Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 4450–4458

Modulating the propeller-like shape of a tripodal $C(CH_2PPh_2)_3$ fragment by the size of the substituent at the pivotal carbon atom in macrobicyclic tri-λ^5-phosphazenes

Mateo Alajarín,* Carmen López-Leonardo* and José Berná

Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain

Received 30 January 2007; revised 8 March 2007; accepted 12 March 2007
Available online 16 March 2007

Abstract—The chiral macrobicyclic tri-λ^5-phosphazenes formed by tripod–tripod coupling of tris(3-azidobenzyl)amines and 1,1,1-tris-[(diphenylphosphino)methyl]methanes present helical topologies as a result of combining two propeller-shaped tripodal fragments with the same sense of twist. The introduction of a series of R_{piv} substituents of increasing size at the pivotal carbon of the lower *tert*-butane fragment R_{piv}–$C(CH_2PPh_2)_3$ causes a gradual decrease of the helicity in the lower propeller. This phenomenon is revealed in their $CDCl_3$ solution NMR spectra, and the activation energies for the racemization process of the tri-λ^5-phosphazenes were calculated by coalescence VT-NMR experiments.

1. Introduction

Macropolycyclic structures are the focus of a continuous and intense research activity within the domain of supramolecular chemistry.[1] Nevertheless, studies related to phosphorus-containing macrobicycles have been scarce[2] and most of them have been limited to those bearing P-bridgehead atoms.[3] By contrast, the work presented here concerns about the synthetic and structural studies of a more unusual kind of molecular cages where the phosphorus atoms are embedded into the arms of the macrobicycle.[4]

We have previously described[5] the tripod–tripod coupling of tris(2- and 3-azidobenzyl)amines with 1,1,1-tris[(diphenylphosphino)methyl]ethane to give the first C_3-symmetric, intrinsically chiral, macrobicyclic triphosphazides **1** and **2** in racemic form by means of a Staudinger phosphane imination reaction.[6] These compounds were shown to possess propeller-like topology and in all the cases studied, their molecular self-assembly[7] occurs with total stereoselectivity in favour of the formation of the macrobicycle in which both propeller units, the upper tribenzylamine core and the lower *tert*-pentane fragment, present the same sense of twist. We proved that such stereoselectivity was not influenced by the variation of R^1–R^6 substituents at the tribenzylamine fragment.[5b,e] The heating of macrobicyclic cages **2** induced a remarkable stepwise triple extrusion of molecular nitrogen to afford tri-λ^5-phosphazenes **3**, which preserved the chiral, propeller-like topology of their precursors[5d,e] (Fig. 1).

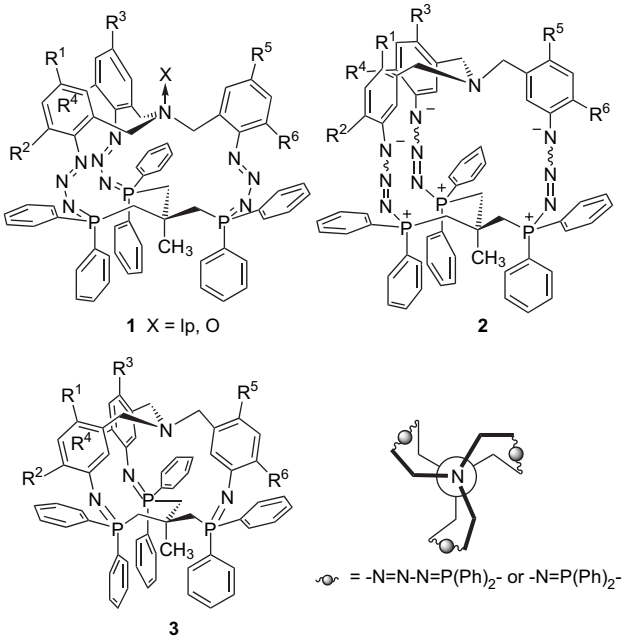


Figure 1. Structure of double propellers **1**–**3** and their schematic representation as viewed along their C_3 axis, showing the same sense of twist of their two pivotal subunits.

Keywords: Triphosphazides; Tri-λ^5-phosphazenes; Macrobicycles; Cage compounds; Propellers; Tripod–tripod coupling.
* Corresponding authors. E-mail addresses: alajarin@um.es; melill@um.es

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.03.076

Recently we have reported[8] that changing the CH_3 group at the pivotal carbon of the lower fragment by a larger Ph group causes a considerable distortion in the optimal conformation of that moiety by 'pushing' the pseudoaxial phenyls at phosphorus away from the sterically-demanding Ph. This deformation occurs with the simultaneous decreasing of the twisting degree of the lower propeller in both triphosphazides and tri-λ^5-phosphazenes (Fig. 2).

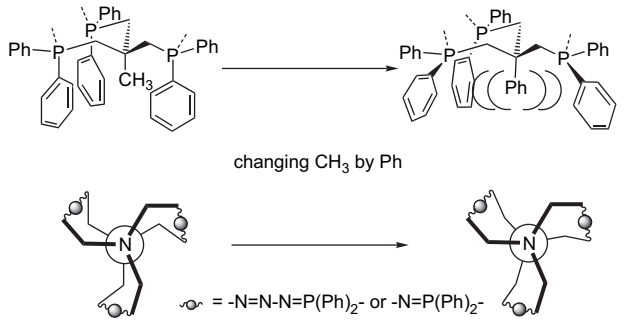


Figure 2. Two schematic representations of the deformation of the lower propeller caused by the introduction of a pivotal Ph group.

Moreover, X-ray analysis of crystals of a tri-λ^5-phosphazene with a pivotal Ph showed two diastereoisomeric macrobicycles, one with the same sense of twist in both propellers, upper and lower (that is, of *P*,P** configuration) and the other in which the sense of twist of the propellers is the opposite (the *P*,M** diastereoisomer)[8] (Fig. 3).

Figure 3. Schematic representations of the two diastereoisomers present in the crystals of a tri-λ^5-phosphazene obtained from $PhC(CH_2PPh_2)_3$ and a tris(3-azidobenzyl)amine.

These results led us to study more systematically the structural consequences of introducing substituents of different size at the pivotal carbon of the tris(phosphane) fragment. Here we disclose the results of such a study in which substituents of increasing size, R_{piv}=H, Me, Et, ^{i}Pr, ^{t}Bu, are positioned at that carbon atom by using the corresponding tris(phosphanes) of general formula $R_{piv}C(CH_2PPh_2)_3$ **4** in the self-assembly reactions with tris(3-azidobenzyl)amines.

2. Results and discussion

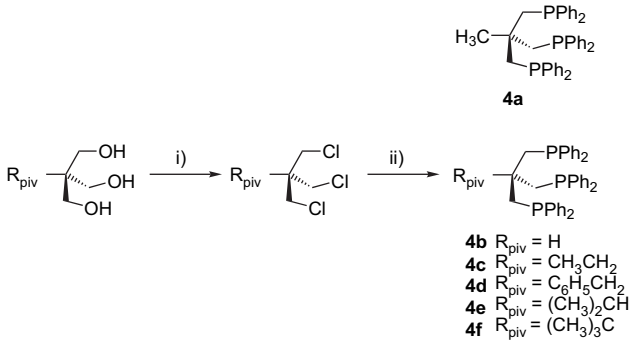
2.1. Preparation of tris(phosphanes) 4

Tris(phosphane) **4a** is commercially available. The known tris(phosphanes) **4b–d** were prepared following previously reported procedures (see Refs. in Table 1), whereas the new compounds **4e** and **4f** were prepared similarly. As outlined in Scheme 1, their syntheses were achieved starting from the corresponding triols, which were converted into their respective trichlorides by reaction with thionyl chloride.

Table 1. Yields (%) of tris(phosphanes) **4b–f** and their trichloride precursors

R_{piv}	$R_{piv}C(CH_2Cl)_3$	$R_{piv}C(CH_2PPh_2)_3$ (**4**)
H	45[9]	42[10] (**4b**)
CH_3CH_2	—	45[11] (**4c**)
$C_6H_5CH_2$	53[12]	63[12] (**4d**)
$(CH_3)_2CH$	80	71 (**4e**)
$(CH_3)_3C$	85	42 (**4f**)

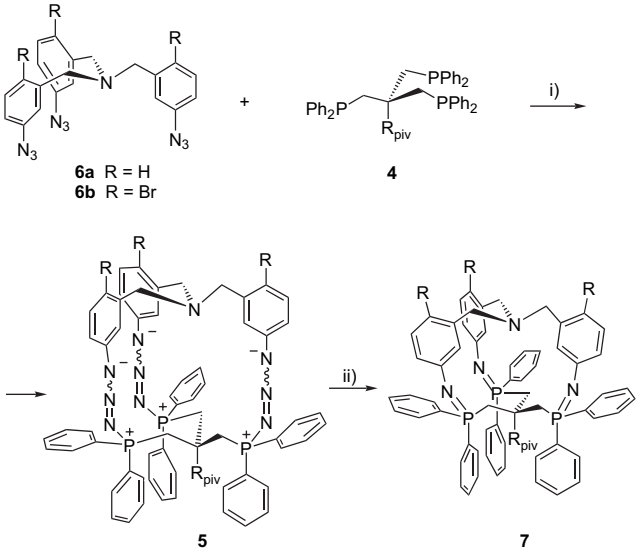
Further chloride substitution with the diphenylphosphide anion gave rise to the tris(phosphanes) **4** (Table 1).



Scheme 1. Synthesis of tris(phosphanes) **4**. *Reagents and conditions*: (i) $SOCl_2$, pyridine, 0–115 °C, 6 h; (ii) $HPPh_2$, KO^{t}Bu, THF, reflux, 16 h.

2.2. Preparation of triphosphazides 5 and tri-λ^5-phosphazenes 7

The new racemic triphosphazides **5** were obtained in moderate yields by the self-assembly of triazides **6a** and **6b** with tris(phosphanes) **4b**, **4c**, **4e**, **4f** (Scheme 2, Table 2). Unfortunately, tris(phosphane) **4d** (R_{piv}=CH_2Ph) did not couple efficiently with tris(3-azidobenzyl)amines **6** either under standard conditions (diethyl ether, room temperature) or at lower temperatures, these reactions always yielding uncharacterized oligomers. This failure may be caused either by the thermodynamic instability of the putative triphosphazide, bearing a benzyl group proximal to the three pseudoapical



Scheme 2. Synthesis of triphosphazides **5** and tri-λ^5-phosphazenes **7**. *Reagents and conditions*: (i) Et_2O, 25 °C, 3 h; (ii) $CDCl_3$, 60 °C, 24 h.

Table 2. Triphosphazides **5** and tri-λ^5-phosphazenes **7** derived from 1,1,1-tris(diphenylphosphanylmethyl)methanes **4b–f**

Entry	R_{piv}	R	Compound (yield %)	
			5	**7**
1	CH_3	H	**5a** (79)[a]	**7a** (75)[a]
2	CH_3	Br	**5b** (63)[a]	**7b** (74)[a]
3	H	H	**5c** (82)[b]	**7c** (58)[d]
4	H	Br	**5d**[b,c]	**7d** (63)
5	CH_3CH_2	H	**5e** (73)	**7e** (74)
6	CH_3CH_2	Br	**5f** (72)	**7f** (81)
7	$(CH_3)_2CH$	H	**5g**[b,c]	**7g** (7)
8	$(CH_3)_2CH$	Br	**5h** (56)	**7h** (72)
9	$(CH_3)_3C$	Br	**5i** (43)	**7i** (56)

[a] Compounds **5a**, **5b**, **7a** and **7b** have been described previously (Ref. 5e) and are included here for a complete discussion of data.
[b] The coupling reaction was carried out at 0 °C.
[c] Not isolated.
[d] The extrusion of dinitrogen occurred at 25 °C.

phenyl rings, or by the lower population of the optimal reactive conformer of **4d** for the self-assembly reaction. The tripod–tripod coupling reactions were carried out under the conditions shown in Scheme 2, except for the entries 3, 4 and 7 of Table 2, which were carried out at 0 °C to obtain the corresponding triphosphazides **5**.

In general compounds **5** were cleanly converted into the corresponding tri-λ^5-phosphazenes **7** by heating at 60 °C in $CDCl_3$ solution, by stepwise triple extrusion of molecular nitrogen (Scheme 2). The dinitrogen expulsion from each PN_3 unit is just the second mechanistic step of a Staudinger P(III) imination reaction.[6,13]

Triphosphazides **5c** and **5d** (R_{piv}=H) are quite unstable, converting at room temperature into the corresponding tri-λ^5-phosphazenes, **7c** and **7d**, respectively. Such instability may be due to the absence of CH···π interactions similar to those contributing to the stability of the analogous R_{piv}=CH_3 derivatives **5a** and **5b** (Fig. 4), as we have previously proposed.[5a,b]

If these stabilizing interactions really exist they would explain why the extrusion of dinitrogen in compounds **5a** or **5b** requires a long thermal treatment. In contrast, their absence in **5c** and **5d** seems to allow their conversion into the respective tri-λ^5-phosphazenes **7c** and **7d** under milder conditions, at room temperature. The chemical shift of the pivotal hydrogen of **5c** in its ^{1}H NMR spectrum (δ=1.82), deshielded 0.29 ppm when compared with that of the free tris(phosphane) **4b** (δ=1.53), is in accord with the absence of shielding CH···π interactions involving that proton. In contrast, the chemical shift of the protons of the pivotal methyl group in the macrobicyclic triphosphazides **5a** and **5b** derived from **4a** (R_{piv}=CH_3) is notably displaced at higher field (δ=−0.26) in relation to the starting tris(phosphane) (δ=0.95).

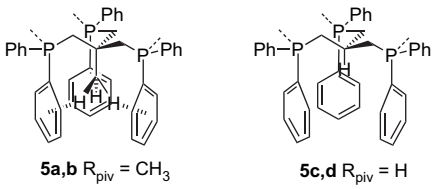


Figure 4. Proposed stabilizing CH···π interactions in the lower fragment of triphosphazides **5a** and **5b** but not in **5c** and **5d**.

From the reaction of the triazide **6a** and the triphosphane **4e** (R_{piv}=^{i}Pr) we could not isolate the corresponding triphosphazide (entry 7, Table 2) under the commonly used reaction conditions, since, as shown by NMR, the equilibrium between reactants and product is not totally displaced to the product side.[14] However, the thermal treatment of the reaction mixture in $CDCl_3$ solution gave rise to the formation of the tri-λ^5-phosphazene **7g**, albeit in very low yield. By contrast, the insolubility of the related triphosphazide **5h** (entry 8, Table 2) in diethyl ether allowed its isolation in medium yield. Probably the accommodation of an isopropyl group in the space delimited by the three pseudoaxial phenyl rings causes a conformational variation in the lower fragment such that these phenyl rings become notably deflected from the pseudoaxial orientation, diminishing notably the stability in solution of the expected triphosphazide. Taking into account the results shown in entries 7 and 8, the triphosphane **4f**, bearing a bulky *tert*-butyl group, was only reacted with triazide **6b**.

2.3. Conformational study of tri-λ^5-phosphazenes 7

Tri-λ^5-phosphazenes **7c** and **7d** show lower conformational stability than the rest of the compounds **7** described in this work. In solution at room temperature, their CH_2N and CH_2P protons and the phenyl rings of their Ph_2P fragments do not appear as diastereotopic in their ^{1}H and ^{13}C NMR spectra, respectively. At low temperature, in $CDCl_3$ solution at −50 °C, their ^{1}H NMR spectra show the splitting of the CH_2N and CH_2P protons as two AB systems, indicating that at room temperature **7c** and **7d** should be equilibrating between the *P*,*P* and *M*,*M*[15] enantiomeric forms. Both spectra correspond to average structures of C_{3v} symmetry, but on cooling the interconversion becomes increasingly slower and it is then possible to observe, in the NMR time-scale, the signals corresponding to species of C_3-symmetry.

The analysis of the room temperature solution NMR data of the rest of the tri-λ^5-phosphazenes **7** serves as the basis for the discussion of the structural arrangement of their molecular skeletons, taking the known triphosphazide **5b** and tri-λ^5-phosphazene **7b** as reference models. To this end, we have also related the larger or smaller shielding of the protons of the pivotal group of the rest of the macrobicyclic species **5** and **7** with the chemical shift values of the same protons in the ^{1}H NMR spectra of the starting tris(phosphanes) **4**. The δ values of the signals corresponding to the protons of the pivotal group of some of the triphosphazides **5** and tri-λ^5-phosphazenes **7** prepared in this work, and their precursor tris(phosphanes) **4** are shown in Table 3. The $\Delta\delta$ values of topologically similar hydrogens between tris(phosphanes) **4** and triphosphazides **5**, $\Delta\delta_{\mathbf{4-5}}$, as well as between tris(phosphanes) **4** and tri-λ^5-phosphazenes **7**, $\Delta\delta_{\mathbf{4-7}}$, and the differences in absolute value between these two increments, $|\Delta\delta_{\mathbf{7-5}}|$, are also collected in that table.

The $\Delta\delta$ value of the CH_3 protons of the ethyl, isopropyl and *tert*-butyl groups diminishes progressively in this order, in both triphosphazides **5** and tri-λ^5-phosphazenes **7**. The

Table 3. Selected ^{1}H NMR data for the protons of pivotal groups in tris(phosphanes) **4**, triphosphazides **5** and tri-λ^5-phosphazenes **7**

R_{piv}	**4**	$\delta_4(R_{piv})$	**5**	$\delta_5(R_{piv})$	**7**	$\delta_7(R_{piv})$	$\Delta\delta_{4-5}$[a]	$\Delta\delta_{4-7}$[a]	$\lvert\Delta\delta_{7-5}\rvert$[a]
CH_3	**4a**	0.95[b]	**5b**	−0.23[b]	**7b**	−0.69[b]	1.18	1.64	0.46
CH_3CH_2	**4c**	0.50[b]	**5f**	−0.68[b]	**7f**	−0.79[b]	1.18	1.29	0.11
		1.51[c]		0.57[c]		0.30[c]	0.94	1.21	0.27
				0.77[c]		0.37[c]	0.74	1.14	0.40
$(CH_3)_2CH$	**4e**	0.80[b]	**5h**	−0.05[b]	**7h**	−0.31[b]	0.85	1.11	0.26
				0.03[b]		−0.06[b]	0.77	0.86	0.09
		2.15[d]		0.87[d]		1.03[d]	1.28	1.12	0.16
$(CH_3)_3C$	**4f**	1.07[b]	**5i**	0.36[b]	**7i**	0.22[b]	0.71	0.85	0.14

[a] $\Delta\delta_{4-5}=\delta_4(R_{piv})-\delta_5(R_{piv})$; $\Delta\delta_{4-7}=\delta_4(R_{piv})-\delta_7(R_{piv})$; $|\Delta\delta_{7-5}|=|\delta_7-\delta_5|$.
[b] CH_3.
[c] CH_2.
[d] CH.

comparison of the $\Delta\delta_{4-5}$ and $\Delta\delta_{4-7}$ values for those protons revealed that the shielding is larger in tri-λ^5-phosphazenes **7** than in triphosphazides **5**. These data suggest that the pivotal groups are closer to the pseudoaxial phenyl rings in compounds **7** than in **5**, as a consequence of the increasing rigidity of the macrobicyclic skeleton after the extrusion of three molecules of dinitrogen on passing from the triphosphazides **5** to triphosphazenes **7**. This effect, in general, is attenuated on going from ethyl to isopropyl to *tert*-butyl pivotal groups, as revealed by the respective $|\Delta\delta_{7-5}|$ values. These data are in agreement with a gradual increment of the volume of the cavity delimited by the three pseudoaxial phenyl groups to accommodate a voluminous pivotal group. Such increment results from a notable distortion of the lower fragment, gradually deviating the three phenyl groups from their pseudoaxial orientation (Fig. 5).

More information on how this distortion takes place can be extracted by analyzing other NMR data such as the ^{1}H NMR chemical shifts of the CH_2N and CH_2P protons (Table 4). We have previously attributed the diastereotopicity of the CH_2N and CH_2P protons to the propeller conformation of the two tripodal units in macrobicycles **5** and **7**, which situates each proton of these groups in a quite different chemical environment (pseudoaxial and pseudoequatorial).[5d,e] In other words, if the lower fragment is not propeller-shaped each pair of CH_2P protons would be equivalent and should appear as a singlet in the ^{1}H NMR spectrum. Thus, we have associated the higher or lower degree of magnetic inequivalence between the pair of protons of each CH_2 group with the corresponding degree of twist of the propeller they belong to. The δ values summarized in Table 4 reveal that increasing the size of the pivotal group results in a gradual reduction of the degree of twist at the lower *tert*-butane propeller (Table 4, $\Delta\delta_{low}$ being gradually smaller). This loss of helicity is interpreted as a consequence of a gradual and simultaneous rotation along the three pivotal carbon–methylenic carbon bonds in the three arms (Fig. 6). In this way, the pseudoaxial phenyl rings are moving gradually towards positions more distant from the C_3 pseudoaxis, and the steric interactions between these phenyls and the pivotal groups are alleviated. This effect is appreciable in both the triphosphazides **5** and tri-λ^5-phosphazenes **7** series.

In contrast, the helicity of the upper tribenzylamine fragment seems to remain approximately constant as long as the volume of the pivotal group is increased [see $\Delta\delta_{up}$ values in Table 4].

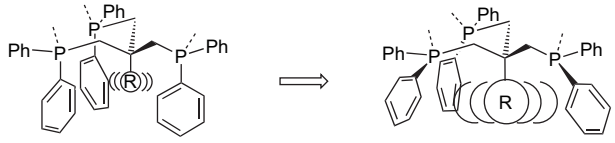


Figure 5. Effect of the increasing size of the pivotal group on the conformation of lower fragment.

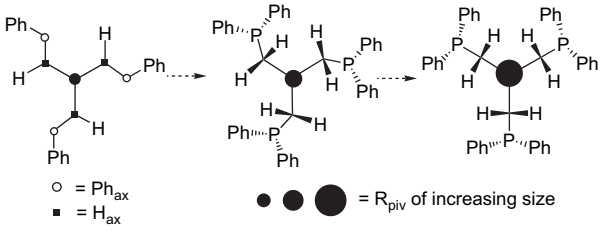


Figure 6. Structural distortion of the lower triphosphane unit of macrobicycles **5** and **7** by increasing the size of the pivotal group.

Table 4. Selected ^{1}H NMR data of CH_2N and CH_2P protons of triphosphazides **5** and tri-λ^5-phosphazenes **7**

R_{piv}	Triphosphazides						Tri-λ^5-phosphazenes					
		δ (CH_2N)			δ (CH_2P)			δ (CH_2N)			δ (CH_2P)	
		H_{eq}	H_{ax}	$\Delta\delta_{up}$[a]	H_{eq}	H_{ax}	$\Delta\delta_{low}$[b]	H_{eq}	H_{ax}	$\Delta\delta_{up}$[a]	H_{eq}	H_{ax}	$\Delta\delta_{low}$[b]
CH_3	**5b**	3.83	4.05	0.22	3.52	3.86	0.34	**7b**	3.45	3.65	0.20	3.23	3.95	0.72
CH_3CH_2	**5f**	3.74	4.00	0.26	3.71	3.84	0.13	**7f**	3.24	3.45	0.21	3.48	4.00	0.52
$(CH_3)_2CH$	**5h**	3.65	3.87	0.22	3.87	3.87	0	**7h**	3.17	3.40	0.23	3.75	4.00	0.25
$(CH_3)_3C$	**5i**	3.58	3.86	0.28	3.84	3.93	0.09	**7i**	2.86	3.25	0.39	4.02	3.89	−0.13

[a] $\Delta\delta_{up}=\delta(H_{ax})-\delta(H_{eq})$ in the upper propeller.
[b] $\Delta\delta_{low}=\delta(H_{ax})-\delta(H_{eq})$ in the lower propeller.

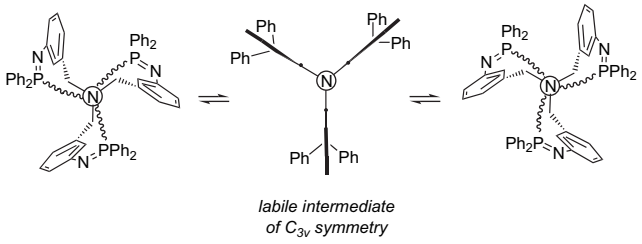
High-temperature ^{1}H NMR experiments demonstrated that the inherently chiral tri-λ^5-phosphazenes **7** experience enantioisomerization processes.[1d] These experiments show the simultaneous coalescence of the CH_2N and CH_2P methylene protons in the ^{1}H NMR spectra, as well as that of the signals corresponding to the two phenyl groups at the phosphorus atom in the corresponding $^{13}C\{^1H\}$ NMR spectra. On cooling to 25 °C, these spectra recovered their original appearance. The calculated activation energy for the racemization process of compound **7b** in *o*-$Cl_2C_6D_4$ solution ($\Delta G^{\ddagger}$= 20.8 kcal mol^{-1}) was discussed in a previous communication.[1d] This barrier is slightly higher than those of some tricyclic[4.4.4]propellanes[16] and the 1-azonia[4.4.4]propellane cation,[17] and notably higher than the values found in other bicyclic molecular propellers.[18] When similar high-temperature NMR experiments were carried out in DMSO-d_6 solution with the rest of the tri-λ^5-phosphazenes **7** the calculated $\Delta G^{\ddagger}$ values[19] were comparable (Table 5), with the exception of **7d** which, as commented above, is less conformationally stable than the rest. It is remarkable that the tri-λ^5-phosphazene with the highest enantioisomerization barrier is **7b**, bearing a pivotal CH_3 group. This fact should be a consequence of the special stabilization of the lower fragment by the three stabilizing CH···π interactions between the methyl protons and the pseudoaxial *P*-phenyl groups, in a similar situation to that represented in Figure 4.

Table 5. Selected data of ^{1}H NMR spectra of tri-λ^5-phosphazenes **7** at high temperature and calculated activation energies for their enantioisomerization processes

Compound	R_{piv}	J (Hz)[a]	$\Delta\nu$ (Hz)[a]	T_c (K)	$\Delta G^{\ddagger}$ (kcal mol^{-1})
7b	CH_3	12.7	51.39	408	20.17
7d	H	12.9	51.50	303	14.79[b]
7f	CH_3CH_2	14.4	19.57	363	18.15
7h	$(CH_3)_3CH$	16.0	66.00	358	17.43
7i	$(CH_3)_3C$	15.9	117.41	408	19.58

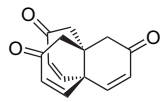
[a] Measured at the CH_2N protons.
[b] Data from experiments in $CDCl_3$ solution.

We have proposed that the equilibrium, at the coalescence temperature, between the two enantiomeric propeller-like forms of **7** should occur via a labile conformation with time-averaged C_{3v} symmetry (Scheme 3).[5d]



Scheme 3. Mechanism of enantioisomerization of tri-λ^5-triphosphazenes **7**.

An alternative mechanism is also conceivable: the sequential isomerization of the three arms, one after another, thus involving species with a degree of symmetry, and in consequence of energy, lower than that of the C_{3v} species. In this sense, a high negative value of $\Delta S^{\ddagger}$ for the enantioisomerization process might support a mechanism through a labile intermediate of C_{3v} symmetry (with one rotation axis and three vertical planes) whereas the involvement of, for instance, a C_3-symmetric species (only one rotation axis) would render a less negative $\Delta S^{\ddagger}$ value as a consequence of a higher molecular disorder (less symmetry elements). In contrast, a nearly zero value of $\Delta S^{\ddagger}$ might be associated with a stepwise process, arm after arm, where the entropic variation of each step should be small. In order to determine $\Delta S^{\ddagger}$, we carried out a line shape analysis[20] of the VT-NMR spectrum of **7b**. The obtained $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were 11.39 kcal mol^{-1} and −24 cal K^{-1} mol^{-1}, respectively. The $\Delta S^{\ddagger}$ is large enough to indicate that the process of enantioisomerization may reasonably occur through a mechanism like that represented in Scheme 3. This value is close to others reported in the literature for similar processes, such as the −16 cal K^{-1} mol^{-1} value of $\Delta S^{\ddagger}$ corresponding to the enantioisomerization of the *P* and *M* forms of the propeller **8** (Fig. 7), which has been qualified as indicative of a mechanism via a C_{3v} intermediate.[21]



8

Figure 7. A tricyclic propeller.

3. Conclusions

Tripod–tripod coupling of triphosphanes derived from the *tert*-butane skeleton with tris(3-azidobenzyl)amines gave rise to a series of chiral macrobicyclic triphosphazides, which were converted by triple dinitrogen extrusion into tri-λ^5-phosphazenes. The structure of these compounds consists of two propellers linked by three P═N units. The introduction of substituents of increasing size at the pivotal carbon atom of the tris(phosphane) fragment causes a gradual loss of helicity at the lower moiety of these double propellers. These conformational changes could be followed by examining some key ^{1}H NMR data. The enantioisomerization barriers of the tri-λ^5-phosphazenes, determined by VT-NMR experiments, show that by changing from a CH_3 pivotal group to H, Et, ^{i}Pr or ^{t}Bu the macrobicycles become less conformationally stable.

4. Experimental

4.1. General method

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 the 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 Bruker AC200 (200 MHz) or a Varian Unity 300 (300 MHz) spectrometer. ^{1}H 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 hydrogenphosphate.

Abbreviations of coupling patterns are as follows: s, singlet; d, doublet; t, triplet; q, quadruplet. Quaternary non-coupled carbons are indicated by *q*. 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 1,1,1-tris(diphenylphosphinomethyl)methane,[9,10] 1,1,1-tris(diphenylphosphinomethyl)propane,[11] 1,1,1-tris(diphenylphosphinomethyl)-2-phenylethane[12] were prepared following previously reported procedures.

4.3. General procedure for the preparation of trichlorides $R_{piv}C(CH_2Cl)_3$

A solution of the corresponding 2-substituted 2-hydroxymethyl-1,3-propanediol (13.5 mmol) in pyridine (3 mL) and thionyl chloride (5.06 g, 42.6 mmol) were simultaneously added dropwise to an ice-cooled round-bottom flask containing pyridine (5 mL). When the addition was over, the resultant mixture was allowed to warm to room temperature (around 1 h) with stirring. Then it was heated at 50 °C for 1 h and at 115 °C for 4 h more. After cooling to room temperature, the mixture was poured on ice/H_2O and extracted with CH_2Cl_2 (3×25 mL). The organic extracts were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the resulting material was chromatographed (silica gel; dichloromethane/*n*-hexane 1:1).

4.3.1. 1-Chloro-2,2-bis(chloromethyl)-3-methylbutane (R_{piv}=^{i}Pr). Yield: 80%; colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.09 (d, J(H,H)=7.1 Hz, 6H; CH_3), 2.06 (sept, J(H,H)=7.1 Hz, 1H; CH), 3.61 (s, 6H; CH_2); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=17.75 (CH_3), 30.77 (CH), 45.17 (*q*), 46.15 (CH_2); IR (film): ν=2972, 1476, 1441, 843, 739, 705 cm^{-1}; MS (70 eV, EI): *m*/*z* (%)=204 (8) [M$^+$+2], 202 (15) [M$^+$], 124 (100); $C_7H_{13}Cl_3$ (203.54): calcd C 41.31, H 6.44; found C 41.19, H 6.40.

4.3.2. 1-Chloro-2,2-bis(chloromethyl)-3,3-dimethylbutane (R_{piv}=^{t}Bu). Yield: 85%; colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.19 (s, 9H; CH_3), 3.81 (s, 6H; CH_2); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=28.14 (CH_3), 36.66 [$C(CH_3)_3$], 46.17 [$C(CH_2Cl)_3$], 47.21 (CH_2); IR (film): ν=2967, 1482, 1443, 965, 864 cm^{-1}; MS (70 eV, EI): *m*/*z* (%)=218 (6) [M$^+$+2], 216 (10) [M$^+$], 124 (100); $C_8H_{15}Cl_3$ (217.56): calcd C 44.16, H 6.95; found C 44.02, H 6.88.

4.4. General procedure for the preparation of 2-substituted 1,1,1-tris(diphenylphosphanylmethyl)propanes (4)

Diphenylphosphane (3 g, 16.5 mmol) was added to a suspension of potassium *tert*-butoxide (2.25 g, 20 mmol) in dry THF (25 mL). The mixture was stirred for 15 min and a solution of the corresponding trichloride (5 mmol) in dry THF (10 mL) was added at once. The reaction mixture was heated at reflux temperature for 16 h. After cooling to room temperature, H_2O (75 mL) was added and the product was extracted with CH_2Cl_2 (3×25 mL). The organic extracts were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude was chromatographed (silica gel; diethyl ether/*n*-hexane 1:1).

4.4.1. 1,1,1-Tris(diphenylphosphanylmethyl)-2-methylpropane (4e). Yield: 71%; white oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.80 (d, J(H,H)=6.8 Hz, 6H; CH_3), 2.15 (sept, J(H,H)=6.8 Hz, 1H; CH), 2.41 (br s, 6H; CH_2), 7.20–7.30 (m, 30H; PhP); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=18.59 (CH_3), 36.56 (CH), 38.75 (m; CH_2P), 44.32 [q, ^2J(C,P)=10.5 Hz; $C(CH_2PPh_2)_3$], 128.04–128.30 (m; *m*C-PhP+*p*C-PhP), 133.56 (d, ^2J(C,P)=19.9 Hz; *o*C-PhP), 140.32 (d, ^1J(C,P)=9.0 Hz; *i*C-PhP); IR (film): ν=2989, 1479, 1386, 1110, 1031, 745, 696 cm^{-1}; MS (70 eV, EI): *m*/*z* (%)=652 (14) [M$^+$], 574 (96), 390 (99), 262 (62), 183 (100); $C_{43}H_{43}P_3$ (652.72): calcd C 79.12, H 6.64; found C 79.03, H 6.54.

4.4.2. 1,1,1-Tris(diphenylphosphanylmethyl)-2,2-dimethylpropane (4f). Yield: 42%; mp 152–154 °C (colourless prisms from chloroform/*n*-pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.07 (s, 9H; CH_3), 2.45 (d, ^2J(H,P)=2.1 Hz, 6H; CH_2), 7.18–7.27 (m, 30H; PhP); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=28.41 (q, ^4J(C,P)=5.0 Hz; CH_3), 38.27 [$C(CH_3)_3$], 39.07 (m; CH_2P), 47.68 [q, ^2J(C,P)=9.3 Hz; $C(CH_2PPh_2)_3$], 128.24 (*p*C-PhP), 128.32 (d, ^3J(C,P)=7.0 Hz; *m*C-PhP), 133.11 (d, ^2J(C,P)=20.3 Hz; *o*C-PhP), 140.39 (d, ^1J(C,P)=13.2 Hz; *i*C-PhP); IR (film): ν=2852, 1465, 1378, 1093, 1025, 968, 736 cm^{-1}; MS (70 eV, EI): *m*/*z* (%)=666 (26) [M$^+$], 586 (82), 404 (85), 389 (99), 262 (83), 181 (99), 106 (100); $C_{44}H_{45}P_3$ (666.75): calcd C 79.26, H 6.80; found C 79.17, H 6.53.

4.5. General procedure for the preparation of the triphosphazides 5

Two solutions of the corresponding tris(3-azidobenzyl)-amine **6** (1.5 mmol) in diethyl ether (10 mL) and the corresponding triphosphane **4** in diethyl ether (10 mL) were simultaneously added dropwise 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.

4.5.1. Triphosphazide 5c. Yield: 82%; mp (decomp.) 306–307 °C (microcrystalline solid from diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.82 (br s, 1H; CH), 3.39–3.63 (m, 12H; CH_2N+CH_2P), 7.00 (d, J(H,H)=7.4 Hz, 3H; H_{arom}), 7.27 (d, J(H,H)=7.6 Hz, 3H; H_{arom}), 7.15–7.50 (m, 24H; H_{arom}), 7.56 (br d, J(H,H)=8.1 Hz, 3H; H_{arom}), 7.64 (dd, 6H, J(H,H),(H,P)=10.2, 8.1 Hz; H_{arom}), 7.76 (br s, 3H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=26.62 (br s; CH), 31.90 (m; CH_2P), 58.11 (CH_2N), 118.61 (br s), 120.80 (br s), 124.20 (d, ^1J(C,P)=110.3 Hz; *i*C-PhP), 126.63, 128.42, 128.90 (d, ^3J(C,P)=11.6 Hz; *m*C-PhP), 129.06 (d, ^3J(C,P)=12.1 Hz; *m*C-PhP), 129.25 (d, ^1J(C,P)=84.6 Hz; *i*C-PhP), 130.91 (d, ^2J(C,P)=9.6 Hz; *o*C-PhP), 131.20 (d, ^4J(C,P)=2.0 Hz; *p*C-PhP), 132.17 (d, ^2J(C,P)=8.1 Hz; *o*C-PhP), 132.20 (d, ^4J(C,P)=1.1 Hz; *p*C-PhP), 141.19 (*q*), 150.99 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=18.20 (br s, $\Delta\nu_{1/2}$=303 Hz); IR (Nujol): ν=1467 (CP), 1113 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%) 1044 (14) [M$^+$+Na], 1021

(6) [M$^+$], 624 (100); $C_{61}H_{55}N_{10}P_3$ (1021.08): calcd C 71.75, H 5.43, N 13.72; found C 71.72, H 5.56, N 13.70.

4.5.2. Triphosphazide 5e. Yield: 73%; mp 309–311 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.60 (pseudot, J(H,H)=6.8 Hz, 3H; CH_3), 0.55 (pseudoq, J(H,H)=7.7 Hz, 1H; $CH_3CH_AH_B$), 0.70 (pseudoq, J(H,H)=7.7 Hz, 1H; $CH_3CH_AH_B$), 3.56 (d, J(H,H)=14.7 Hz, 3H; CH_AH_BN), 3.78–3.94 (m, 9H; CH_AH_BN+CH_AH_BP+CH_AH_BP), 6.85–7.00 (m, 9H; H_{arom}), 7.13 (t, J(H,H)=7.1 Hz, 3H; H_{arom}), 7.26 (t, J(H,H)=7.6 Hz, 3H; H_{arom}), 7.30–7.45 (m, 15H; H_{arom}), 7.57 (d, J(H,H)=8.1 Hz, 3H; H_{arom}), 8.00–8.10 (m, 9H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=9.21 (CH_3CH_2), 31.38 (CH_3CH_2), 39.72 (m; CH_2P), 45.97 (q, ^2J(C,P)=3.5 Hz; CH_3CH_2C), 57.16 (CH_2N), 119.71 (br s, two signals), 125.55, 127.35 (d, ^1J(C,P)=94.0 Hz; *i*C-PhP), 128.56 (d, ^3J(C,P)=11.0 Hz; *m*C-PhP), 128.59, 128.61(d, ^3J(C,P)=10.5 Hz; *m*C-PhP), 129.92 (d, ^1J(C,P)=84.1 Hz; *i*C-PhP), 131.09 (d, ^2J(C,P)=8.7 Hz; *o*C-PhP), 131.25 (br s; *p*C-PhP), 132.18 (br s; *p*C-PhP), 132.99 (d, ^2J(C,P)=7.0 Hz; *o*C-PhP), 141.49 (*q*), 150.24 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=5.80 (br s, $\Delta\nu_{½}$=1210 Hz); IR (Nujol): ν=1440 (CP), 1109 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%) 1072 (16) [M$^+$+Na], 1049 (12) [M$^+$], 653 (100); $C_{63}H_{59}N_{10}P_3$ (1049.13): calcd C 72.12, H 5.67, N 13.35; found C 71.98, H 5.81, N 13.37.

4.5.3. Triphosphazide 5f. Yield: 72%; mp 312–314 °C (yellow prisms from chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.68 (pseudot, J(H,H)=7.3 Hz, 3H; CH_3), 0.57 (pseudoq, J(H,H)=7.6 Hz, 1H; $CH_3CH_AH_B$), 0.77 (pseudoq, J(H,H)=7.6 Hz, 1H; $CH_3CH_AH_B$), 3.71 (m, 3H; CH_AH_BP), 3.74 (d, J(H,H)=16.8 Hz, 3H; CH_AH_BN), 3.84 (pseudot, J(H,H),(H,P)=15.0 Hz, 3H; CH_AH_BP), 4.00 (d, J(H,H)=16.8 Hz, 3H; CH_AH_BN), 6.89–6.93 (m, 6H; H_{arom}), 7.16–7.28 (m, 9H; H_{arom}), 7.37–7.44 (m, 15H; H_{arom}), 8.05–8.07 (m, 6H; H_{arom}), 8.18 (br s, 3H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=8.87 (CH_3CH_2), 31.22 (CH_3CH_2), 39.52 (m; CH_2P), 46.18 (q, ^2J(C,P)=3.0 Hz; CH_3CH_2C), 58.19 (CH_2N), 117.52 (br s), 119.70 (*q*), 120.65 (br s), 127.25 (d_{right}; *i*C-PhP), 128.53 (d, ^3J(C,P)=12.2 Hz; *m*C-PhP), 128.60 (d, ^3J(C,P)=11.0 Hz; *m*C-PhP), 129.54 (d_{left}; *i*C-PhP), 130.80 (d, ^2J(C,P)=9.3 Hz; *o*C-PhP), 131.40 (br s; *p*C-PhP), 132.13 (br s; *p*C-PhP), 132.74 (d, ^2J(C,P)=7.0 Hz; *o*C-PhP), 133.24, 139.32 (*q*), 149.22 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=4.76 (br s, $\Delta\nu_{½}$=484 Hz); IR (Nujol): ν=1462 (CP), 1114 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%) 1284 (7) [M$^+$+2], 655 (100); $C_{63}H_{56}Br_3N_{10}P_3$ (1285.82): calcd C 58.85, H 4.39, N 10.89; found C 58.94, H 4.48, N 10.87.

4.5.4. Triphosphazide 5h. Yield: 56%; mp (decomp.) 301–303 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.05 [d, J(H,H)=6.3 Hz, 3H; $(CH_3)_A$], 0.03 [d, J(H,H)=6.0 Hz, 3H; $(CH_3)_B$], 0.87 (m, 1H; CH), 3.65 (d, J(H,H)=16.5 Hz, 3H; CH_AH_BN), 3.77–3.96 (m, 9H; CH_AH_BN+CH_2P), 6.81–6.85 (m, 6H; H_{arom}), 7.13–7.15 (m, 3H; H_{arom}), 7.30–7.46 (m, 21H; H_{arom}), 8.06–8.15 (m, 9H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=19.89 [$(CH_3)_A$], 20.48 [$(CH_3)_B$], 33.21 [$(CH_3)_2CH$], 37.82 (m; CH_2P), 51.84 [q, ^2J(C,P)=3.4 Hz; $(CH_3)_2CHC$], 58.15 (CH_2N), 117.80 (br s), 119.88 (*q*), 120.83 (br s), 128.43 (d, ^1J(C,P)=106.7 Hz; *i*C-PhP), 128.59 (br d, ^3J(C,P)=11.6 Hz; 2 *m*C-PhP), 129.69 (d, ^1J(C,P)=84.3 Hz; *i*C-PhP), 130.68 (d, ^2J(C,P)=9.1 Hz; *o*C-PhP), 131.34 (br s; *p*C-PhP), 132.24 (br s; *p*C-PhP), 133.27, 133.35 (d, ^2J(C,P)=8.3 Hz; *o*C-PhP), 139.33 (*q*), 149.25 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=6.46 (br s, $\Delta\nu_{½}$=447 Hz); IR (Nujol): ν=1463 (CP), 1112 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%) 1301 (11) [M$^+$+5], 1299 (13) [M$^+$+3], 666 (100); $C_{64}H_{58}Br_3N_{10}P_3$ (1299.85): calcd C 59.14, H 4.50, N 10.78; found C 58.99, H 4.43, N 10.69.

4.5.5. Triphosphazide 5i. Yield: 43%; mp 297–299 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.36 (br s, 9H; CH_3), 3.58 (d, J(H,H)=16.4 Hz, 3H; CH_AH_BN), 3.84 (pseudoquint, J(H,H),(H,P)=12.0 Hz, 3H; CH_AH_BP), 3.86 (d, J(H,H)=16.4 Hz, 3H; CH_AH_BN), 3.93 (pseudot, J(H,H),(H,P)=15.9 Hz, 3H; CH_AH_BP), 6.65–6.72 (m, 6H; H_{arom}), 7.22–7.50 (m, 24H; H_{arom}), 8.01–8.08 (m, 6H; H_{arom}), 8.12 (br s, 3H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=29.07 [$(CH_3)_3C$], 34.14 [$(CH_3)_3C$], 37.80 (m; CH_2P), 57.92 [q, ^2J(C,P)=3.0 Hz, $(CH_3)_3CC$], 58.15 (CH_2N), 117.50 (br s), 119.49 (*q*), 123.04 (br s), 128.12 (d, ^3J(C,P)=11.7 Hz; *m*C-PhP), 128.30 (d, ^3J(C,P)=11.2 Hz; *m*C-PhP), 128.80 (d, ^1J(C,P)=105.6 Hz; *i*C-PhP), 130.40 (d, ^2J(C,P)=9.0 Hz; *o*C-PhP), 130.67 (d, ^1J(C,P)=82.6 Hz; *i*C-PhP), 130.75 (br s; *p*C-PhP), 131.79 (br s; *p*C-PhP), 133.10, 134.14 (d, ^2J(C,P)=7.3 Hz; *o*C-PhP), 139.31 (*q*), 148.83 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=7.00 (br s, $\Delta\nu_{½}$=242 Hz); IR (Nujol): ν=1462 (CP), 1115 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%) 1314 (12) [M$^+$+4], 1312 (15) [M$^+$+2], 1310 (7) [M$^+$], 684 (100); $C_{65}H_{60}Br_3N_{10}P_3$ (1313.87): calcd C 59.42, H 4.60, N 10.66; found C 59.30, H 4.52, N 10.45.

4.6. General procedure for the preparation of the tri-λ^5-phosphazenes 7

A solution of the corresponding triphosphazide **5** (1 mmol) in $CDCl_3$ (10 mL) was heated at 60 °C in an oil bath for 24 h. After cooling, the solvent was removed under reduced pressure and the crude product was crystallized.

4.6.1. Tri-λ^5-phosphazene 7c. Yield: 58%; mp 210–212 °C (colourless prisms from chloroform/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.16 (br s, 1H; CH), 3.39 (br s, 6H; CH_2P), 3.40 (br s, 6H; CH_2N), 6.26 (s, 3H; H_{arom}), 6.59 (d, J(H,H)=7.2 Hz, 3H; H_{arom}), 6.97 (d, J(H,H)=7.8 Hz, 3H; H_{arom}), 7.08 (dt, J(H,H),(H,P)=8.1, 2.2 Hz, 3H; H_{arom}), 7.10–7.45 (m, 30H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=26.17 (br s; CH), 27.05 (dt, ^1J(C,P)=46.6 Hz, ^3J(C,P)=8.0 Hz; CH_2P), 58.03 (CH_2N), 118.69, 123.20 (d, ^3J(C,P)=11.1 Hz; *s-cis-C*H=C–N=P), 124.87 (d, ^3J(C,P)=27.7 Hz; *s-trans-C*H=C–N=P), 128.41, 128.56 (br s; *m*C-PhP), 130.92 (br s; *p*C-PhP), 131.29 (br s; *p*C-PhP), 142.04 (*q*), 151.52 (*q*), the resonance of the *i*C-PhP was not observed; ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=1.11; IR (Nujol): ν=1465 (CP), 1115 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%)=938 (55) [M$^+$+1], 937 (100) [M$^+$], 936 (64) [M$^+$−1]; $C_{61}H_{55}N_4P_3$ (937.04): calcd C 78.19, H 5.92, N 5.98; found C 78.05, H 5.79, N 5.87.

4.6.2. Tri-λ^5-phosphazene 7d. Yield: 63%; mp 171–173 °C (colourless prisms from chloroform); ^{1}H NMR (300 MHz,

$CDCl_3$, 25 °C): δ=1.48 (br s, 1H; CH), 3.33 (br s, 6H; CH_2P), 3.69 (br s, 6H; CH_2N), 6.47 (d, J(H,H)=2.7 Hz, 3H; H_{arom}), 6.84 (dd, J(H,H)=8.7, 3.0 Hz, 3H; H_{arom}), 7.23–7.52 (m, 33H; H_{arom}); ^{1}H NMR (300 MHz, $CDCl_3$, 60 °C): δ=1.30 (pseudoq, J(H,H),(H,P)=8.4 Hz, 1H; CH), 3.32 (br s, 6H; CH_2P), 3.70 (s, 6H; CH_2N), 6.49 (d, J(H,H)=2.7 Hz, 3H; H_{arom}), 6.82 (dd, J=8.7, 3.0 Hz, 3H; H_{arom}), 7.23–7.44 (m, 33H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 60 °C): δ=26.18 (q, ^2J(C,P)=2.5 Hz; CH), 28.12 (dt, ^1J(C,P)=46.4 Hz, ^3J(C,P)=8.2 Hz; CH_2P), 56.96 (CH_2N), 111.74 (*q*), 124.73 (d, ^3J(C,P)=10.4 Hz; *s-cis-C*H=C–N=P), 126.86 (d, ^3J(C,P)=27.8 Hz; *s-trans-C*H=C–N=P), 128.74 (d, ^3J(C,P)=12.2 Hz; *m*C-PhP), 131.05 (d, ^2J(C,P)=9.3 Hz; *o*C-PhP), 131.50 (d, ^4J(C,P)= 2.3 Hz; *p*C-PhP), 132.68 (d, ^4J(C,P)=4.1 Hz), 140.07 (*q*), 150.99 (*q*), the resonance of the *i*C-PhP was not observed; ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=2.68; IR (Nujol): ν=1474 (CP), 1116 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%)= 1175 (45) [M$^+$+5], 1173 (89) [M$^+$+3], 1171 (100) [M$^+$+1]; $C_{61}H_{52}Br_3N_4P_3$ (1173.73): calcd C 62.42, H 4.47, N 4.77; found C 62.34, H 4.38, N 4.81.

4.6.3. Tri-λ^5-phosphazene 7e. Yield: 74%; mp 321–323 °C (yellow prisms from chloroform/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.92 (pseudot, J(H,H)=7.3 Hz, 3H; CH_3), 0.18 (pseudoq, J(H,H)=7.3 Hz, 1H; $CH_3CH_AH_B$), 0.32 (pseudoq, J(H,H)=7.3 Hz, 1H; $CH_3CH_AH_B$), 2.86 (d, J(H,H)=12.3 Hz, 3H; CH_AH_BN), 3.41 (pseudoquint, J(H,H),(H,P)=8.1 Hz, 3H; CH_AH_BP), 3.45 (d, J(H,H)= 12.3 Hz, 3H; CH_AH_BN), 3.97 (pseudot, J(H,H),(H,P)= 15.2 Hz, 3H; CH_AH_BP), 6.36–6.38 (m, 3H; H_{Ar}), 6.47 (d, J(H,H)=6.8 Hz, 3H; H_{arom}), 7.00–7.60 (m, 30H; H_{arom}), 7.90–7.96 (m, 6H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=8.98 (CH_3CH_2), 33.48 (CH_3CH_2), 36.98 (m; CH_2P), 44.53 (q, ^2J(C,P)=3.5 Hz; CH_3CH_2C), 57.56 (CH_2N), 118.40, 122.64 (d, ^3J(C,P)=12.7 Hz; *s-cis-C*H=C–N=P), 125.41 (d, ^3J(C,P)=27.8 Hz; *s-trans-C*H=C–N=P), 128.22 (d, ^4J(C,P)=4.0 Hz), 128.36 (d, ^3J(C,P)=12.8 Hz; *m*C-PhP), 128.70 (d, ^3J(C,P)=11.0 Hz; *m*C-PhP), 130.94 (d, ^4J(C,P)=1.2 Hz; *p*C-PhP), 131.41 (d, ^4J(C,P)=1.0 Hz; *p*C-PhP), 131.61 (d, ^2J(C,P)=8.7 Hz; *o*C-PhP), 131.86 (d, ^1J(C,P)=91.5 Hz; *i*C-PhP), 132.23 (d, ^2J(C,P)=9.3 Hz; *o*C-PhP), 132.51 (d, ^1J(C,P)=88.9 Hz; *i*C-PhP), 141.80 (*q*), 151.24 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=2.17; IR (Nujol): ν=1451 (CP), 1117 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%)=988 (12) [M$^+$+Na], 966 (100) [M$^+$+1]; $C_{63}H_{59}N_4P_3$ (965.09): calcd C 78.40, H 6.16, N 5.81; found C 78.29, H 6.11, N 5.92.

4.6.4. Tri-λ^5-phosphazene 7f. Yield: 81%; mp (decomp.) 348–350 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.79 (pseudot, J(H,H)=7.4 Hz, 3H; CH_3), 0.30 (pseudoq, J(H,H)=7.4 Hz, 1H; $CH_3CH_AH_B$), 0.37 (pseudoq, J(H,H)=7.4 Hz, 1H; $CH_3CH_AH_B$), 3.24 (d, J(H,H)=14.4 Hz, 3H; CH_AH_BN), 3.45 (d, J(H,H)=14.4 Hz, 3H; CH_AH_BN), 3.48 (m, 3H; CH_AH_BP), 4.00 (pseudot, J(H,H),(H,P)=15.3 Hz, 3H; CH_AH_BP), 6.68 (d, J(H,H)=2.4 Hz, 3H; H_{arom}), 6.81 (dd, J(H,H)=8.7, 2.7 Hz, 3H; H_{arom}), 7.17–7.39 (m, 27H; H_{arom}), 7.89–7.95 (m, 6H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=9.12 (CH_3CH_2), 33.62 (CH_3CH_2), 37.23 (m; CH_2P), 44.75 (q, ^2J(C,P)=3.4 Hz; CH_3CH_2C), 56.95 (CH_2N), 111.04 (*q*), 122.77 (d, ^3J(C,P)=11.6 Hz; *s-cis-C*H=C–N=P), 126.88 (d, ^3J(C,P)=27.8 Hz; *s-trans-C*H=C–N=P), 128.48 (d, ^3J(C,P)=12.8 Hz; *m*C-PhP), 128.82 (d, ^3J(C,P)=11.0 Hz; *m*C-PhP), 130.80 (d_{right}; *i*C-PhP), 131.00 (d, ^2J(C,P)=8.7 Hz; *o*C-PhP), 131.25 (br s; *p*C-PhP), 131.57 (br s; *p*C-PhP), 131.92 (d, ^2J(C,P)=9.3 Hz; *o*C-PhP), 132.86, 138.97 (*q*), 150.98 (*q*), the resonance of one *i*C-PhP was not observed; ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=0.63; IR (Nujol): ν=1440 (CP), 1119 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%)=1202 (95) [M$^+$+4], 1200 (100) [M$^+$+2], 1198 (31) [M$^+$]; $C_{63}H_{56}Br_3N_4P_3$ (1201.78): calcd C 62.96, H 4.70, N 4.66; found C 62.85, H 4.64, N 4.60.

4.6.5. Tri-λ^5-phosphazene 7g. Yield: 7%; mp 258–260 °C (colourless prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.41 [d, J(H,H)=7.0 Hz, 3H; $(CH_3)_A$], −0.21 [d, J(H,H)=6.8 Hz, 3H; $(CH_3)_B$], 0.96 (m, 1H; CH), 2.81 (d, J(H,H)=12.4 Hz, 3H; CH_AH_BN), 3.34 (d, J(H,H)=12.4 Hz, 3H; CH_AH_BN), 3.66 (pseudoquint, J(H,H),(H,P)=7.6 Hz, 3H; CH_AH_BP), 3.94 (pseudot, J(H,H),(H,P)=15.9 Hz, 3H; CH_AH_BP), 6.37 (d, J(H,H)= 7.0 Hz, 3H; H_{arom}), 6.40 (br s, 3H; H_{arom}), 7.02 (dt, J(H,H)= 7.2, 1.8 Hz, 3H; H_{arom}), 7.12 (d, J(H,H)=6.9 Hz, 3H; H_{arom}), 7.34–7.39 (m, 15H; H_{arom}), 7.46–7.56 (m, 9H; H_{arom}), 7.98–8.03 (m, 6H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=19.53 [$(CH_3)_A$], 20.11 [$(CH_3)_B$], 35.48 [$(CH_3)_2CH$], 36.75 (dd, ^1J(C,P)=45.8 Hz, ^3J(C,P)=12.2 Hz; CH_2P), 50.12 [q, ^2J(C,P)=3.1 Hz; $(CH_3)_2CHC$], 57.42 (CH_2N), 118.14, 122.75 (d, ^3J(C,P)=12.8 Hz; *s-cis-C*H=C–N=P), 125.49 (d, ^3J(C,P)=27.8 Hz; *s-trans-C*H=C–N=P), 128.21, 128.30 (d, ^3J(C,P)=13.3 Hz; *m*C-PhP), 128.71 (d, ^3J(C,P)=11.0 Hz; *m*C-PhP), 130.69 (br s; *p*C-PhP), 131.10 (d, ^1J(C,P)=90.7 Hz; *i*C-PhP), 131.28 (br s; *p*C-PhP), 131.63 (d, ^2J(C,P)=8.7 Hz; *o*C-PhP), 132.45 (d, ^2J(C,P)= 9.3 Hz; *o*C-PhP), 132.80 (d, ^1J(C,P)=105.1 Hz; *i*C-PhP), 141.63 (*q*), 151.33 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=3.50; IR (Nujol): ν=1459 (CP), 1109 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%)=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 6.15, N 5.61.

4.6.6. Tri-λ^5-phosphazene 7h. Yield: 72%; mp (decomp.) 328–330 °C (colourless prisms from chloroform/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.31 [d, J(H,H)=7.1 Hz, 3H; $(CH_3)_A$], −0.06 [d, J(H,H)=7.0 Hz, 3H; $(CH_3)_B$], 1.03 (m, 1H; CH), 3.17 (d, J(H,H)=16.0 Hz, 3H; CH_AH_BN), 3.40 (d, J(H,H)=16.0 Hz, 3H; CH_AH_BN), 3.75 (pseudoquint, J(H,H),(H,P)=7.7 Hz, 3H; CH_AH_BP), 4.00 (pseudot, J(H,H),(H,P)=16.3 Hz, 3H; CH_AH_BP), 6.83 (d, J(H,H)=2.4 Hz, 3H; H_{arom}), 6.97 (dd, J(H,H)=8.7, 2.4 Hz, 3H; H_{arom}), 7.12 (dt, J(H,H)=7.6, 2.9 Hz, 6H; H_{arom}), 7.20 (dd, J(H,H)=8.4, 1.8 Hz, 3H; H_{arom}), 7.24–7.33 (m, 9H; H_{arom}), 7.38–7.41 (m, 9H; H_{arom}), 7.98–8.04 (m, 6H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=19.66 [$(CH_3)_A$], 19.84 [$(CH_3)_B$], 35.58 [$(CH_3)_2CH$], 37.73 (m; CH_2P), 50.38 [q, ^2J(C,P)=3.3 Hz; $(CH_3)_2CHC$], 57.75 (CH_2N), 110.17 (*q*), 121.51 (d, ^3J(C,P)=11.0 Hz; *s-cis-C*H=C–N=P), 126.31 (d, ^3J(C,P)=27.2 Hz; *s-trans-C*H=C–N=P), 128.36 (d, ^3J(C,P)=12.8 Hz; *m*C-PhP), 128.69 (d, ^3J(C,P)=10.4 Hz; *m*C-PhP), 130.63 (d, ^2J(C,P)=8.1 Hz; *o*C-PhP), 130.75 (br s; *p*C-PhP), 131.23, 131.47 (d, ^1J(C,P)=92.4 Hz; *i*C-PhP), 131.76 (d, ^2J(C,P)=9.3 Hz; *o*C-PhP), 133.30 (d, ^4J(C,P)=3.2 Hz; *p*C-PhP), 133.81 (d_{left}; *i*C-PhP), 138.12 (*q*), 151.29 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=0.88; IR (Nujol):

ν=1446 (CP), 1116 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%)= 1216 (89) [M$^+$+4], 1214 (100) [M$^+$+2], 1212 (39) [M$^+$]; $C_{64}H_{58}Br_3N_4P_3$ (1215.81): calcd C 63.22, H 4.81, N 4.61; found C 63.35, H 4.69, N 4.76.

4.6.7. Tri-λ^5-phosphazene 7i. Yield: 56%; mp (decomp.) 324–326 °C (colourless prisms from chloroform/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.22 (s, 9H; CH_3), 2.86 (d, *J*(H,H)=15.9 Hz, 3H; CH_AH$_B$N), 3.25 (d, *J*(H,H)= 15.9 Hz, 3H; CH$_A$$H_B$N), 3.89 (pseudot, *J*(H,H),(H,P)=16.4 Hz, 3H; CH_AH$_B$P), 4.02 (pseudoquint, *J*(H,H),(H,P)= 7.8 Hz, 3H; CH$_A$$H_B$P), 6.88 (br s, 3H; H_{arom}), 7.04 (dt, *J*(H,H)=7.7, 2.6 Hz, 9H; H_{arom}), 7.17–7.21 (m, 6H; H_{arom}), 7.28–7.37 (m, 15H; H_{arom}), 8.10–8.14 (m, 6H; H_{arom}); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=28.79 [(*C*H$_3$)$_3$C], 34.80 [(CH$_3$)$_3$*C*], 38.12 (m; CH_2P), 56.24 [q, ^{2}*J*(C,P)= 3.1 Hz; (CH$_3$)$_3$C*C*], 57.83 (CH_2N), 109.75 (*q*), 121.29 (d, ^{3}*J*(C,P)=10.4 Hz; *s-cis-C*H=C–N=P), 126.09 (d, ^{3}*J*(C,P)=29.7 Hz; *s-trans-C*H=C–N=P), 128.08 (d, ^{3}*J*(C,P)=12.2 Hz; *m*C-PhP), 128.56 (d, ^{3}*J*(C,P)=10.4 Hz; *m*C-PhP), 130.34 (br s; *p*C-PhP), 130.40 (d, ^{2}*J*(C,P)=8.1 Hz; *o*C-PhP), 130.95 (br s; *p*C-PhP), 131.44 (d, ^{1}*J*(C,P)= 74.8 Hz; *i*C-PhP), 132.44 (d, ^{2}*J*(C,P)=8.7 Hz; *o*C-PhP), 133.02 (d, ^{1}*J*(C,P)=74.8 Hz; *i*C-PhP), 133.67, 137.71 (*q*), 151.67 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=−0.02; IR (Nujol): ν=1451 (CP), 1116 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%)=1231 (100) [M$^+$+5], 1229 (97) [M$^+$+3], 1227 (18) [M$^+$+1]; $C_{65}H_{60}Br_3N_4P_3$ (1229.83): calcd C 63.48, H 4.92, N 4.56; found C 63.51, H 4.78, N 4.47.

Acknowledgements

This work was supported by the MEC and FEDER (Project CTQ2005-02323/BQU) and Fundación Séneca-CARM (Project 00458/PI/04). J.B. also thanks the MEC for a fellowship.

References and notes

1. (a) Dietrich, B.; Voiut, P.; Lehn, J. M. *Macrocyclic Chemistry: Aspects of Organic and Inorganic Supramolecular Chemistry*; VCH: Weinheim, 1992; (b) Schneider, H. J.; Yatsimirski, A. K. *Principles and Methods in Supramolecular Chemistry*; Wiley: Chichester, UK, 1999.
2. Caminade, A. M.; Majoral, J. P. *Chem. Rev.* **1994**, *94*, 1183.
3. (a) Caminade, A. M.; Kraemer, R.; Majoral, J. P. *New J. Chem.* **1997**, *21*, 627; (b) Bauer, I.; Gruner, M.; Goutal, S.; Habicher, W. D. *Chem.—Eur. J.* **2004**, *10*, 4011; (c) Bauer, I.; Sergeenko, G. G.; Nizamov, I. S.; Theumer, G.; Froehlich, R.; Burilov, A. R.; Maslennikova, V. I.; Habicher, W. D. *ARKIVOC* **2004**, *12*, 38.
4. (a) Badri, M.; Caminade, A. M.; Majoral, J. P.; Gorgues, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *56*, 123; (b) Mitjaville, J.; Caminade, A. M.; Majoral, J. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2161; (c) Mitjaville, J.; Caminade, A. M.; Mathieu, R.; Majoral, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 5007; (d) Houalla, D.; Moureau, L.; Skouta, S.; Mazieres, M. R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *103*, 199.
5. (a) Alajarín, M.; Molina, P.; López-Lázaro, A.; Foces-Foces, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 67; (b) Alajarín, M.; López-Lázaro, A.; Vidal, A.; Berná, J. *Chem.—Eur. J.* **1998**, *4*, 2558; (c) Alajarín, M.; Vidal, A.; López-Leonardo, C.; Berná, J.; Ramírez de Arellano, M. C. *Tetrahedron Lett.* **1998**, *39*, 7807; (d) Alajarín, M.; López-Leonardo, C.; Vidal, A.; Berná, J.; Steed, J. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 1205; (e) Alajarín, M.; López-Leonardo, C.; Berná, J. *Tetrahedron* **2006**, *62*, 6190.
6. (a) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635; (b) Gololobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437; (c) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353; Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley: New York, NY, 1993; p 403.
7. (a) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: New York, NY, 1995; p 140; (b) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: New York, NY, 2000; p 461.
8. Alajarín, M.; López-Leonardo, C.; Berná, J.; Steed, J. W. *Tetrahedron* **2007**, *63*, 2078.
9. Global yield of a sequence of two reactions: (a) conversion of 2-hydroxy-2-nitro-1,3-propanediol to 1,3-dichloro-2-chloromethyl-2-nitropropane (53%): Fort, G.; McLean, A. *J. Am. Chem. Soc.* **1948**, 1902; and (b) conversion of 1,3-dichloro-2-chloromethyl-2-nitropropane to 1,3-dichloro-2-chloromethyl-propane (84%): Latour, S.; Wuest, J. D. *Synthesis* **1987**, 742.
10. Janssen, B. C.; Asam, A.; Huttner, G.; Sernau, V.; Zsolnai, L. *Chem. Ber.* **1994**, *127*, 501.
11. Ott, J.; Venanzi, L. M.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1985**, *291*, 89.
12. Janssen, B. C.; Sernau, V.; Huttner, G.; Asam, A.; Water, O.; Büchner, M.; Zsolnai, L. *Chem. Ber.* **1995**, *128*, 63.
13. For high level calculations on the mechanism of the Staudinger P(III) imination reaction see: (a) Alajarín, M.; Conesa, C.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1811; (b) Widauer, C.; Grützmacher, H.; Shevchenko, Y.; Gramlich, V. *Eur. J. Inorg. Chem.* **1999**, 1659; (c) Tian, W. Q.; Wang, Y. A. *J. Chem. Theory Comput.* **2005**, *1*, 353.
14. For examples of phosphazides that equilibrate in solution with their phosphane and azide counterparts, see: (a) Leffler, J. E.; Honsberg, U.; Tsuno, Y.; Forsblad, I. *J. Org. Chem.* **1961**, *26*, 4810; (b) Leffler, J. E.; Tsuno, Y. *J. Org. Chem.* **1963**, *28*, 902; (c) Leffler, J. E.; Temple, R. D. *J. Am. Chem. Soc.* **1967**, *89*, 5235.
15. The conventional assignment of the stereochemical descriptor *P* or *M* (helical twist sense) to the propeller units of the chiral macrobicycles was made by looking at the molecule along its threefold axis from the side of the tribenzylamine fragment.
16. Gilboa, H.; Altman, J.; Loewenstein, A. *J. Am. Chem. Soc.* **1969**, *91*, 6062.
17. Alder, R. W.; Arrowsmith, R. J. *J. Chem. Res., Synop.* **1980**, 163.
18. (a) Nakazaki, M.; Yamamoto, K.; Toya, T. *J. Org. Chem.* **1981**, *46*, 1611; (b) L'Esperance, R. P.; West, A. P., Jr.; Engen, D. V.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 2672.
19. The activation energies were calculated from the equation: $\Delta G^{\ddagger}=(4.57\times10^{-3})T_c(10.32+\log(T_c2/\pi\Delta\nu))$ following: Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; McGraw-Hill: New York, NY, 1989; p 103.
20. (a) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411; (b) Martin, M. L.; Delpuech, J. J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: London, 1980; (c) Lamber, J. B.; Nienhuis, R. J.; Keepers, J. W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 487; (d) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: London, 1990.
21. Jendralla, H.; Doecke, C. W.; Paquette, L. A. *J. Chem. Soc., Chem. Commun.* **1984**, 942.