, 25 °C, 16 h; (iv) $SOCl_2$, CH_2Cl_2, 0 °C, 3 h; (v) potassium phthalimide (KNPhth), DMF, 80 °C, 12 h; (vi) $N_2H_4\cdot H_2O$, EtOH, reflux, 3 h; (vii) 5-azido-2-bromobenzyl bromide, 1,4-dioxane, reflux, 3 h, then Et_3N, 25 °C, 2 h, (viii) 3-azidobenzyl iodide, 1,4-dioxane, reflux, 8 h, then Et_3N, 25 °C, 3 h.

$^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra. The structural determination of compounds **3** was accomplished by means of their analytical and spectral data. Full characterization of **3a** was discussed in a previous communication.[6c]

Selected physical data of new triphosphazides **3b–g** were essentially coincident with those of the previously reported **3a**, indicative of their tridimensional arrangements where the lone pair and CH_3 group on the bridgehead atoms are directed in and out, respectively, from the bicyclic cavity and possessing propeller-like topology in solution and in the solid state. The intrinsic chirality of these species was shown by the anisochronous CH_2N and CH_2P methylene protons in their ^1H NMR spectra, as well as by the appearance of the *ipso*, *ortho*, *meta*, and *para* carbons of the *Ph*P rings as two sets of signals. The observed magnetic equivalence of the three arms of macrobicycles **3a** and **3b** in their solution ^1H and $^{13}C\{^1H\}$ NMR spectra is in contrast with their inequivalence in the solid state. The X-ray crystal structure of **3a**, shows two zwitterionic PN_3 fragments ($^+P–N{=}N–N^-$) of *Z* configuration with respect to the central N=N bond whereas the third one is *E*. This dissimilitude of NMR data can only be understood if, in $CDCl_3$ solution at 298 K, the fluxionality of **3a** and **3b** involves *E*/*Z* equilibration of the phosphazide fragments to yield a bicyclic skeleton of C_3-symmetric mean conformation. Indicative of such equilibration is the observed broad signals in their ^1H and $^{13}C\{^1H\}$ NMR spectra, and more notoriously in their $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ at 298 K, where a very broad singlet around δ 3.0 ($\Delta\nu_{½}$=972 Hz for **3a** and 608 Hz for **3b**) is observed. This signal is somewhat thinner when the spectra were run in CD_2Cl_2 solution, appearing at δ 8.93 ($\Delta\nu_{½}$=425 Hz) and 5.36 ($\Delta\nu_{½}$=484 Hz) for **3a** and **3b**, respectively. The assumption of this equilibration is also in accord with the results of low temperature NMR experiments. Thus, on cooling at 253 K in $CDCl_3$ solution, the broad singlet in the $^{31}P\{^1H\}$ NMR spectrum of **3a** separated out into two broad singlets, which at 213 K resolved into two well-separated multiplets of complex fine structure, centered at δ 2 and 24, which probably are associated with the two types of phosphorus atoms: those included into PN_3 units of *Z* and *E* configuration, respectively (Fig. 2). These values are similar to those observed in the solid state by the CPMAS-NMR spectrum of **3a**, which shows one signal at δ 1.31 and other at 24.13, the first one of double intensity.

To our knowledge, the characterization of phosphazides as *Z* or *E* geometrical isomers (in their zwitterionic $^+P–N{=}N–N^-$ forms, equivalent to *s-cis* or *s-trans* in the neutral P=N–N=N form, respectively) by spectroscopic means has not been generalized up to now. From the $^{31}P\{^1H\}$ NMR data of compounds **3** in solution, we conclude that the chemical shifts for the phosphorus atoms belonging to intracyclic phosphazide units are quite different depending on their geometry. Thus, we propose the approximate shift values of δ 23 and δ 0 for phosphazides with *E* and *Z* geometry, respectively.

The molecular fluxionality of **3f** and **3g** is not so accused as that of their counterparts commented above. Their $^{31}P\{^1H\}$ NMR spectra show two well-defined singlets in the ranges established above for *E* and *Z* phosphazide units. Thus, compound **3f** shows two signals at δ 2.14 and 21.58, this last one of double intensity, assignable to the phosphorus atoms of the units with *Z* (arm without CH_3) and *E* configuration (arms with CH_3), respectively. By contrary, the triphosphazide **3g** shows a slightly broad singlet at δ 5.12 of double intensity than that appearing at δ 21.50. These data can be interpreted by assuming that the CH_3 group in *ortho*-position to the N terminus of a PN_3 function exerts some steric influence on the geometry of the nearby phosphazide fragment. This may result in preference for the *E* configuration of that phosphazide arm in order to minimize repulsive interactions with the *ortho*-methyl group (Fig. 3).

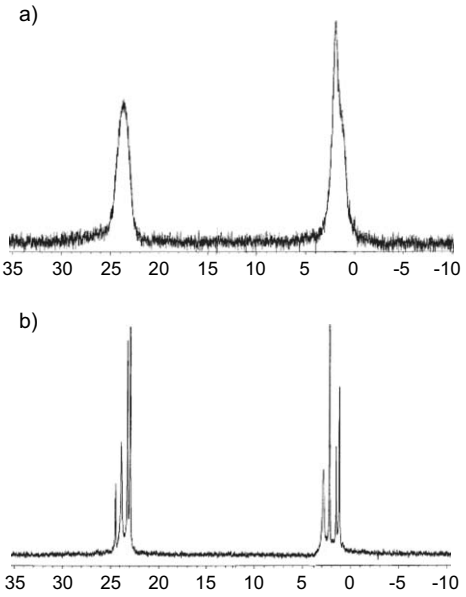


Figure 2. $^{31}P\{^1H\}$ NMR spectra of triphosphazide **3a** recorded at (a) 253 K and (b) 213 K.

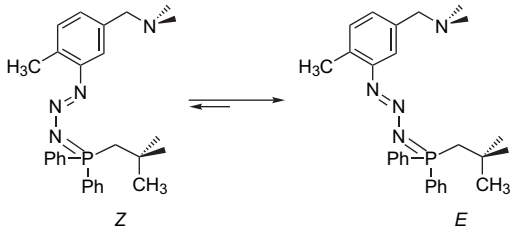
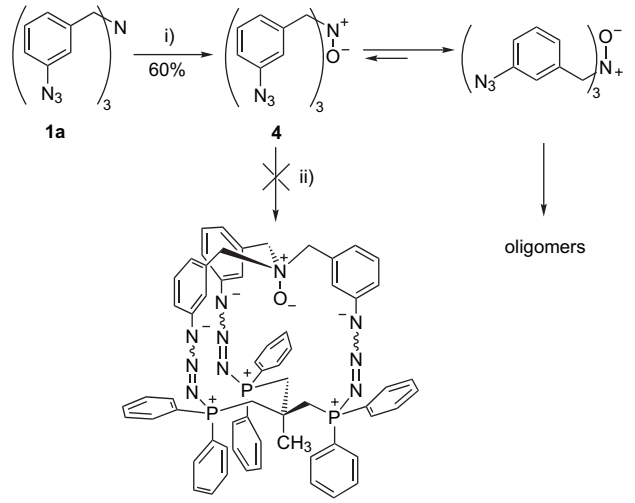


Figure 3. *E*/*Z* equilibrium of the phosphazide fragments, displaced toward *E* as a result of the presence of the *ortho*-CH_3 group.

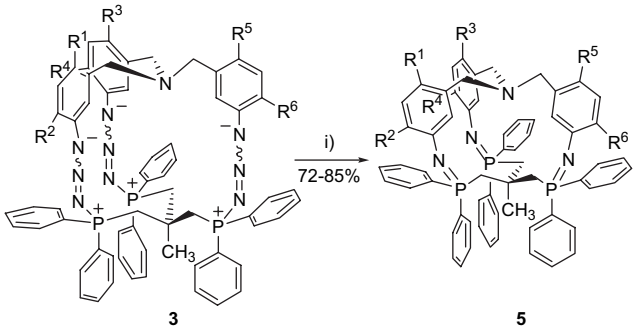
The coupling of triphos with tris(3-azidobenzyl)amine *N*-oxide **4**, prepared by reaction of **1a** with *m*CPBA in 60% yield, did not yield the expected triphosphazide, instead giving rise to oligomeric products (Scheme 3). We reasoned that this result can be a consequence of a low population, in the conformational equilibrium of **4**, of the reactive conformer with the optimal tridimensional structure for the success of the tripod–tripod coupling, other more populated conformations leading to oligomers. Alternatively, the putative macrobicycle could be highly unstable as a result of electronic repulsions between the negatively charged O and N atoms.



Scheme 3. Reaction of tris(3-azidobenzyl)amine *N*-oxide (**4**) with triphosphane **2**. Reagents and conditions: (i) *m*CPBA, $CHCl_3$, 0 °C, 4 h; (ii) 2, Et_2O, 25 °C, 3 h.

2.3. Macrobicyclic tri-λ^5-phosphazenes from triphosphazides

When compounds **3** were heated at 333 K in $CDCl_3$ solution for 24 h they were cleanly converted into tri-λ^5-phosphazenes **5** in 72–85% yields, by triple extrusion of molecular N_2 (Scheme 4). The dinitrogen expulsion from each PN_3 unit can be understood as the second mechanistic step of Staudinger imination reaction.[4,7]



	R^1	R^2	R^3	R^4	R^5	R^6
5a	H	H	H	H	H	H
5b	Br	H	Br	H	Br	H
5c	Br	H	Br	H	Cl	H
5d + 5d'	Br	H	Cl	H	H	H
5e	H	CH_3	H	CH_3	H	CH_3
5f	H	CH_3	H	CH_3	H	H
5g	H	CH_3	H	H	H	H

Scheme 4. Synthesis of tri-λ^5-phosphazenes **5**. Conditions: (i) $CDCl_3$, 60 °C, 24 h.

The structural determination of the cage compounds **5** was accomplished by its analytical and spectroscopic data. Full characterization of **5a** and **5b** was discussed in our previous communication.[6d] The X-ray analysis of **5b** was described there, and is shown here for convenience (Fig. 4). The molecule is located on a noncrystallographic threefold axis passing through the two bridgehead atoms of the bicyclic cage, and its propeller-like shape is clearly apparent when the molecule is viewed along this axis. Both propeller units, the upper tribenzylamine core and the lower *tert*-pentane fragment, present the same helical twist sense.[8]

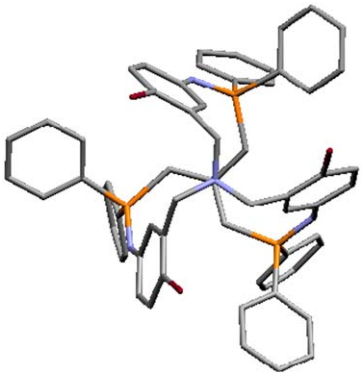


Figure 4. A perspective view of compound **5b** as projected along the threefold axis.

Since the physical data of the new tri-λ^5-phosphazenes **5c–g** were essentially coincident with those of the previously reported **5a** and **5b**, we assumed the same tridimensional arrangements for the new members of the series prepared here.

In the ^{1}H NMR spectra of compounds **5**, the protons of the pivotal CH_3 group appear as a singlet between −0.78 and −0.69 ppm, notably upfield relative to those in the phosphane (δ 0.95).[9] These data are consistent with a conformation in solution in which the three pseudoaxial phenyl groups are flanking the pivotal methyl group, situation that is favored by stabilizing [CH···π] interactions.[10]

The simplicity of the NMR of C_3-symmetric **5a**, **5b**, and **5e** indicates high symmetry. The ^{31}P{^{1}H} NMR spectra of these compounds show only one sharp singlet between −1.43 and 0.49 ppm, shifted 25.87–27.79 ppm downfield relative to that of the parent triphosphane δ −27.3,[11] in accordance with previous reports on acyclic λ^5-phosphazenes.[4b–d] In their ^{1}H and ^{13}C{^{1}H} NMR spectra, only one set of signals is observed for the three equivalent arms of the bicyclic structure. The methylene protons of the CH_2N and CH_2P groups are magnetically inequivalent as a consequence of their diastereotopic nature, accounting for the chirality of these propeller-shaped compounds.

The different coupling patterns shown by the two CH_2P protons (an apparent triplet and an apparent quintuplet) in the ^{1}H NMR spectra are particularly significant. The first signal is due to what may be called the *pseudoaxial* (nearly parallel to the local C_3-axis) methylene proton, ^3J(H,H)≈ ^2J(H,P)=14.4–14.5 Hz, whereas the second one, with a separation between lines of 6.8–8.4 Hz, corresponds to the *pseudoequatorial* proton, which is further split by a long-distance coupling with the phosphorus atom in one of the other arms in relative *M* planar disposition to that proton, as revealed by the crystal structure of **5b**. The observation of these coupling patterns in the solution spectrum of **5b** clearly indicates that the solid state and the room temperature solution conformation of compounds **5** could be nearly identical.

In the ^{13}C{^{1}H} NMR spectra of compounds **5a**, **5b**, and **5e**, the two phenyl rings linked to each phosphorus atom are

magnetically inequivalent, and show notable differences in the ^1J(C,P) coupling constants of their two *ipso* carbons (see Section 4). This is a consequence of the environment of the phosphorus atoms,[6a] which causes the neat differentiation of the two *Ph*P rings: one *pseudoaxial* and the other *pseudoequatorial*.

Compounds **5c**, **5f**, and **5g** with only two chemically identical arms, exhibit two singlets in a 2:1 intensity ratio in their $^{31}P\{^1H\}$ NMR. Their ^1H and $^{13}C\{^1H\}$ MNR spectra are very complex as a result of the diastereotopicity of the two chemically equivalent arms (see Section 4).

The tri-λ^5-phosphazene derived from the constitutionally chiral, benzyl 4-bromobenzyl 4-chlorobenzyl amine **1d** was obtained as an approximately equimolecular mixture of two diastereoisomers, **5d** and **5d′**. These two diastereoisomers were not separated, the composition of the mixture (1:1) being deduced by integration in its ^1H NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of this mixture shows six singlets of equal intensity, which correspond to the two sets of three inequivalent phosphorus atoms, each one associated to one diastereoisomer. The equimolecular diastereomeric composition of the mixture is also evidenced in some regions of its $^{13}C\{^1H\}$ NMR spectrum, such as the CH_2N zone in the range δ 55.13–58.10.

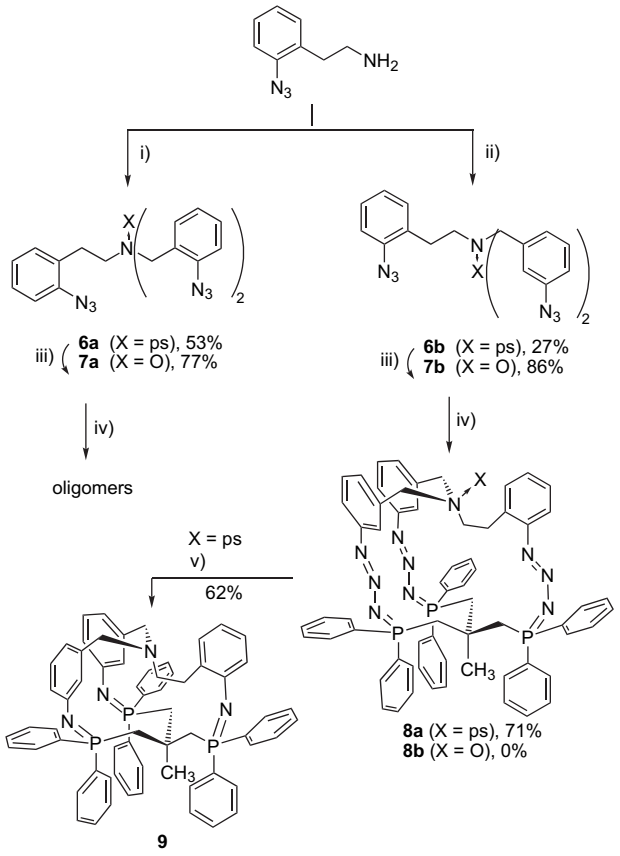
We wondered if the triple extrusion of dinitrogen in **3** leading to **5** takes place either simultaneously in the three arms or stepwise, in one arm after the other. The mass spectrometric data, MS-FAB+, of the reaction mixture at different times, from 10 min up to 6 h, revealed that the dinitrogen extrusion occurs stepwise, since we could detect in those spectra molecular ions corresponding to macrobicyclic species in which phosphazide arms coexisted with λ^5-phosphazene arms.

2.4. Structural variations in the triazide component

Having established the efficiency of the self-assembly between triphosphane **2** and triazides derived from tribenzylamine with its three azido groups situated either in *ortho*[6a,b] or *meta* positions, we next examined if this coupling strategy is still valid for the assembly of **2** with other tripodal triazides of slightly different structure, as for instance those bearing one arm of different length and/or nature than the other benzylic ones. With this aim, we prepared the triazides **6a** and **6b** by alkylation of 2-(2-azidophenyl)ethylamine[12] with 2 equiv of the appropriate azidobenzyl iodide. The quaternization of the pivotal nitrogen atom of **6** with *m*CPBA gave rise to the corresponding *N*-oxides **7** (Scheme 5).

The tripodal coupling of these new azides with **2** was successful only in the case of triazide **6b** giving rise to triphosphazide **8a**, whereas **6a**, **7a**, and **7b** afforded oligomeric products (Scheme 5).

The structure determination of **8a** was accomplished by comparison of its spectroscopic data with those previously obtained for other triphosphazides. Its ^{31}P NMR spectrum shows three signals, two (at δ 19.93 and 21.28) attributed to the benzylic diastereotopic *E* arms and the third one (at δ −0.55) corresponding to the phenethylic *Z* arm. In the solid state, its CPMAS-NMR shows similar shift values, δ −3.12,



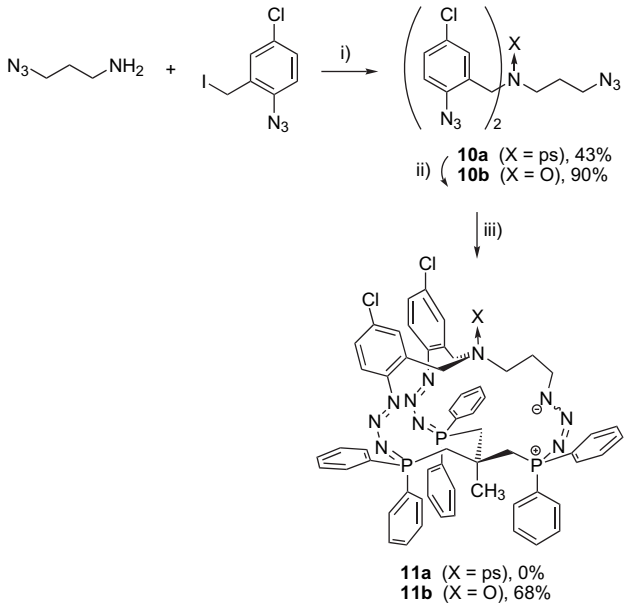
Scheme 5. Synthesis of tri-λ^5-phosphazene **9**. Reagents and conditions: (i) (a) 2-azidobenzyl iodide, 1,4-dioxane, reflux, 4 h; (b) excess Et_3N, rt, 2 h; (ii) (a) 3-azidobenzyl iodide, 1,4-dioxane, reflux, 4 h; (b) excess Et_3N, rt, 2 h; (iii) *m*CPBA, $CHCl_3$, 0 °C, 4 h; (iv) triphos (**2**), Et_2O, 25 °C, N_2 atm, 3 h; (v) $CDCl_3$, 60 °C, 24 h.

21.02, and 25.24. Molecular models (CPK) accommodate best an out arrangement for the lone pair on the bridgehead nitrogen atom.

The thermal treatment of **8a** yielded tri-λ^5-phosphazene **9** in 62%, which shows spectroscopic data in accordance with its structure (Scheme 5).

Finally, we tested if the change of one benzylic arm by other aliphatic one of similar length (three carbon atoms) allowed the tripod–tripod coupling. Thus, we prepared triazide **10a** by alkylation of 3-azidopropylamine[13] with 2-azido-5-chlorobenzyl iodide (Scheme 6). The quaternization of its pivotal nitrogen with *m*CPBA gave rise to the corresponding *N*-oxide **10b**.

The reaction of bis(2-azido-5-chlorobenzyl)(3-azidopropyl)amine (**10a**) with triphosphane **2** did not provide the expected macrobicycle, instead oligomeric products were obtained. However, the reaction of the *N*-oxide **10b** afforded a yellow microcrystalline solid, its spectroscopic data and elemental analysis were in agreement with the structure of triphosphazide **11b** (Scheme 6). Probably, macrobicycle **11a** could not be obtained because of its instability in solution caused by the pyramidal inversion of its pivotal nitrogen atom, which favors the dissociation of the phosphazide arms, as we have demonstrated in other similar cases.[6b] In contrast, the stability of triphosphazide **11b** is notably greater as a



Scheme 6. Synthesis of triphosphazide **11b**. Reagents and conditions: (i) (a) 1,4-dioxane, reflux, 4 h; (b) excess Et_3N, rt, 2 h; (ii) *m*CPBA, $CHCl_3$, 0 °C, 4 h; (iii) 2, Et_2O, 25 °C, N_2 atm, 3 h.

result of the higher configurational stability imposed by the *N*-oxide function, which obviously blocks such inversion. Moreover, the pivotal oxygen atom of **11b** avoids electronic repulsive interferences with the phosphazide nitrogen atoms by orienting itself out from the internal cavity.

3. Conclusions

A wide range of examples of chiral macrobicyclic triphosphazides have been prepared by tripod–tripod coupling of several triazides derived from the tribenzylamine skeleton with 1,1,1-tris[diphenylphosphino]methyl]ethane. These cage compounds show molecular fluxionality, associated with the *E*/*Z* isomerization of its PN_3 units, and could be converted into tri-λ^5-phosphazenes by nonsimultaneous dinitrogen extrusion in its three phosphazide fragments. The reported method was also suitable for the synthesis of macrobicyclic triphosphazides where one benzylic arm has been substituted by another *ortho*-phenethylic or propylenic fragment.

4. Experimental

4.1. General

Coupling reactions were carried out under nitrogen and using solvents that were dried by routine procedures. Column chromatography was performed with the use of silica gel (70–200 μm) as a stationary phase. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were determined as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded at 25 °C on a Brucker AC200 (200 MHz) or a Varian Unity 300 (300 MHz). ^1H and ^{13}C chemical shifts were reported in parts per million downfield of internal tetramethylsilane (TMS) and ^{31}P chemical shifts were externally referenced to 85% aqueous phosphoric acid or ammonium hydrogen phosphate. Abbreviations of coupling patterns are as follows: s, singlet; d, doublet; t, triplet; q, quadruplet. The mass spectra were recorded on a Hewlett-Packard 5993C spectrometer (EI) or on a VG-Autospec spectrometer (FAB^+). Microanalyses were performed on an EA 1108 Carlo Erba instrument.

4.2. Materials

Compounds 2-chloro-5-nitrobenzyl alcohol,[14] 5-amino-2-chlorobenzyl alcohol,[15] 3-azidobenzyl alcohol,[16] 3-azidobenzyl bromide,[17] and 2-azidobenzyl iodide[6b] were prepared following previously reported procedures. The syntheses and data of 3-azido-4-methylbenzyl alcohol, 3-azidobenzyl chloride, 3-azido-4-methylbenzyl chloride, 3-azido-4-methylbenzyl iodide, 3-azidobenzylamine, 3-azido-4-methylbenzylamine, bis(3-azidobenzyl)amine, bis(3-azido-4-methylbenzyl)-amine, bis(5-azido-2-bromobenzyl)amine, tris(3-azidobenzyl)amine (**1a**), tris(5-azido-2-bromobenzyl)-amine (**1b**), tris(3-azido-4-methylbenzyl)amine (**1e**), bis(3-azido-4-methylbenzyl)(3-azidobenzyl)amine (**1f**), bis(3-azidobenzyl)(3-azido-4-methylbenzyl)amine (**1g**), tris(3-azidobenzyl)amine *N*-oxide (**4**), bis(2-azidobenzyl)[(2-azidophenyl)ethyl]amine (**6a**), bis(3-azidobenzyl)[(2-azidophenyl)ethyl]amine (**6b**), bis(2-azidobenzyl)[(2-azidophenyl)ethyl]amine *N*-oxide (**7a**), bis(3-azidobenzyl)[(2-azidophenyl)ethyl]amine *N*-oxide (**7b**), bis(2-azido-5-chlorobenzyl)(3-azidopropyl)amine (**10a**), and bis(2-azido-5-chlorobenzyl)(3-azidopropyl)amine *N*-oxide (**10b**) are given in Supplementary data.

4.3. Preparation of 5-azido-2-chlorobenzyl alcohol

A solution of sodium nitrite (3.30 g, 48 mmol) in H_2O (30 mL) was added dropwise to an ice-cooled solution of 5-amino-2-chlorobenzyl alcohol (5.20 g, 33 mmol) in a mixture of H_2O (40 mL) and concentrated sulfuric acid (7.3 mL). The resulting mixture was stirred at that temperature for 30 min. A solution of sodium azide (4.42 g, 68 mmol) in H_2O (25 mL) was then added dropwise. After stirring for 16 h at room temperature, the precipitated solid was isolated by filtration, washed with H_2O (100 mL), air-dried, and recrystallized from abs EtOH. Yield: 57%; mp 86–87 °C (colorless prisms); ^1H NMR (200 MHz, $CDCl_3$): δ=2.55 (br s, 1H, OH), 4.72 (s, 2H, CH_2), 6.86 (dd, J(H,H)=8.5, 2.5 Hz, 1H, H4), 7.17 (d, J(H,H)=2.5 Hz, 1H, H6), 7.29 (d, J(H,H)=8.5 Hz, 1H, H3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ=62.27 (CH_2), 118.67, 119.05, 128.06 (*q*), 130.41, 139.12 (*q*), 139.94 (*q*); IR (Nujol): ν=3251 (OH), 2122 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%)=185 (8) [M^++2], 183 (15) [M^+], 157 (100); $C_7H_6ClN_3O$ (183.59): Calcd C 45.79, H 3.29, N 22.89; found C 45.64, H 3.17, N 22.96.

4.4. Preparation of 5-azido-2-chlorobenzyl chloride

Thionyl chloride (4.16 g, 35 mmol) was added dropwise to an ice-cooled solution of 5-azido-2-chlorobenzyl alcohol (5.51 g, 30 mmol) in dry CH_2Cl_2 (40 mL) and the reaction mixture was stirred at 0 °C for 3 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel; diethyl ether/*n*-hexane 1:1). Yield: 71%; yellow oil; ^1H NMR (200 MHz,

$CDCl_3$): δ=4.64 (s, 2H, CH_2), 6.92 (dd, J(H,H)=8.6, 2.6 Hz, 1H, H4), 7.12 (d, J(H,H)=2.6 Hz, 1H, H6), 7.35 (d, J(H,H)=8.6 Hz, 1H, H3); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ=43.09 (CH_2), 120.31 (q), 121.09, 129.75, 131.00, 136.59 (q), 139.33 (q); IR (film): ν=2117 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%)=205 (8) [M^++4], 203 (38) [M^++2], 201 (42) [M^+], 175 (61), 77 (100); $C_7H_5Cl_2N_3$ (202.04): Calcd C 41.61, H 2.49, N 20.80; found C 41.43, H 2.53, N 20.71.

4.5. Preparation of 5-azido-2-bromobenzyl bromide

A solution of bromine (3.5 g, 22 mmol) in C_6H_6 (35 mL) was added dropwise to a cooled solution of triphenylphosphane (5.8 g, 22 mmol) in C_6H_6 (100 mL). The mixture was stirred at that temperature for 45 min, when a solution of 5-azido-2-bromobenzyl alcohol (5 g, 22 mmol) in C_6H_6 (20 mL) and triethylamine (2.2 g, 22 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. The triethylammonium bromide was separated by filtration, and the solvent removed under reduced pressure. The resulting material was chromatographed (silica gel; ethyl acetate/*n*-hexane 1:4). Yield: 81%; mp 50–51 °C (yellow prisms from ethyl acetate/*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$): δ=4.54 (s, 2H, CH_2), 6.84 (dd, J(H,H)=8.6, 2.6 Hz, 1H, H4), 7.11 (d, J(H,H)=2.6 Hz, 1H, H6), 7.53 (d, J(H,H)=8.6 Hz, 1H, H3); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=32.54 (CH_2), 119.70 (q), 120.70, 121.62, 134.56, 138.70 (q), 140.20 (q); IR (Nujol): ν=2113 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%)=293 (6) [M^++4], 291 (4) [M^++2], 289 (4) [M^+], 103 (100); $C_7H_5Br_2N_3$ (290.94): Calcd C 28.90, H 1.73, N 14.44; found C 28.83, H 1.89, N 14.31.

4.6. Preparation of 3-azidobenzyl iodide

Sodium iodide (2.85 g, 19 mmol) was added to a solution of 3-azidobenzyl chloride (2.2 g, 13 mmol) in dry acetone (25 mL), and this reaction mixture was stirred at room temperature for 12 h. The precipitated sodium chloride was separated by filtration. From the filtrate, the solvent was removed under reduced pressure and the resulting material was chromatographed (silica gel; diethyl ether/*n*-hexane 1:1). Yield: 91%; yellow oil; ^1H NMR (200 MHz, $CDCl_3$): δ=4.37 (s, 2H, CH_2), 6.88 (d, J(H,H)=7.7 Hz, 1H, H4), 7.00 (s, 1H, H2), 7.12 (d, J(H,H)=7.7 Hz, 1H, H6), 7.25 (t, J(H,H)=7.7 Hz, 1H, H5); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ=4.34 (CH_2), 118.46, 119.15, 125.22, 130.12, 140.31 (q), 141.15 (q); IR (film): ν=2114 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%)=259 (6) [M^+], 207 (100); $C_7H_6IN_3$ (259.05): Calcd C 32.46, H 2.33, N 16.22; found C 32.39, H 2.28, N 16.20.

4.7. Preparation of *N*-(5-azido-2-chlorobenzyl)-phthalimide

A mixture of 5-azido-2-chlorobenzyl chloride (4.54 g, 25 mmol) and potassium phthalimide (5.56 g, 30 mmol) in dry DMF (30 mL) was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture was poured on ice/H_2O (500 mL) and the precipitated solid was isolated by filtration, washed with H_2O (2×100 mL), and air-dried under vacuum. The solid was then recrystallized from chloroform/diethyl ether. Yield: 89%; mp 225–227 °C (white needles); ^1H NMR (300 MHz, $CDCl_3$): δ=4.94 (s, 2H, CH_2), 6.82 (d, J(H,H)=2.5 Hz, 1H, H6), 6.90 (dd, J(H,H)=8.4, 2.5 Hz, 1H, H4), 7.35 (d, J(H,H)=8.4 Hz, 1H, H3), 7.73–7.82 (m, 2H, H_{arom}), 7.86–7.90 (m, 2H, H_{arom}); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=39.28 (CH_2), 119.25, 119.49, 123.69, 129.04 (q), 130.90, 131.96 (q), 134.31, 135.27 (q), 139.14 (q), 167.69 (q, CO); IR (Nujol): ν=2116 (N_3), 1725 (CO) cm^{-1}; MS (70 eV, EI): m/z (%)=314 (4) [M^++2], 312 (8) [M^+], 249 (82), 130 (100); $C_{15}H_9ClN_4O_2$ (312.71): Calcd C 57.61, H 2.90, N 17.92; found C 57.73, H 2.84, N 17.89.

4.8. Preparation of 5-azido-2-chlorobenzylamine

$N_2H_4\cdot H_2O$ (5 mL) was added to a solution of *N*-(5-azido-2-chlorobenzyl)phthalimide (5.26 g, 18 mmol) in EtOH (75 mL), and the mixture was stirred at reflux temperature for 3 h. After cooling to room temperature, NaOH 10% (50 mL) was added and the resulting solution was extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were washed with brine (100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was chromatographed (silica gel; ethyl acetate/methanol 1:1). Yield: 80%; yellow oil; ^1H NMR (200 MHz, $CDCl_3$): δ=1.58 (br s, 2H, NH_2), 3.90 (s, 2H, CH_2), 6.84 (dd, J(H,H)=8.6, 2.6 Hz, 1H, H4), 7.08 (d, J(H,H)=2.6 Hz, 1H, H6), 7.30 (d, J(H,H)=8.6 Hz, 1H, H5); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ=44.22 (CH_2), 118.49, 118.24, 129.08 (q), 130.56, 139.03 (q), 142.24 (q); IR (film): ν=3397, 3326 (NH_2), 2115 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%)=184 (26) [M^++2], 182 (39) [M^+], 154 (100); $C_7H_7ClN_4$ (259.05): Calcd C 46.04, H 3.86, N 30.68; found C 45.89, H 3.80, N 30.83.

4.9. Preparation of (5-azido-2-bromobenzyl)(5-azido-2-chlorobenzyl)amine and bis(5-azido-2-bromobenzyl)(5-azido-2-chlorobenzyl)amine (1c)

5-Azido-2-bromobenzyl bromide (4.4 g, 15 mmol) was added to a solution of 5-azido-2-chlorobenzylamine (3.65 g, 20 mmol) in dry dioxane (100 mL). The mixture was heated at reflux temperature for 3 h. After cooling to room temperature, triethylamine (2.0 g, 20 mmol) was added, and the mixture then stirred for 2 h. The triethylammonium bromide was separated by filtration, and the solvent was removed under reduced pressure. From the resulting residue, a mixture of secondary and tertiary amines was separated by chromatography (silica gel; ethyl acetate/*n*-hexane 1:9). (5-Azido-2-bromobenzyl)(5-azido-2-chlorobenzyl)-amine: Yield: 35%; mp 111–113 °C (yellow prisms from chloroform); ^1H NMR (200 MHz, $CDCl_3$): δ=1.87 (br s, 1H, NH), 3.85 (s, 2H, CH_2), 3.87 (s, 2H, CH_2), 6.79 (dd, J(H,H)=8.5, 2.8 Hz, 1H, H4/H4′), 6.86 (dd, J(H,H)=8.5, 2.8 Hz, 1H, H4/H4′), 7.14 (d, J(H,H)=2.8 Hz, 2H, H6+H6′), 7.31 (d, J(H,H)=8.5 Hz, 1H, H3/H3′), 7.48 (d, J(H,H)=8.5 Hz, 1H, H3/H3′); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ=50.43 (CH_2), 52.89 (CH_2), 118.95, 119.13 (q), 119.29, 120.40, 120.55, 129.62 (q), 130.69, 133.92, 139.01 (q), 139.13 (q), 139.71 (q), 140.73 (q); IR (Nujol): ν=3166 (NH), 2116 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%)=396 (12) [M^++5], 394 (36) [M^++3], 392 (36) [M^++1], 363 (39), 103 (100); $C_{14}H_{11}BrClN_7$ (392.64): Calcd C 42.83, H 2.82, N 24.97; found C 42.91, H 2.77, N 24.82. Bis(5-azido-2-bromobenzyl)(5-azido-2-chlorobenzyl)amine (**1c**): Yield: 11%; mp 125–127 °C (brown prisms from ethyl

acetate/*n*-hexane); ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.80 (s, 4H, CH_2), 3.82 (s, 2H, CH_2), 6.72 (dd, *J*(H,H)=8.5, 2.8 Hz, 2H, H4), 6.79 (dd, *J*(H,H)=8.5, 2.8 Hz, 1H, H4′), 7.25–7.30 (m, 4H, H3′+H6+H6′), 7.45 (d, *J*(H,H)=8.5 Hz, 2H, H3); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ=56.27 (CH_2), 58.78 (CH_2), 119.21, 119.28 (*q*), 119.54, 120.25, 120.34, 129.80 (*q*), 130.77, 133.99, 137.91 (*q*), 139.08 (*q*), 139.58 (*q*), 139.79 (*q*); IR (Nujol): ν=2113 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%)=604 (27) [M$^+$+4], 602 (36) [M$^+$+2], 600 (22) [M$^+$], 102 (100); $C_{21}H_{15}Br_2ClN_{10}$ (602.67): Calcd C 41.85, H 2.51, N 23.24; found C 41.70, H 2.47, N 23.09.

4.10. Preparation of (3-azidobenzyl)(5-azido-2-bromobenzyl)(5-azido-2-chlorobenzyl)amine (1d)

3-Azidobenzyl iodide (2.6 g, 10 mmol) was added to a solution of (5-azido-2-bromobenzyl)(5-azido-2-chlorobenzyl)-amine (3.9 g, 10 mmol) in dry dioxane (100 mL), and the mixture was stirred at reflux temperature for 8 h. After cooling to room temperature, triethylamine (1.5 g, 13 mmol) was added, and the mixture was stirred for 3 h. The triethylammonium iodide was separated by filtration. From the filtrate, the dioxane was evaporated to dryness and the residue was purified by column chromatography (silica gel; ethyl acetate/*n*-hexane 1:9); Yield: 40%; brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.68 (s, 2H, CH_2), 3.71 (s, 2H, CH_2), 3.73 (s, 2H, CH_2), 6.72 (dd, *J*(H,H)=8.4, 2.9 Hz, 1H, H_{arom}), 6.79 (dd, *J*(H,H)=8.5, 2.8 Hz, 1H, H_{arom}), 6.91 (br d, *J*(H,H)=7.9 Hz, 1H, H_{arom}), 7.06 (br s, 1H, H_{arom}), 7.16 (br d, *J*(H,H)=7.6 Hz, 1H, H_{arom}), 7.25–7.32 (m, 4H, H_{arom}), 7.44 (d, *J*(H,H)=8.4 Hz, 1H, H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=55.50 (CH_2), 58.08 (CH_2), 58.88 (CH_2), 118.10, 119.00, 119.11, 119.35, 120.29, 120.41, 121.05 (*q*), 125.15, 129.78 (*q*), 129.89, 130.69, 133.90, 138.21 (*q*), 139.01 (*q*), 139.72 (*q*), 139.87 (*q*), 140.31 (*q*), 140.60 (*q*); IR (film): ν=2112 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%)=524 (26) [M$^+$+2], 522 (25) [M$^+$], 103 (100); $C_{21}H_{16}BrClN_{10}$ (523.78): Calcd C 48.16, H 3.08, N 26.74; found C 48.00, H 3.21, N 26.67.

4.11. General procedure for the preparation of the triphosphazides 3

Two solutions, one of the corresponding tris(3-azidobenzyl)-amine **1** (1.5 mmol) in diethyl ether or dichloromethane (10 mL) and the other of 1,1,1-tris[(diphenylphosphino)-methyl]ethane (**2**) (1.3 g, 1.5 mmol) in diethyl ether (10 mL), were simultaneously added to a round-bottom flask containing diethyl ether (15 mL) under nitrogen atmosphere at room temperature over a period of 30 min with stirring. The resulting mixture was then stirred for 3 h. The precipitated pale yellow solid was filtered, washed with diethyl ether (3×10 mL), and dried under vacuum.

4.11.1. Triphosphazide 3a. Yield: 79%; mp>350 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.26 (br s, 3H, CH_3), 3.52–3.62 (m, 3H, CH_AH$_B$P), 3.63 (d, *J*(H,H)=14.3 Hz, 3H, CH_AH$_B$N), 3.81–3.93 (m, 6H, CH$_A$$H_B$N+CH$_A$$H_B$P), 6.80–7.10 (m, 9H, H_{arom}), 7.18 (t, *J*(H,H)=7.5 Hz, 3H, H_{arom}), 7.25–7.50 (m, 18H, H_{arom}), 7.59 (d, *J*(H,H)=7.8 Hz, 3H, H_{arom}), 7.90–8.10 (m, 9H, H_{arom}); ^{1}H NMR (200 MHz, CD_2Cl_2): δ=−0.23 (s, 3H, CH_3), 3.59–3.73 (m, 3H, CH_AH$_B$P), 3.78 (d, *J*(H,H)=14.7 Hz, 3H, CH_AH$_B$N), 3.85 (d, *J*(H,H)=14.7 Hz, 3H, CH$_A$$H_B$N), 3.94 (pseudot, *J*(H,H)(H,P)=14.5 Hz, 3H, CH$_A$$H_B$P), 7.07–7.16 (m, 9H, H_{arom}), 7.31–7.52 (m, 21H, H_{arom}), 7.63 (br d, *J*(H,H)=8.0 Hz, 3H, H_{arom}), 7.95 (br s, 3H, H_{arom}), 8.03–8.13 (m, 6H, H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=26.58 (br s, CH_3), 40.05 (m, CH_2P), 40.68 (q, ^{2}*J*(C,P)=3.5 Hz, CH_3*C*), 57.35 (CH_2N), 119.00 (br s, two signals), 125.78 (*q*), 128.65, 128.71 (d, ^{3}*J*(C,P)=10.1 Hz, *m*C-PhP), 128.73 (d, ^{3}*J*(C,P)=11.6 Hz, *m*C-PhP), 129.85 (d, ^{1}*J*(C,P)=83.6 Hz, *i*C-PhP), 131.09 (d, ^{2}*J*(C,P)=9.1 Hz, *o*C-PhP), 131.48 (d, ^{4}*J*(C,P)=2.0 Hz, *p*C-PhP), 132.16 (d, ^{1}*J*(C,P)=105.8 Hz, *i*C-PhP), 132.26 (d, ^{4}*J*(C,P)=1.0 Hz, *p*C-PhP), 132.92 (d, ^{2}*J*(C,P)=7.5 Hz, *o*C-PhP), 141.55 (*q*), 150.39 (*q*); ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ=26.49 (CH_3), 39.81 (m, CH_2P), 40.62 (q, ^{2}*J*(C,P)=3.5 Hz, CH_3*C*), 57.17 (CH_2N), 117.21 (br s), 121.96 (br s), 125.86 (*q*), 127.40 (d, ^{1}*J*(C,P)=108.8 Hz, *i*C-PhP), 128.75, 128.78 (d, ^{3}*J*(C,P)=11.6 Hz, *m*C-PhP), 128.85 (d, ^{3}*J*(C,P)=11.2 Hz, *m*C-PhP), 130.14 (d, ^{1}*J*(C,P)=82.4 Hz, *i*C-PhP), 130.96 (d, ^{2}*J*(C,P)=9.1 Hz, *o*C-PhP), 131.54 (d, ^{4}*J*(C,P)=2.8 Hz, *p*C-PhP), 132.30 (d, ^{4}*J*(C,P)=2.2 Hz, *p*C-PhP), 132.90 (d, ^{2}*J*(C,P)=7.5 Hz, *o*C-PhP), 142.01 (*q*), 150.25 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=3.76 (br s, $\Delta\nu_{½}$=972 Hz); ^{31}P{^{1}H} NMR (81.01 MHz, $CDCl_3$): δ=8.93 (br s, $\Delta\nu_{½}$=425 Hz); ^{31}P{^{1}H} NMR (CPMAS, 121.4 MHz, H_3PO_4 85%): δ=1.31 (s, 2P, *Z*-PN_3), 24.13 (s, 1P, *E*-PN_3); ^{31}P{^{1}H} NMR (CPMAS, 121.4 MHz, $(NH_4)_2HPO_4$): δ=2.72 (s, 2P, *Z*-PN_3), 25.44 (s, 1P, *E*-PN_3); IR (Nujol): ν=1440 (CP), 1122 (NP) cm^{-1}; MS (FAB+): *m*/*z* (%)=1036 (9) [M$^+$+1], 307 (100); $C_{62}H_{57}N_{10}P_3$ (1035.10): Calcd C 71.94, H 5.55, N 13.53; found C 71.79, H 5.68, N 13.39.

4.11.2. Triphosphazide 3b. Yield: 63%; mp (decomp.) 291–293 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.23 (br s, 3H, CH_3), 3.46–3.58 (m, 3H, CH_AH$_B$P), 3.83 (d, *J*(H,H)=16.6 Hz, 3H, CH_AH$_B$N), 3.86 (pseudot, *J*(H,H)(H,P)=14.2 Hz, 3H, CH$_A$$H_B$P), 4.05 (d, *J*(H,H)=16.6 Hz, 3H, CH$_A$$H_B$N), 6.92–6.94 (m, 6H, H_{arom}), 7.14–7.26 (m, 9H, H_{arom}), 7.34–7.41 (m, 12H, H_{arom}), 7.49 (dd, *J*(H,H)=8.4, 1.8 Hz, 3H, H_{arom}), 7.99–8.04 (m, 6H, H_{arom}), 8.22 (br s, 3H, H_{arom}); ^{1}H NMR (200 MHz, CD_2Cl_2): δ=−0.29 (br s, 3H, CH_3), 3.48–3.54 (m, 3H, CH_AH$_B$P), 3.84 (d, *J*(H,H)=16.7 Hz, 3H, CH_AH$_B$N), 3.86 (pseudot, *J*(H,H)(H,P)=12.9 Hz, 3H, CH$_A$$H_B$P), 4.11 (d, *J*(H,H)=16.7 Hz, 3H, CH$_A$$H_B$N), 6.95–6.98 (m, 6H, *m*H-PhP), 7.15 (dd, *J*(H,H)(H,P)=8.5, 8.1 Hz, 6H, *o*H-PhP), 7.26 (t, *J*=7.4 Hz, 3H, *p*H-PhP), 7.40–7.44 (m, 9H, H_{arom}), 7.47 (br d, *J*(H,H)=8.7 Hz, 3H, H_{arom}), 7.58 (d, *J*(H,H)=8.7 Hz, 3H, H_{arom}), 7.96–8.02 (m, 6H, *o*H-PhP), 8.20 (br s, 3H, H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=26.41 (br s, CH_3), 40.54 (m, CH_2P), 40.87 (q, ^{2}*J*(C,P)=3.0 Hz, CH_3*C*), 58.45 (CH_2N), 118.10 (br s), 119.89 (*q*), 121.20 (br s), 127.20 (d, ^{1}*J*(C,P)=110.0 Hz, *i*C-PhP), 128.73 (d, ^{3}*J*(C,P)=11.5 Hz, *m*C-PhP), 128.80 (d, ^{3}*J*(C,P)=11.3 Hz, *m*C-PhP), 129.04 (d, ^{1}*J*(C,P)=81.8 Hz, *i*C-PhP), 130.96 (d, ^{2}*J*(C,P)=9.3 Hz, *o*C-PhP), 131.70 (br s, *p*C-PhP), 132.31 (br s, *p*C-PhP), 132.84 (d, ^{2}*J*(C,P)=7.0 Hz, *o*C-PhP), 133.47, 139.52 (*q*), 149.53 (*q*); ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2): δ=26.35 (CH_3), 39.97 (m, CH_2P), 40.82 (q, ^{2}*J*(C,P)=3.6 Hz, CH_3*C*), 58.43 (CH_2N), 117.56 (br s), 119.62 (*q*), 121.96 (br s), 127.38 (d, ^{1}*J*(C,P)=107.2 Hz, *i*C-PhP), 128.77 (d,

^3J(C,P)=11.7 Hz, *m*C-PhP), 128.91 (d, ^3J(C,P)=11.3 Hz, *m*C-PhP), 129.39 (d, ^1J(C,P)=82.0 Hz, *i*C-PhP), 130.90 (d, ^2J(C,P)=9.2 Hz, *o*C-PhP), 131.69 (d, ^4J(C,P)=2.9 Hz, *p*C-PhP), 132.32 (d, ^4J(C,P)=2.2 Hz, *p*C-PhP), 132.81 (d, ^2J(C,P)=7.6 Hz, *o*C-PhP), 133.54, 139.89 (*q*), 149.66 (*q*); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=2.46 (br s, $\Delta\nu_{1/2}$= 608 Hz); $^{31}P\{^1H\}$ NMR (81.01 MHz, $CDCl_3$): δ=5.36 (br s, $\Delta\nu_{1/2}$=484 Hz); $^{31}P\{^1H\}$ NMR (CPMAS, 121.4 MHz, $(NH_4)_2HPO_4$): δ=−0.91 (s, *Z*-PN_3); IR (Nujol): ν=1438 (CP), 1109 (NP) cm^{-1}; MS (FAB+): *m*/*z* (%)=1275 (10) [M^++7], 1273 (7) [M^++5], 1271 (4) [M^++3], 1269 (6) [M^++1], 638 (100); $C_{62}H_{54}Br_3N_{10}P_3$ (1271.79): Calcd C 58.55, H 4.28, N 11.01; found C 58.42, H 4.43, N 10.88.

4.11.3. Triphosphazide 3c. Yield: 80%; >350 °C (yellow prisms from chloroform-*d*/diethyl ether); ^1H NMR (300 MHz, $CDCl_3$): δ=−0.25 (br s, 3H, CH_3), 3.46–3.59 (m, 3H, CH_AH_BP), 3.78–3.90 (m, 6H, CH_AH_BN+ CH_AH_BP), 4.01–4.15 (m, 3H, CH_AH_BN), 6.91–6.93 (m, 3H, H_{arom}), 7.13–7.26 (m, 9H, H_{arom}), 7.35–7.58 (m, 18H, H_{arom}), 7.98–8.06 (m, 6H, *o*H-PhP), 8.23 (br s, H_{arom}); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=26.40 (br s, CH_3), 39.97 (m, CH_2P), 40.82 (q, ^2J(C,P)=3.1 Hz, CH_3C), 55.87 (CH_2N), 58.44 (CH_2N), 118.26 (br s, two signals), 119.86 (*q*), 121.72 (br s, two signals), 127.19 (d, ^1J(C,P)= 106.8 Hz, *i*C-PhP), 128.72 (d, ^3J(C,P)=11.5 Hz, *m*C-PhP), 128.78 (d, ^3J(C,P)=11.0 Hz, *m*C-PhP), 129.04 (d, ^1J(C,P)= 82.0 Hz, *i*C-PhP), 129.59 (*q*), 130.20, 130.97 (d, ^2J(C,P)= 9.3 Hz, *o*C-PhP), 131.67 (br s, *p*C-PhP), 132.29 (br s, *p*C-PhP), 132.82 (d, ^2J(C,P)=6.9 Hz, *o*C-PhP), 133.47, 138.00 (*q*), 139.54 (*q*), 149.02 (*q*), 149.54 (*q*); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=2.90 (br s, $\Delta\nu_{1/2}$=545 Hz); IR (Nujol): ν=1459 (CP), 1111 (NP) cm^{-1}; MS (FAB+): *m*/*z* (%)=1252 (10) [M^++5+Na], 1229 (6) [M^++5], 1227 (4) [M^++3], 638 (100); $C_{62}H_{54}Br_2ClN_{10}P_3$ (1227.34): Calcd C 60.67, H 4.44, N 11.41; found C 60.54, H 4.57, N 11.34.

4.11.4. Triphosphazide 3d/3d′. Yield: 66%; ^1H NMR (300 MHz, $CDCl_3$): δ=−0.25 [s, 6H, CH_3 (d+d′)], 3.44–3.62 [m, 6H, CH_AH_BP (d+d′)], 3.78–4.07 [m, 18H, CH_2N (d+d′)+CH_AH_BP (d+d′)], 6.87–6.97 [m, 12H, H_{arom} (d+d′)], 7.04 [d, J(H,H)=7.5 Hz, 4H, H_{arom} (d+d′)], 7.16–7.22 [m, 18H, H_{arom} (d+d′)], 7.35–7.38 [m, 20H, H_{arom} (d+d′)], 7.47–7.59 [m, 8H, H_{arom} (d+d′)], 7.90–8.06 [m, 12H, H_{arom} (d+d′)], 8.20 [br s, 4H, H_{arom} (d+d′)], 8.25 [br s, 2H, H_{arom} (d+d′)]; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=26.44 [br s, CH_3 (d+d′)], 38.80–40.50 [m, 3 CH_2P (d+d′)], 40.75 [q, ^2J(C,P)=3.5 Hz, CH_3C (d+d′)], 55.13 [CH_2N (d/d′)], 55.54 [CH_2N (d/d′)], 57.75 [CH_2N (d/d′)], 57.87 [2 CH_2N (d/d′)], 58.10 [CH_2N (d/d′)], 118.26 [br s, d/d′)], 119.90 [*q*, (d/d′)], 120.04 [*q*, (d/d′)], 121.72 [br s, (d+d′)], 125.44 [*q*, (d+d′)], 126.97 [br d, ^1J(C,P)=107.3 Hz, *i*C-PhP (d+d′)], 128.30–130.26 (a+b), 130.97 [br d, ^2J(C,P)=9.1 Hz, *o*C-PhP (d/d′)], 131.02 [br d, ^2J(C,P)=8.7 Hz, 2 *o*C-PhP (d/d′)], 131.49 [br s, *p*C-PhP (d/d′)], 131.64 [br s, 2 *p*C-PhP (d/d′)], 132.21 [br s, *p*C-PhP (d/d′)], 132.22 [br s, 2 *p*C-PhP (d/d′)], 132.83 [m, 2 *o*C-PhP (d/d′)], 133.22 [d, ^2J(C,P)=6.4 Hz, *o*C-PhP (d/d′)], 138.15 [*q*, (d/d′)], 138.31 [*q*, (d/d′)], 139.71 [*q*, (d/d′)], 139.85 [*q*, (d/d′)], 140.92 [2 *q*, (d/d′)], 148.86 [*q*, (d/d′)], 148.91 [*q*, (d/d′)], 149.36 [*q*, (d/d′)], 149.41 [*q*, (d/d′)], 150.76 [2 *q*, (d/d′)]; $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=2.40 (br s, $\Delta\nu_{1/2}$=726 Hz); IR (Nujol): ν=1455 (CP), 1108 (NP) cm^{-1}; MS (FAB+): *m*/*z* (%)=1171 (6) [M^++2+Na], 1148 (4) [M^++2], 638 (100); $C_{62}H_{55}BrClN_{10}P_3$ (1148.45): Calcd C 64.84, H 4.83, N 12.20; found C 64.71, H 4.92, N 12.17.

4.11.5. Triphosphazide 3e. Yield: 30%; mp (decomp.) >350 °C (microcrystalline solid from diethyl ether); IR (Nujol): ν=1445 (CP), 1091 (NP) cm^{-1}; MS (FAB+): *m*/*z* (%)=1100 (8) [M^++Na], 1077 (6) [M^+], 641 (100); $C_{65}H_{63}N_{10}P_3$ (1077.18): Calcd C 72.48, H 5.90, N 13.00; found C 72.35, H 5.76, N 12.86.

4.11.6. Triphosphazide 3f. Yield: 77%; mp (decomp.) >350 °C (microcrystalline solid from diethyl ether); ^1H NMR (300 MHz, $CDCl_3$): δ=−0.28 (br s, 3H, CH_3), 2.50 (s, 3H, CH_3-Ar), 2.53 (s, 3H, CH_3-Ar), 3.34 (d, J(H,H)= 15.0 Hz, 2H, CH_AH_BN), 3.39 (d, J(H,H)=14.8 Hz, 1H, CH_AH_BN), 3.44–3.82 (m, 6H, CH_AH_BN+CH_AH_BP), 4.08 (pseudot, J(H,H)=15.2 Hz, 3H, CH_AH_BP), 6.88–6.96 (m, 9H, H_{arom}), 7.12–7.28 (m, 4H, H_{arom}), 7.38–7.49 (m, 18H, H_{arom}), 7.99–8.05 (m, 6H, H_{arom}), 8.08 (br s, 1H, H_{arom}), 8.17 (br s, 1H, H_{arom}), 8.19 (br s, 1H, H_{arom}); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=2.14 (br s, 1P, *Z*-PN_3), 21.58 (br s, 2P, *E*-PN_3); IR (Nujol): ν=1450 (CP), 1108 (NP) cm^{-1}; MS (FAB+): *m*/*z* (%)=1086 (13) [M^++Na], 1064 (7) [M^++1], 638 (100); $C_{64}H_{61}N_{10}P_3$ (1063.16): Calcd C 72.30, H 5.78, N 13.17; found C 72.17, H 5.63, N 13.04.

4.11.7. Triphosphazide 3g. Yield: 79%; mp (decomp.) 316–318 °C (microcrystalline solid from diethyl ether); ^1H NMR (300 MHz, $CDCl_3$): δ=−0.27 (br s, 3H, CH_3), 2.55 (s, 3H, CH_3-Ar), 3.39–3.90 (m, 9H, CH_AH_BN+CH_AH_BP), 3.95 (pseudot, J(H,H)(H,P)=14.4 Hz, 3H, CH_AH_BP), 6.92–7.04 (m, 10H, H_{arom}), 7.14–7.57 (m, 22H, H_{arom}), 7.80–8.05 (m, 8H, H_{arom}), 8.20 (br s, 1H, H_{arom}); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=19.97 (CH_3-Ar), 26.68 (CH_3C), 39.50–40.20 (m, 3 CH_2P), 40.82 (q, ^2J(C,P)=3.3 Hz, CH_3C), 57.31 (CH_2N), 57.35 (CH_2N), 58.24 (CH_2N), 115.57, 119.00 (br s), 125.77, 126.26, 128.70–133.24, 138.21 (2 *q*), 141.60 (*q*), 149.64 (br s, 3 *q*); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=5.12 (br s, 2P, *Z*-PN_3), 21.50 (br s, 1P, *E*-PN_3); IR (Nujol): ν=1440 (CP), 1114 (NP) cm^{-1}; MS (FAB+): *m*/*z* (%) 1049 (12) [M^+], 640 (100); $C_{63}H_{59}N_{10}P_3$ (1049.13): Calcd C 72.12, H 5.67, N 13.35; found C 71.99, H 5.56, N 13.27.

4.12. General procedure for the preparation of tri-λ^5-phosphazenes 5

A solution of the corresponding triphosphazide (1 mmol) in $CDCl_3$ (10 mL) was heated at 60 °C in a flask immersed in an oil bath for 24 h. After cooling, the solvent was removed under reduced pressure and the crude product was crystallized.

4.12.1. Tri-λ^5-phosphazene 5a. Yield: 75%; mp 236–238 °C (colorless prisms from chloroform/*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$): δ=−0.78 (s, 3H, CH_3), 2.94 (d, J(H,H)=12.3 Hz, 3H, CH_AH_BN), 3.20 (pseudoquint, J(H,H) (H,P)=7.5 Hz, 3H, CH_AH_BP), 3.57 (d, J(H,H)=12.3 Hz, 3H, CH_AH_BN), 3.97 (pseudot, J(H,H)(H,P)=14.4 Hz, 3H, CH_AH_BP), 6.37 (s, 3H, H_{arom}), 6.49–6.52 (m, 3H, H_{arom}), 7.09–7.11 (m, 6H, H_{arom}), 7.20–7.50 (m, 24H, H_{arom}), 7.85

(dd, J(H,H)=7.5, 2.1 Hz, 6H, *o*H-PhP); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=27.42 (CH_3), 37.48 (m, CH_2P), 39.05 (q, ^2J(C,P)=3.4 Hz, CH_3C), 57.68 (CH_2N), 118.56, 122.52 (d, ^3J(C,P)=12.6 Hz, *s-cis-C*H=C–N=P), 125.29 (d, ^3J(C,P)=28.7 Hz, *s-trans-C*H=C–N=P), 128.20, 128.37 (d, ^3J(C,P)=12.6 Hz, *m*C-PhP), 128.71 (d, ^3J(C,P)=11.5 Hz, *m*C-PhP), 130.66 (d, ^1J(C,P)=85.1 Hz, *i*C-PhP), 131.21 (d, ^4J(C,P)=1.8 Hz, *p*C-PhP), 131.49 (d, ^2J(C,P)=8.6 Hz, *o*C-PhP), 131.70 (d, ^4J(C,P)=1.1 Hz, *p*C-PhP), 132.12 (d, ^2J(C,P)=9.2 Hz, *o*C-PhP), 132.41 (d, ^1J(C,P)=102.1 Hz, *i*C-PhP), 141.99 (*q*), 151.33 (*q*); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=0.22; IR (Nujol): ν=1459 (CP), 1114 (NP) cm^{-1}; MS (FAB+): *m/z* (%)=950 (100) [M^+ −1]; $C_{62}H_{57}N_4P_3$ (951.06): Calcd C 78.30, H 6.04, N 5.89; found C 78.15, H 5.89, N 5.75.

4.12.2. Tri-λ^5-phosphazene 5b. Yield: 74%; mp (decomp.) 316–318 °C (colorless prisms from chloroform); ^1H NMR (300 MHz, $CDCl_3$): δ=−0.69 (s, 3H, CH_3), 3.23 (pseudoquint, J(H,H)(H,P)=8.4 Hz, 3H, CH_AH$_B$P), 3.45 (d, J(H,H)=13.3 Hz, 3H, CH_AH$_B$N), 3.65 (d, J(H,H)=13.3 Hz, 3H, CH$_A$$H_B$N), 3.95 (pseudot, J(H,H)(H,P)=14.5 Hz, 3H, CH$_A$$H_B$P), 6.55–6.57 (m, 3H, H_{arom}), 6.96 (dd, J(H,H)=8.6, 2.5 Hz, 6H, H_{arom}), 7.25–7.42 (m, 24H, H_{arom}), 7.81–7.87 (m, 6H, H_{arom}); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=27.59 (CH_3), 38.09 (m, CH_2P), 39.10 (q, ^2J(C,P)=3.2 Hz, CH_3C), 56.46 (CH_2N), 111.71 (*q*), 123.69 (d, ^3J(C,P)=12.2 Hz, *s-cis-C*H=C–N=P), 127.07 (d, ^3J(C,P)=27.8 Hz, *s-trans-C*H=C–N=P), 128.50 (d, ^3J(C,P)=12.8 Hz, *m*C-PhP), 128.87 (d, ^3J(C,P)=11.0 Hz, *m*C-PhP), 130.23 (d, ^1J(C,P)=90.5 Hz, *i*C-PhP), 131.13 (d, ^2J(C,P)=9.3 Hz, *o*C-PhP), 131.60 (br s, *p*C-PhP), 131.81 (br s, *p*C-PhP), 131.91 (d, ^1J(C,P)=105.2 Hz, *i*C-PhP), 131.99 (d, ^2J(C,P)=9.3 Hz, *o*C-PhP), 132.60, 139.65 (*q*), 150.77 (*q*); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=0.49; IR (Nujol): ν=1457 (CP), 1119 (NP) cm^{-1}; MS (FAB+): *m/z* (%)=1190 (48) [M^++6], 1188 (84) [M^++4], 1186 (60) [M^++2], 1184 (15) [M^+], 154 (100); $C_{62}H_{54}Br_3N_4P_3$ (1187.75): Calcd C 62.70, H 4.58, N 4.72; found C 62.58, H 4.44, N 4.57.

4.12.3. Tri-λ^5-phosphazene 5c. Yield: 79%; mp (decomp.) 325–326 °C (colorless prisms from chloroform); ^1H NMR (300 MHz, $CDCl_3$): δ=−0.73 (s, 3H, CH_3), 3.23 (pseudoquint, J(H,H)(H,P)=6.8 Hz, 3H, CH_AH$_B$P), 3.34 (d, J(H,H)=13.3 Hz, 2H, CH_AH$_B$N), 3.38 (d, J(H,H)=13.1 Hz, 1H, CH_AH$_B$N), 3.61 (d, J(H,H)=13.3 Hz, 2H, CH$_A$$H_B$N), 3.65 (d, J(H,H)=13.1 Hz, 1H, CH$_A$$H_B$N), 3.89 (pseudot, J(H,H)(H,P)=14.7 Hz, 3H, CH$_A$$H_B$P), 6.48–6.50 (m, 3H, H_{arom}), 6.96 (dd, J(H,H)(H,P)=8.6, 2.7 Hz, 2H, H_{arom}), 7.01 (dd, J(H,H)(H,P)=8.6, 2.7 Hz, 1H, H_{arom}), 7.13 (d, J(H,H)=8.7 Hz, 2H, H_{arom}), 7.15 (d, J(H,H)=8.7 Hz, 1H, H_{arom}), 7.27–7.49 (m, 24H, H_{arom}), 7.78–7.89 (m, 6H, H_{arom}); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=27.50 (CH_3), 37.91 (ddd, ^1J(C,P)=46.5 Hz, ^3J(C,P)=11.9, 3.9 Hz, 3 CH_2P), 38.96 (q, ^2J(C,P)=3.9 Hz, CH_3C), 53.59 (2 CH_2N), 56.19 (CH_2N), 111.52 (2 *q*), 121.99 (*q*), 123.40 (d, ^3J(C,P)=12.3 Hz, *s-cis-C*H=C–N=P), 123.72 (d, ^3J(C,P)=12.3 Hz, 2 *s-cis-C*H=C–N=P), 126.62 (d, ^3J(C,P)=26.6 Hz, *s-trans-C*H=C–N=P), 127.16 (d, ^3J(C,P)=28.2 Hz, 2 *s-trans-C*H=C–N=P), 128.61 (d, ^3J(C,P)=13.4 Hz, *m*C-PhP), 128.86 (d, ^3J(C,P)=11.9 Hz, *m*C-PhP), 129.43 (d, ^4J(C,P)=4.5 Hz), 131.08 (d, ^2J(C,P)=8.8 Hz, *o*C-PhP), 131.46 (d, ^1J(C,P)=81.2 Hz, *i*C-PhP), 131.66 (d, ^4J(C,P)=2.7 Hz, *p*C-PhP), 131.91 (d, ^4J(C,P)=2.1 Hz, *p*C-PhP), 131.96 (d, ^2J(C,P)=9.3 Hz, *o*C-PhP), 132.54 (d, ^4J(C,P)=4.1 Hz), 137.99 (*q*), 139.67 (*q*), 150.33 (d, ^2J(C,P)=1.4 Hz, *q*), 150.95 (d, ^2J(C,P)=1.6 Hz, *q*), the resonance of one *i*C-PhP was not observed; $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=0.29 (s, 2P), 0.39 (s, 1P); IR (Nujol): ν=1437 (CP), 1110 (NP) cm^{-1}; MS (FAB+): *m/z* (%)=1146 (10) [M^++6], 1144 (29) [M^++4], 1142 (38) [M^++2], 1140 (21) [M^+], 154 (100); $C_{62}H_{54}ClBr_2N_4P_3$ (1143.30): Calcd C 65.13, H 4.76, N 4.90; found C 65.01, H 4.65, N 4.77.

4.12.4. Tri-λ^5-phosphazenes 5d+5d′. Yield: 83%; ^1H NMR (300 MHz, $CDCl_3$): δ=−0.74 [s, 6H, CH_3 (d+d′)], 3.05–3.70 [m, 36H, CH_AH$_B$P (d+d′)+CH_2N (d+d′)], 3.80–4.04 [m, 12H, CH$_A$$H_B$P (d+d′)], 6.39–6.52 [m, 5H, H_{arom} (d+d′)], 6.93–7.04 [m, 5H, H_{arom} (a+b)], 7.10–7.13 [m, 4H, H_{arom} (d+d′)], 7.26–7.48 [m, 34H, H_{arom} (a+b)], 7.80–7.88 [m, 8H, H_{arom} (d+d′)]; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=27.48 [CH_3 (d+d′)], 37.34–38.41 [m, CH_2P (d+d′)], 39.02 [q, ^2J(C,P)=3.5 Hz, CH_3C (d+d′)], 53.26 [CH_2N (d/d′)], 53.54 [CH_2N (d/d′)], 56.81 [CH_2N (d/d′)], 56.13 [CH_2N (d/d′)], 57.88 [CH_2N (d/d′)], 57.91 [CH_2N (d/d′)], 111.81 [*q* (d/d′)], 111.94 [*q* (d/d′)], 118.59 (d+d′), 122.21 [*q* (d/d′)], 122.25 [d, ^3J(C,P)=11.6 Hz, *s-cis-C*H=C–N=P (d+d′)], 122.30 [*q* (d/d′)], 123.97 [d, ^3J(C,P)=12.7 Hz, *s-cis-C*H=C–N=P (d+d′)], 124.20 [d, ^3J(C,P)=12.2 Hz, *s-cis-C*H=C–N=P (d/d′)], 124.27 [d, ^3J(C,P)=12.2 Hz, *s-cis-C*H=C–N=P (d/d′)], 125.41 [d, ^3J(C,P)=28.4 Hz, *s-trans-C*H=C–N=P (d+d′)], 126.57 [d, ^3J(C,P)=29.0 Hz, *s-trans-C*H=C–N=P (d+d′)], 127.11 [d, ^3J(C,P)=28.4 Hz, *s-trans-C*H=C–N=P (d+d′)], 128.35–132.60 (d+d′), 138.25 [*q* (d/d′)], 138.31 [*q* (d/d′)], 139.95 [*q* (d/d′)], 139.99 [*q* (d/d′)], 141.57 [*q* (d+d′)], 149.99 [*q* (d/d′)], 150.19 [*q* (d/d′)], 150.65 [*q* (d/d′)], 150.83 [*q* (d/d′)], 151.35 [*q* (d+d′)]; $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=−0.11 (s, 1P), −0.05 (s, 1P), 0.84 (s, 1P), 0.88 (s, 1P), 1.04 (s, 1P), 1.16 (s, 1P); IR (Nujol): ν=1442 (CP), 1123 (NP) cm^{-1}; MS (FAB+): *m/z* (%)=1066 (31) [M^++4], 1064 (89) [M^++2], 1062 (74) [M^+], 154 (100); $C_{62}H_{55}ClBrN_4P_3$ (1064.41): Calcd C 69.96, H 5.21, N 5.26; found C 69.82, H 5.08, N 5.12.

4.12.5. Tri-λ^5-phosphazene 5e. Yield: 85%; mp 301–303 °C (colorless prisms from chloroform/*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$): δ=−0.69 (s, 3H, CH_3), 2.50 (s, 9H, CH_3-Ar), 2.87 (d, J(H,H)=12.3 Hz, 3H, CH_AH$_B$N), 3.14 (pseudoquint, J(H,H)(H,P)=6.8 Hz, 3H, CH_AH$_B$P), 3.58 (d, J(H,H)=12.3 Hz, 3H, CH$_A$$H_B$N), 4.04 (pseudot, J(H,H)(H,P)=14.4 Hz, 3H, CH$_A$$H_B$P), 6.43 (d, J(H,H)=7.2 Hz, 3H, H_{arom}), 6.48 (s, 3H, H_{arom}), 7.05 (dd, J(H,H)=7.1, 2.7 Hz, 3H, H_{arom}), 7.20–7.36 (m, 27H, H_{arom}), 7.84–7.89 (m, 3H, H_{arom}); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=19.56 (CH_3-Ar), 28.26 (CH_3C), 37.46 (m, CH_2P), 38.86 (q, ^2J(C,P)=3.5 Hz, CH_3C), 57.52 (CH_2N), 118.16, 122.09 (d, ^3J(C,P)=12.2 Hz, *s-cis-C*H=C–N=P), 128.18, 128.40 (d, ^3J(C,P)=11.6 Hz, *m*C-PhP), 128.62 (br s, *p*C-PhP), 131.05 (d, ^3J(C,P)=8.7 Hz, *m*C-PhP), 131.33 (br s, *p*C-PhP), 132.19 (d, ^1J(C,P)=81.8 Hz, *i*C-PhP), 132.21 (d, ^2J(C,P)=9.3 Hz, *o*C-PhP), 133.19 (d_{left} *i*C-PhP), 139.88 (*q*), 149.59 (*q*), the resonance of one *o*C-PhP and the quaternary atom *s-trans-C*=C–N=P was not observed; $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=−1.43; IR (Nujol): ν=1437

(CP), 1116 (NP) cm^{-1}; MS (FAB+): *m/z* (%)=994 (55) [M^++1], 993 (100) [M^+], 992 (78) [M^+−1]; $C_{65}H_{63}N_4P_3$ (993.14): Calcd C 78.61, H 6.39, N 5.64; found C 78.46, H 6.25, N 5.49.

4.12.6. Tri-λ^5-phosphazene 5f. Yield: 82%; mp 288–290 °C (colorless prisms from chloroform/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.73 (s, 3H, CH_3), 2.51 (s, 3H, CH_3-Ar), 2.52 (s, 3H, CH_3-Ar), 2.88 (d, *J*(H,H)=12.3 Hz, 1H, CH_AH$_B$N), 2.89 (d, *J*(H,H)=12.3 Hz, 1H, CH_AH$_B$N), 2.91 (d, *J*(H,H)=12.1 Hz, 1H, CH_AH$_B$N), 3.12–3.23 (m, 3H, CH_AH$_B$P), 3.56 (d, *J*(H,H)=12.1 Hz, 1H, CH_AH$_B$N), 3.58 (d, *J*(H,H)=12.2 Hz, 2H, CH$_A$$H_B$N), 3.94 (pseudot, *J*(H,H)(H,P)=14.6 Hz, 1H, CH$_A$$H_B$P), 4.02 (pseudot, *J*(H,H)(H,P)=14.4 Hz, 1H, CH$_A$$H_B$P), 4.10 (pseudot, *J*(H,H)(H,P)=14.4 Hz, 1H, CH$_A$$H_B$P), 6.40–6.50 (m, 4H, H_{arom}), 7.06–7.10 (m, 3H, H_{arom}), 7.15–7.43 (m, 30H, H_{arom}), 7.87 (m, 3H, H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=19.58 (CH_3-Ar), 19.61 (CH_3-Ar), 27.89 (*C*H$_3$C), 36.20–38.80 (m, CH_2P), 38.86 (q, ^{2}*J*(C,P)=3.5 Hz, CH_3*C*), 57.35 (CH_2N), 57.58 (CH_2N), 57.65 (CH_2N), 118.10, 118.14, 118.74, 122.04 (d, ^{3}*J*(C,P)=12.0 Hz, *s-cis-C*H=C–N=P), 122.08 (d, ^{3}*J*(C,P)=12.8 Hz, *s-cis-C*H=C–N=P), 122.39 (d, ^{3}*J*(C,P)=12.8 Hz, *s-cis-C*H=C–N=P), 125.01 (d, ^{3}*J*(C,P)=28.4 Hz, *s-trans-C*H=C–N=P), 128.10–133.10, 139.74 (*q*), 139.78 (*q*), 142.11 (*q*), 149.59 (2 *q*), 150.99 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=−1.90 (s, 1P, CH_3–Ar–N=P), −1.23 (s, 1P, CH_3–Ar–N=P), 1.98 (s, 1P, H–Ar–N=P); IR (Nujol): ν=1439 (CP), 1117 (NP) cm^{-1}; MS (FAB+): *m/z* (%)=1022 (3) [M^++Na], 980 (56) [M^++1], 979 (100) [M^+]; $C_{64}H_{61}N_4P_3$ (979.12): Calcd C 78.51, H 6.28, N 5.72; found C 78.38, H 6.16, N 5.58.

4.12.7. Tri-λ^5-phosphazene 5g. Yield: 78%; mp 269–270 °C (colorless prisms from chloroform/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.75 (s, 3H, CH_3), 2.52 (s, 3H, CH_3-Ar), 2.90 (d, *J*(H,H)=12.3 Hz, 1H, CH_AH$_B$N), 2.91 (d, *J*(H,H)=12.2 Hz, 1H, CH_AH$_B$N), 2.92 (d, *J*(H,H)=12.2 Hz, 1H, CH_AH$_B$N), 3.13–3.26 (m, 3H, CH_AH$_B$P), 3.56 (d, *J*(H,H)=12.1 Hz, 2H, CH$_A$$H_B$N), 3.58 (d, *J*(H,H)=12.2 Hz, 1H, CH$_A$$H_B$N), 3.92 (pseudot, *J*(H,H)(H,P)=14.6 Hz, 1H, CH$_A$$H_B$P), 4.00 (pseudot, *J*(H,H)(H,P)=14.4 Hz, 1H, CH$_A$$H_B$P), 4.07 (pseudot, *J*(H,H)(H,P)=14.4 Hz, 1H, CH$_A$$H_B$P), 6.39 (s, 1H, H_{arom}), 6.44–6.50 (m, 4H, H_{arom}), 7.07–7.10 (m, 3H, H_{arom}), 7.18–7.48 (m, 30H, H_{arom}), 7.80–7.91 (m, 3H, H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=19.58 (CH_3-Ar), 27.58 (*C*H$_3$C), 36.83–38.15 (m, 3 CH_2P), 38.91 (q, ^{2}*J*(C,P)=4.1 Hz, CH_3*C*), 57.44 (CH_2N), 57.50 (CH_2N), 57.73 (CH_2N), 118.08, 118.61, 118.65, 122.06 (d, ^{3}*J*(C,P)=12.3 Hz, *s-cis-C*H=C–N=P), 122.40 (d, ^{3}*J*(C,P)=12.0 Hz, *s-cis-C*H=C–N=P), 122.44 (d, ^{3}*J*(C,P)=13.4 Hz, *s-cis-C*H=C–N=P), 125.06 (d, ^{3}*J*(C,P)=28.4 Hz, *s-trans-C*H=C–N=P), 125.15 (d, ^{3}*J*(C,P)=28.4 Hz, *s-trans-C*H=C–N=P), 128.20–132.90, 139.66 (*q*), 141.99 (*q*), 142.02 (*q*), 149.61 (*q*), 151.11 (2 *q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=−1.76 (s, 1P, CH_3–Ar–N=P), 1.35 (s, 1P, H–Ar–N=P), 1.95 (s, 1P, H–Ar–N=P); IR (Nujol): ν=1438 (CP), 1118 (NP) cm^{-1}; MS (FAB+): *m/z* (%)=965 (55) [M^+], 964 (100) [M^+−1]; $C_{63}H_{59}N_4P_3$ (965.09): Calcd C 78.40, H 6.16, N 5.81; found C 78.45, H 6.02, N 5.68.

4.13. Procedure for the preparation of triphosphazides 8a and 11b

Two solutions, one of bis(3-azidobenzyl)[2-(2-azidophenyl)-ethyl]amine (**6b**) (0.64 g, 1.5 mmol) or bis(2-azido-5-chlorobenzyl)(3-azidopropyl)amine *N*-oxide (**10b**) (0.67 g, 1.5 mmol) in diethyl ether or dichloromethane (10 mL) and the other of 1,1,1-tris[(diphenylphosphino)methyl]-ethane (**2**) (1.3 g, 1.5 mmol) in diethyl ether (10 mL) were simultaneously added to a round-bottom flask containing diethyl ether (15 mL) under nitrogen atmosphere at room temperature over a period of 30 min with stirring. The resulting mixture was then stirred for 3 h. The precipitated pale yellow solid was filtered, washed with diethyl ether (3×10 mL), and dried under vacuum.

4.13.1. Triphosphazide 8a. Yield: 71%; mp 298–300 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.06 (br s, 3H, CH_3), 2.70–2.79 (m, 2H, ArCH_2CH$_2$N), 3.16 (td, *J*(H,H)=12.4, 5.2 Hz, 1H, CH$_2$CH_AH$_B$N), 3.32–3.85 (m, 8H, CH$_2$CH$_A$$H_B$N+2 CH$_2$N+3 C$H_AH_B$P), 3.91 (pseudot, *J*(H,H)(H,P)=16.0 Hz, 1H, CH$_A$$H_B$P), 4.03 (pseudot, *J*(H,H)(H,P)=16.0 Hz, 1H, CH$_A$$H_B$P), 4.07 (pseudot, *J*(H,H)(H,P)=10.1 Hz, 1H, CH$_A$$H_B$P), 6.61 (td, *J*=7.9, 2.9 Hz, 1H, H_{arom}), 6.86 (td, 1H, *J*=7.8, 3.1 Hz, H_{arom}), 6.93–7.57 (m, 34H, H_{arom}), 7.81–8.25 (m, 6H, H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=26.06 (*C*H$_3$C), 31.11 (Ar*C*H$_2$CH$_2$N), 36.90 (m, CH_2P), 39.40 (m, CH_2P), 40.09 (q, ^{2}*J*(C,P)=3.2 Hz, CH_3*C*), 40.50 (m, CH_2P), 51.37 (ArCH$_2$*C*H$_2$N), 59.06 (CH_2N), 59.25 (CH_2N), 114.61, 116.08, 117.61, 122.91, 125.05, 125.08 (d, ^{1}*J*(C,P)=109.6 Hz, *i*C-PhP), 125.51, 126.05, 126.32, 127.27 (d, ^{1}*J*(C,P)=82.9 Hz, *i*C-PhP), 127.56 (d_{right}, *i*C-PhP), 128.48–128.14, 129.50 (d_{left}, *i*C-PhP), 129.77 (d, ^{1}*J*(C,P)=91.6 Hz, *i*C-PhP), 129.90 (d, ^{2}*J*(C,P)=9.3 Hz, *o*C-PhP), 130.88 (d, ^{2}*J*(C,P)=8.7 Hz, *o*C-PhP), 130.95, 131.22 (d, $^2J_{CP}$=8.7 Hz, *o*C-PhP), 131.65, 131.93 (d, ^{2}*J*(C,P)=7.5 Hz, *o*C-PhP), 132.47, 132.72 (d, ^{2}*J*(C,P)=8.7 Hz, *o*C-PhP), 132.93, 133.29 (d, ^{2}*J*(C,P)=8.1 Hz, *o*C-PhP), 133.74 (*q*), 141.36 (*q*), 141.83 (*q*), 147.38 (*q*), 151.34 (*q*), 152.04 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=−0.55 (s, 1P, *Z*-PN$_3$), 19.93 (s, 1P, *E*-PN$_3$), 21.28 (s, 1P, *E*-PN$_3$); ^{31}P{^{1}H} NMR (CPMAS, 121.4 MHz, $(NH_4)_2HPO_4$): δ=−3.12 (*Z*-PN$_3$), 21.02 (*E*-PN$_3$), 25.24 (*E*-PN$_3$); IR (Nujol): ν=1440 (CP), 1106 (NP) cm^{-1}; MS (FAB+): *m/z* (%)=1072 (M^++Na, 2), 1050 (M^++1, 2), 154 (100); $C_{63}H_{59}N_{10}P_3$ (1049.13): Calcd C 72.12, H 5.67, N 13.35; found C 71.85, H 5.58, N 13.08.

4.13.2. Triphosphazide 11b. Yield: 68%; mp 206–208 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.20 (br s, 3H, CH_3), 1.96–1.99 (m, 1H, CH$_2$CH_AH$_B$CH$_2$N), 2.47–2.49 (m, 1H, CH$_2$CH$_A$$H_BCH_2$N), 2.81 (br s, 2H, C$H_2CH_2CH_2$N), 2.97–3.17 (m, 2H, CH$_2CH_2CH_AH_B$N+C$H_AH_B$P), 3.47 (pseudot, *J*(H,H)(H,P)=17.4 Hz, 1H, CH_AH$_B$P), 3.51 (pseudot, *J*(H,H)(H,P)=17.4 Hz, 1H, CH_AH$_B$P), 3.57–3.74 (m, 2H, CH$_A$$H_B$P), 3.90 (d, *J*(H,H)=12.4 Hz, 2H, CH_AH$_B$N), 3.99–4.07 (m, 1H, CH$_2$CH$_2$CH$_A$$H_B$N), 4.31 (d, *J*(H,H)=16.0 Hz, 1H, CH$_A$$H_B$N), 4.66–4.73 (m, 1H, CH$_A$$H_B$P), 5.00 (d, *J*(H,H)=16.0 Hz, 1H, CH$_A$$H_B$N), 6.98–7.05 (m, 3H, H_{arom}), 7.25–7.57 (m, 23H, H_{arom}), 7.91–8.02 (m, 6H, H_{arom}), 8.16–8.20 (m, 2H, H_{arom}), 8.33 (d, *J*(H,H)=2.0 Hz, 1H, H_{arom}),

8.45 (d, J(H,H)=1.8 Hz, 1H, H_{arom}); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=23.31 ($PN_3CH_2\mathit{C}H_2CH_2N$), 26.14 ($\mathit{C}H_3C$), 36.20 (m, CH_2P), 38.41 (dd, ^1J(C,P)=42.8 Hz, ^3J(C,P)=13.9 Hz, CH_2P), 40.02 (q, ^2J(C,P)=3.2 Hz, $CH_3\mathit{C}$), 40.09 (dd, ^1J(C,P)=40.5 Hz, ^3J(C,P)=13.2 Hz, CH_2P), 57.39 ($PN_3CH_2CH_2\mathit{C}H_2N$), 65.44 ($CH_2N$), 67.08 ($CH_2N$), 68.17 ($CH_2N$), 116.99, 117.54, 125.43 (d, ^1J(C,P)=101.7 Hz, *i*C-PhP), 128.77 (d, ^3J(C,P)=11.6 Hz, *m*C-PhP), 128.93 (d, ^3J(C,P)=12.2 Hz, *m*C-PhP), 129.01, 129.08 (d, ^3J(C,P)=10.4 Hz, *m*C-PhP), 129.49 (d, ^3J(C,P)=11.6 Hz, *m*C-PhP), 129.88, 130.57 (d, ^2J(C,P)=9.5 Hz, *o*C-PhP), 131.17 (br s, *p*C-PhP), 131.74–132.85, 145.97 (*q*); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=−0.40 (s, 1P, *Z*-PN_3), 0.40 (s ancho, 1P), 5.95 (s, 1P, *Z*-PN_3); IR (Nujol): ν=1406 (CP), 1106 (NP) cm^{-1}; MS (FAB+): *m*/*z* (%)=1094 (M^++1+Na, 8), 1074 (M^++4, 4), 1073 (M^++3, 3), 1072 (M^++2, 6), 183 (100); $C_{58}H_{55}Cl_2N_{10}OP_3$ (1071.95): Calcd C 64.99, H 5.17, N 13.07; found C 65.13, H 5.29, N 13.11.

4.14. Preparation of tri-λ-phosphazene 9

This compound was prepared following the procedure described above for the preparation of tri-λ-phosphazenes **4**.

4.14.1. Tri-λ-phosphazene 9. Yield: 62%; mp 228–230; ^1H NMR (300 MHz, $CDCl_3$): δ=−0.44 (s, 3H, CH_3), 2.40–2.78 (m, 5H, 3 $C\mathit{H}_A\mathit{H}_BP$+Ar$C\mathit{H}_2C\mathit{H}_2N$), 3.02 (d, J(H,H)=13.5 Hz, 1H, $C\mathit{H}_A\mathit{H}_BN$), 3.10 (d, J(H,H)=12.4 Hz, 1H, $C\mathit{H}_A\mathit{H}_BN$), 3.27–3.42 (m, 1H, $C\mathit{H}_A\mathit{H}_BN$), 3.53–3.58 (m, 1H, $CH_A\mathit{H}_BN$), 3.64 (d, J(H,H)=12.4 Hz, 1H, $CH_A\mathit{H}_BN$), 3.76–3.81 (m, 1H, $CH_A\mathit{H}_BP$), 3.91 (d, J(H,H)=13.4 Hz, 1H, $CH_A\mathit{H}_BN$), 4.21 (pseudot, J(H,H)(H,P)=13.9 Hz, 1H, $CH_A\mathit{H}_BP$), 5.49 (pseudot, J(H,H)(H,P)=13.9 Hz, 1H, $CH_A\mathit{H}_BP$), 6.04 (d, J(H,H)=7.6 Hz, 2H, H_{arom}), 6.50–6.65 (m, 2H, H_{arom}), 6.88–7.56 (m, 32H, H_{arom}), 7.67–7.93 (m, 6H, H_{arom}); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ=29.07 ($\mathit{C}H_3C$), 34.01 (Ar$\mathit{C}H_2CH_2N$), 37.12 (dd, ^1J(C,P)=47.6 Hz, ^3J(C,P)=7.1 Hz, CH_2P), 38.59 (q, ^2J(C,P)=3.6 Hz, $CH_3\mathit{C}$), 39.92 (dd, ^1J(C,P)=47.6 Hz, ^3J(C,P)=7.1 Hz, CH_2P), 44.82 (dd, ^1J(C,P)=95.1 Hz, ^3J(C,P)=7.1 Hz, CH_2P), 53.73 (CH_2N), 56.01 (CH_2N), 61.04 (CH_2N), 116.42, 117.48, 118.15, 120.29 (d, ^3J(C,P)=11.6 Hz), 122.33 (d, ^3J(C,P)=13.9 Hz), 123.23 (d, ^3J(C,P)=12.8 Hz), 124.76 (d, ^3J(C,P)=28.4 Hz), 125.02 (d, ^3J(C,P)=29.0 Hz), 125.98, 128.24–133.15, 133.48 (d, ^2J(C,P)=9.3 Hz, *o*C-PhP), 134.73 (d, ^3J(C,P)=23.8 Hz, *q*), 141.66 (*q*), 143.90 (*q*), 149.90 (*q*), 151.50 (*q*), 151.53 (*q*); $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ=0.76 (s, 1P), 1.44 (s, 1P), 8.16 (s, 1P); IR (Nujol): ν=1436 (CP), 1122 (NP) cm^{-1}; MS (FAB+): *m*/*z* (%)=966 (M^++1, 57), 965 (M^+, 100); $C_{63}H_{59}N_4P_3$ (965.09): Calcd C 78.40, H 6.16, N 5.81; found C 8.23, H 5.88, N 5.58.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.04.056.

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