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Macrobicyclic triphosphazides and tri-λ⁵-phosphazenes derived from $PhC(CH_2PPh_2)_3$. Two propeller-shaped diastereoisomers in the crystals

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Abstract—New macrobicyclic cage-compounds composed of two tripodal, propeller-shaped fragments linked by phosphazide and phosphazene units have been synthesized by reaction of $PhC(CH_2PPh_2)_3$ with tris(*m*-azidobenzyl)amines. Two diastereoisomers of one of these cages have been characterized in the solid state by X-ray crystallography, one presenting two propellers with the same sense of twist *P**,*P** whereas in the second one the helical sense of both propellers is the opposite, *P**,*M**. In contrast, only one species is apparent in $CDCl_3$ solution.

1. Introduction

We have previously described[1] the tripod–tripod coupling of tris(*o*- and *m*-azidobenzyl)amines with 1,1,1-tris[(diphenylphosphino)methyl]ethane $CH_3C(CH_2PPh_2)_3$ to give the first intrinsically chiral, C_3-symmetric, macrobicyclic triphosphazides **1** and **2** by self-assembly[2] processes, which involve a triple Staudinger phosphane-imination reaction.[3] These compounds were shown to possess propeller-like topology and, in all the cases studied by us, their formation occurs with total diastereoselectivity in favor of the stereoisomer in which both propeller units, the upper tribenzylamine core and the lower *tert*-pentane fragment, present the same sense of twist. The heating of macrobicyclic cages **2** induced a remarkable stepwise triple extrusion of molecular nitrogen to afford tri-λ⁵-phosphazenes **3**, which preserved the chiral, propeller-like topology of their precursors[1e] (Fig. 1).

All the examples of triphosphazides **1** and **2** and triphosphazenes **3** prepared so far and which have been characterized in the solid state by X-ray diffraction show only one type of molecules in the crystals, those with coincident senses of twist in both propeller fragments, upper and lower.[1a–d] At the same time, their NMR data in solution are in agreement with the structures determined in the solid state, thus suggesting a high degree of conformational stability of these macrobicycles. Here we disclose a result that deviates from this general trend when the lower tris(phosphane) fragment is changed from $CH_3C(CH_2PPh_2)_3$, bearing a methyl group at the pivotal carbon atom, to $PhC(CH_2PPh_2)_3$, in which a larger phenyl group occupies that position instead.

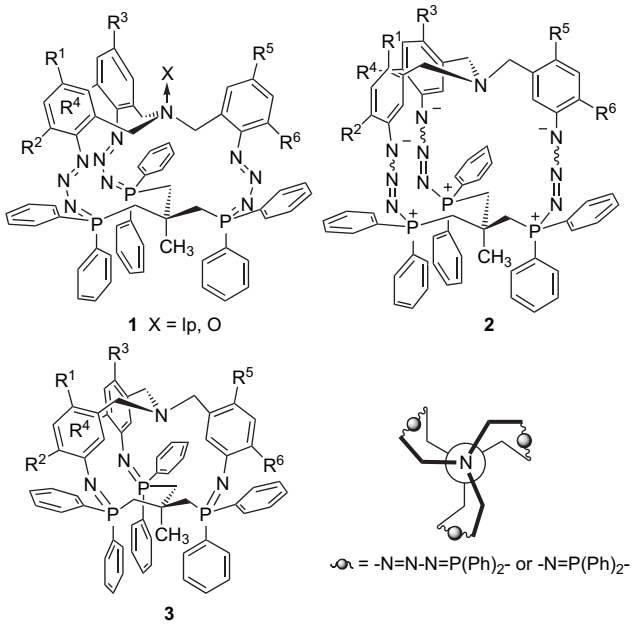

Figure 1. Structure of triphosphazides **1** and **2** and tri-λ⁵-phosphazenes **3**, and schematic representation, as viewed along the C_3 axis, of the bis(propeller) shape of these compounds.

Keywords: Triphosphazide; Tri-λ⁵-phosphazene; Macrobicycle; Cage-compound; Propeller; Tripod–tripod coupling.
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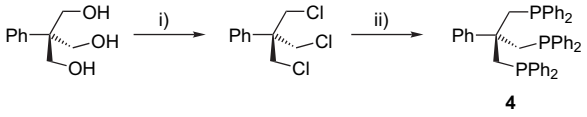
2. Results and discussion

Tris(phosphane) **4** has been reported only once in the chemical literature.[4] We have prepared it essentially by following the reported procedure, but with some minor modifications aimed at making it more reproducible and resulting in a slightly improved total yield. As outlined in Scheme 1, the appropriate triol, 2-hydroxymethyl-2-phenylpropane-1,3-diol, easily available from phenylacetaldehyde and paraformaldehyde,[5] was converted into its trichloride in 61% yield by reaction with thionyl chloride in pyridine. Further triple substitution with potassium diphenylphosphide gave rise to tris(phosphane) **4** in 76% yield.



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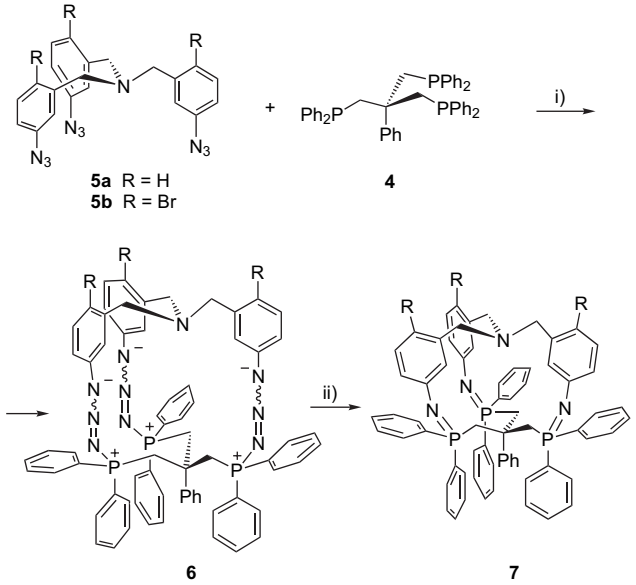
Scheme 1. Synthesis of tris(phosphanes) **4**. Reagents and conditions: (i) $SOCl_2$, pyridine, 0–115 °C, 6 h; (ii) $HPPh_2$, KO^{t}Bu, THF, reflux, 16 h.

With the tris(phosphane) **4** in our hands we prepared the triphosphazides **6a** and **6b** in 49 and 50% yields, respectively, by the tripod–tripod coupling reaction of **4** with the tris(*m*-azidobenzyl)amines **5a** and **5b**, respectively (Scheme 2). These self-assembly reactions were run in Et_2O at room temperature, and the products precipitated out from this solvent. The new triphosphazides **6** are quite stable in $CDCl_3$ solution at room temperature for days, as checked by NMR, and their spectral data are similar to those of the several compounds **2** prepared in advance.[1c,e]



Scheme 2. Synthesis of triphosphazides **6** and tri-λ^5-phosphazenes **7**. Reagents and conditions: (i) Et_2O, 25 °C, 3h; (ii) $CDCl_3$, 60 °C, 24 h.

The existence and stability of **6** seems to indicate that the phenyl group at the pivotal carbon of the lower propeller could be accommodated inside the space delimited by the three pseudoaxial phenyl groups at the phosphorus atoms. However, the insignificant anisochrony of the CH_2P methylene protons in the ^1H NMR spectra of **6** ($\Delta\delta$=0–0.05), when compared with triphosphazides **2** ($\Delta\delta$=0.35), is an indication of the apparent absence of a propeller arrangement in the lower fragment, thus positioning the two methylene protons in a similar, or nearly similar, chemical environment. The reason for this striking conformational change should be attributed to the sterically demanding pivotal phenyl and could be explained by assuming that it distorts the optimal, propeller-like conformation of the triphosphane fragment by 'pushing' the pseudoaxial phenyls at phosphorus away from the C_3 axis passing through the pivotal carbon (Fig. 2).

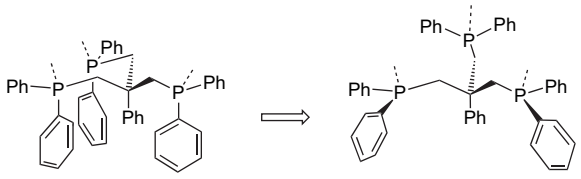


Figure 2. Deformation in the conformation of the lower fragment on introducing a larger phenyl group.

This conformational deformation, originated by the pivotal phenyl group and requiring just a few bond rotations, determines that now both phenyls at P and the CH_2P methylene protons are practically no longer diastereotopic. It seems reasonable that the flexibility that the three phosphazide functions impart to the macrobicyclic cage (due to their easy *s*-cis to *s*-trans isomerization,[6] or *E* to *Z* in the dipolar form N^-–N=N–P^+, as well as the easy reversibility of the equilibrium with their precursors, azide and phosphane[7]) may play a decisive role in allowing the conformational change related above. Moreover, the solution conformation of the lower part of triphosphazides **6**, as deduced from their NMR data [note that the upper part is still propeller-like, as indicated by the anisochrony of the methylene CH_2N protons ($\Delta\delta$=0.24–0.37)] may be just the mean equilibrium situation representing the center of the conformational continuum in the extremes of which the two lower propellers with different sense of twist, *P** and *M**,[8] would be positioned whereas the helical sense of the upper propeller is kept unchanged (Fig. 3).

By examining molecular models we found that this conformational equilibrium can be apparently established without disturbing the propeller at the upper part of the cage. Additionally we did not find, at first sight, reasons for a clear preference in favor of either one of the two possible extreme helical senses at the lower fragment or the putative mean, non-propeller-shaped conformation. For instance, the two diastereoisomeric triphosphazides **6** differing only in the propeller configuration of the lower fragment, *P**,*P** and *P**,*M**, can be built easily and do not show, at first sight, notable differences as far as steric interferences between atoms

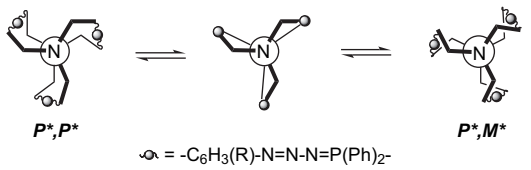


Figure 3. Conformational equilibrium of triphosphazides **6** at the lower propeller.

or groups of atoms are concerned. In conclusion, the lower propeller of triphosphazides **6** seems to be conformationally labile in $CDCl_3$ solution at room temperature, whereas the upper part appears clearly propeller-shaped as indicated by the anisochrony of its methylene CH_2N protons in the ^1H NMR spectra.

As expected, triphosphazides **6** cleanly extruded N_2 in their three arms when heated at 60 °C for 24 h in $CDCl_3$ solution, yielding the respective triphosphazenes **7a** and **7b** in 62 and 87% yields, respectively.

These new tri-λ^5-phosphazenes **7** seem to be, as the rest of their partners **3** prepared before, C_3-symmetric chiral species in $CDCl_3$ solution at room temperature, as revealed by their ^1H, ^{13}C, and ^{31}P NMR spectra, which are otherwise similar to those of the compounds **3** described so far for which only one diastereoisomeric, *P**,*P** propeller-like cage has been characterized. In contrast to what was observed in triphosphazides **6**, in tri-λ^5-triphosphazenes **7** the anisochrony of the methylene CH_2P protons is considerable, $\Delta\delta$=0.21–0.22, but to a lesser degree than in compounds **3**, $\Delta\delta$=0.70. Thus, we can attribute to **7** the propeller-like conformation of their lower tris(phosphane) fragments, but the helicity seems to be quite less pronounced than in compounds **3** bearing a methyl group at the pivotal carbon. At this point, it should be noted that on passing from triphosphazides **2** and **6** to triphosphazenes **3** and **7** the macrobicycles become more rigid in conformational terms, as a consequence of the smaller size of their rings, the smaller inner cavity, and the absence of flexible PN_3 functions. A new element entered into this conformational playfield when an X-ray structure determination of **7b** showed that two different diastereoisomers, **A** and **B**, are equally present in the unit cell of the crystals[9] (Fig. 4), *which only differ notably in the helical sense of the lower propeller-shaped fragment*. In the *P**,*P** diastereoisomer **A** the helical sense of the upper and lower propellers is the same (as viewed from any extreme of the C_3 axis) whereas in **B** (*P**,*M**) both have different helical senses.

Another relevant difference between structures **A** and **B** is that the P═N double bonds and the aryl groups linked to their nitrogen atoms are nearly coplanar in diastereoisomer **A** but much less in diastereoisomer **B**, as reflected by the torsion (τ) angles of the C1–C2–N–P fragments (averaged for the three branches): τ_m(**A**)=4.20° versus τ_m(**B**)=17.83°. Semiempirical MNDO calculations[10] of the relative energies of both diastereoisomers of the less substituted triphosphazene **7a** gave a result that its diastereoisomer **A** is 12.43 kcal mol^{-1} more stable than **B**. This result suggests that the delocalization of the partial negative charge at the nitrogen atom of the P═N bonds (P^+–N^- canonical forms) over the *N*-phenyl groups should contribute notably to the stability of these species. Such delocalization must be greater in diastereoisomer **A** than in **B** as in the former the P═N and *N*-phenyl groups are nearly coplanar.

The fact that **7b** exhibits two diastereoisomeric forms in the solid state while only one is apparently observed in $CDCl_3$ solution at room temperature poses the question of which is the species observed in solution, either one of these two diastereoisomers, both but they did not differ in NMR data

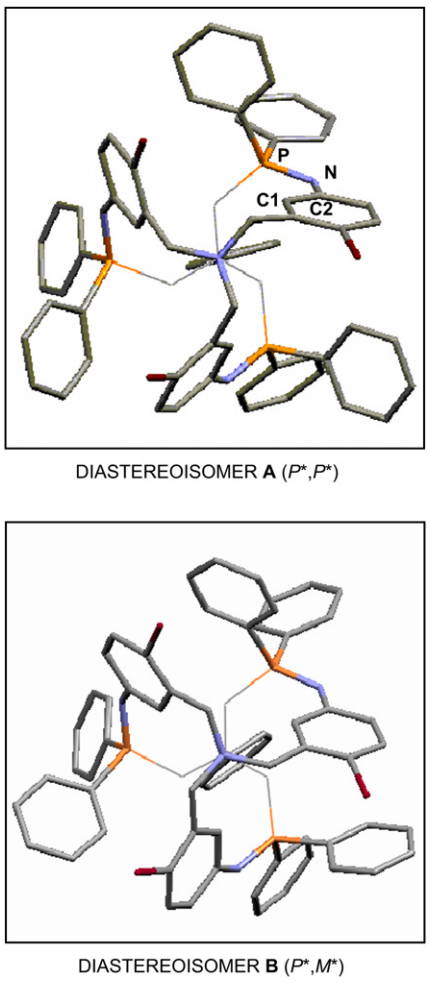


Figure 4. Molecular structure of the two diastereoisomers **A** and **B** of tri-λ^5-phosphazene **7b** in the crystals, as viewed approximately along their respective C_3 axes.

(highly improbable), or the mean conformation resulting from a conformational equilibrium between both? Low temperature VT-NMR experiments in CD_2Cl_2 from 25 to −70 °C showed no splitting of the signals in the ^1H and ^{31}P NMR spectra of **7a**,**b**, so if a conformational equilibrium is occurring it should involve quite low energy barriers. High temperature ^1H VT-NMR experiments (*o*-$Cl_2C_6D_4$, 25–120 °C) showed the simultaneous coalescence of the methylene CH_2P and CH_2N protons of **7b** at 80 °C indicating that the cage is no longer propeller-shaped as a result of an equilibration process with a calculated barrier[11] of 17.53 kcal mol^{-1}. This value is lower than that calculated[1d] in a similar way for a triphosphazene type **3**, which was 20.8 kcal mol^{-1}. This set of data is understandable by assuming that the two diastereoisomers in the crystal, **A** and **B**, quickly equilibrate in solution to a species with its lower fragment presenting a conformation, which is slightly propeller-shaped between −70 and 75 °C and which, attending to the semiempirical calculations, should be of *P**,*P** relative configuration. This conformational equilibrium must involve low energy barriers as the crystal packing forces operating in the crystallization process allow both diastereoisomers to be present in the solid state. The flexibility of the lower tripodal fragment renders triphosphazenes **7** more conformationally labile than their analogous **3** bearing

a pivotal methyl group. This is a consequence of the more sterically demanding nature of the pivotal phenyl group present in **7**, which is the origin of these differences, and also probably the absence of the stabilizing CH···π interactions present when the pivotal group is methyl.[1b,d]

To the best of our knowledge, the presence of these two diastereoisomers in the solid state is totally unusual in related macrobicycles and cryptands reported in the literature, where a cage formed by two propeller units most usually showed the same sense of twist of both.[12] The observation, for the first time in our macrobicycles, of a species with its two propellers in opposite sense of twist makes worthy of study the conformational effects that can be originated by introducing at the pivotal carbon atom substituents other than methyl and phenyl (the only ones checked up to now) such as H, Et, ^{i}Pr, and ^{t}Bu. We are currently engaged in such investigations whose results will be disclosed in due course.

3. Conclusions

Tripod–tripod coupling of triphosphane $PhC(CH_2PPh_2)_3$ with two different tris(*m*-azidobenzyl)amines gave rise to the corresponding chiral macrobicyclic triphosphazides, which by triple dinitrogen extrusion were converted into tri-λ^5-phosphazenes. The structure of these cage-compounds consists of two propellers linked by three P═N units. The presence of the phenyl group at the pivotal carbon causes a loss of helicity in the lower propeller, and two diastereoisomeric bis(propellers) of one triphosphazene (*P**,*P** and *P**,*M**) have been characterized in the solid state. This represents the first observation of a *P**,*M** relative configuration in this kind of macrobicyclic bis(propellers).

4. Experimental

4.1. General method

The self-assembly 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 Brucker 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. Abbreviations of coupling patterns are as follows: s, singlet; d, doublet; t, triplet; q, quadruplet. Other abbreviations: *q*, quaternary carbon. 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

Tris(*m*-azidobenzyl)amines **5a** and **5b** were prepared following previously reported procedures.[1e]

4.2.1. α,α,α-Tris(diphenylphosphinomethyl)toluene (4). A solution of 2-hydroxymethyl-2-phenylpropane-1,3-diol (2.46 g, 13.5 mmol) in pyridine (3 ml) and neat thionyl chloride (5.06 g, 42.6 mmol) were simultaneously added in 1 h to a cold (0–5 °C) round-bottom flask containing pyridine (2 ml), immersed in an ice-water bath. After the addition was completed, the resulting mixture was stirred for 1 h allowing it to reach room temperature. After that, the reaction mixture was heated at 50 °C for 1 h and then at 115 °C for 3 h. The cooled mixture was poured onto crushed ice (25 g), stirred, and extracted with dichloromethane (3×25 ml). The combined organic extracts were washed with a saturated aqueous solution of sodium bisulfite, dried over anhydrous Na_2SO_4, filtered, and the solvents evaporated under reduced pressure. The crude trichloride so obtained was purified by elution in a column through a pad of silica gel (20 g) with a mixture of CH_2Cl_2/*n*-hexane 1:1 (v/v) as eluent. The 1,3-dichloro-2-chloromethyl-2-phenylpropane (1.95 g, 61%; mp 114–116 °C; yellow prisms, from $CHCl_3$) thus obtained showed to be pure by ^{1}H NMR [300 MHz, $CDCl_3$, δ=4.02 (s, 6H), 7.35 (m, 5H)] and ^{13}C NMR [75.4 MHz, $CDCl_3$, δ=47.42 (*C*H$_2$), 49.10 (*C*Ph), 126.56, 127.92, 128.73, 137.70] and was used as such in the next step.

Diphenylphosphane (0.61 g, 3.3 mmol) was added by syringe, under N_2 atmosphere, to a suspension of KO^{t}Bu (0.45 g, 4.0 mmol) in dry THF (5 ml). The resulting mixture is stirred for 15 min at room temperature and then a solution of 1,3-dichloro-2-chloromethyl-2-phenylpropane (0.24 g, 1.0 mmol) in the same solvent (2 ml) is added. The reaction mixture is refluxed for 16 h with stirring, and then left to cool at room temperature. Water (15 ml) is then added slowly at the same temperature. The resulting solution is extracted with dichloromethane and the combined extracts were dried over anhydrous Na_2SO_4, filtered, and the volatiles eliminated under reduced pressure. The crude tris(phosphane) was purified by a short column chromatography by using Et_2O/*n*-hexane 5:95 (v/v) as eluent to give pure α,α,α-tris(diphenylphosphinomethyl)toluene (**4**) (0.52 g, 76% yield). An analytically pure sample was obtained by crystallization from $CHCl_3$/*n*-pentane as colorless prisms, mp 74–76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.14 (br s, 6H, C*H*$_2$), 6.71 (t, *J*(H,H)=7.6 Hz, 2H; *H*$_3$), 6.80 (t, *J*(H,H)=7.6 Hz, 1H; *H*$_4$), 7.01 (d, *J*(H,H)=7.6 Hz, 2H; *H*$_2$), 7.15 (m, 18H, *Ph*$_2$P), 7.26 (m, 12H, *Ph*$_2$P); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=41.39 (m, *C*H$_2$P), 44.65 (q, ^{2}*J*(C,P)=16.2 Hz; *C*Ph), 126.01 (*C*$_4$), 127.27 (*C*$_2$/*C*$_3$), 127.53 (*C*$_3$/*C*$_2$), 127.95–128.15 (m, *C*$_m$+*C*$_p$), 133.19 (d, ^{2}*J*(C,P)=20.9 Hz; *C*$_o$), 139.28 (d, ^{1}*J*(C,P)=11.2 Hz; *C*$_i$), 143.66 (*C*$_1$); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=−24.65 (s); IR (Nujol): ν=3075, 1498, 1443, 1388, 1030, 1002, 651 cm^{-1}; MS (EI): *m*/*z* (%) 686 (4) [M$^+$], 609 (71) [M$^+$−77], 501 (26), 424 (55), 409 (41), 379 (27), 315 (43), 293 (26), 199 (46), 185 (100), 121 (79), 91 (66); $C_{46}H_{41}P_3$ (686.74): calcd C 80.45, H 6.02; found C 80.32, H 6.13.

4.3. General procedure for the preparation of the triphosphazides 6

Two solutions of the corresponding tris(*m*-azidobenzyl)amine **5a** or **5b** (1.5 mmol) in diethyl ether (10 ml) and the corresponding tris(phosphane) **4** in the same solvent (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.

4.3.1. Triphosphazide 6a. Yield: 49%; mp>350 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.49 (d, J(H,H)=14.3 Hz, 3H; CH_AH$_B$N), 3.86 (d, J(H,H)=14.3 Hz, 3H; CH$_A$$H_B$N), 4.17 (pseudot, J(H,H),(H,P)=14.8 Hz, 3H; CH_AH$_B$P), 4.22 (m, 3H; CH$_A$$H_B$P), 5.83 (t, J(H,H)=6.9 Hz, 2H; H$_{arom}$), 6.16 (t, J(H,H)=7.2 Hz, 1H; H$_{arom}$), 6.66 (d, J(H,H)=7.4 Hz, 2H; H$_{arom}$), 6.92–6.95 (m, 9H; H$_{arom}$), 7.11–7.13 (m, 9H; H$_{arom}$), 7.23–7.26 (m, 6H; H$_{arom}$), 7.43 (t, J(H,H)=9.0 Hz, 6H; H$_{arom}$), 7.53 (d, J(H,H)=7.4 Hz, 3H; H$_{arom}$), 7.66 (d, J(H,H)=9.2 Hz, 6H; H$_{arom}$), 8.11 (br s, 3H; H$_{arom}$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=40.24 (m; CH_2P), 48.81 (q, ^2J(C,P)=3.9 Hz; Ph*C*), 57.33 (CH_2N), 118.80 (br s), 119.20 (br s), 125.72, 126.26, 126.63, 128.24 (d, ^3J(C,P)=12.2 Hz; *m*C–PhP), 128.39, 128.49, 128.61 (d, ^1J(C,P)=81.3 Hz; *i*C–PhP), 128.67 (d, ^3J(C,P)=11.6 Hz; *m*C–PhP), 130.89 (d, ^1J(C,P)=83.5 Hz; *i*C–PhP), 131.40 (d, ^2J(C,P)=9.3 Hz; *o*C–PhP), 131.45 (br s; *p*C–PhP), 131.57 (br s; *p*C–PhP), 132.87 (d, ^2J(C,P)=7.5 Hz; *o*C–PhP), 135.00 (*q*), 141.30 (*q*), 150.50 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=8.60 (br s, $\Delta\nu_{1/2}$=1105 Hz); IR (Nujol): ν=1462 (CP), 1112 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%) 1098 (19) [M$^+$+1], 700 (100); $C_{67}H_{59}N_{10}P_3$ (1097.17): calcd C 73.34, H 5.42, N 12.77; found C 73.20, H 5.27, N 12.64.

4.3.2. Triphosphazide 6b. Yield: 50%; mp 279–281 °C (yellow prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, CD_2Cl_2): δ=3.76 (d, J(H,H)=16.5 Hz, 3H; CH_AH$_B$N), 4.00 (d, J(H,H)=16.5 Hz, 3H; CH$_A$$H_B$N), 4.16 (br d, J(H,H)=12.3 Hz, 6H; CH_2P), 5.84 (t, J(H,H)=7.6 Hz, 2H; H$_{arom}$), 6.18 (t, J(H,H)=7.6 Hz, 1H; H$_{arom}$), 6.69 (d, J(H,H)=8.1 Hz, 2H; H$_{arom}$), 6.93–6.97 (m, 6H; H$_{arom}$), 7.14–7.31 (m, 18H; H$_{arom}$), 7.45 (dd, J(H,H)=8.4, 1.7 Hz, 3H; H$_{arom}$), 7.54 (d, J(H,H)=8.4 Hz, 3H; H$_{arom}$), 7.61–7.66 (m, 6H; H$_{arom}$), 8.23 (br s, 3H; H$_{arom}$); ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ=40.57 (m; CH_2P), 49.32 (q, ^2J(C,P)=4.2 Hz; Ph*C*), 58.52 (CH_2N), 119.90 (br s), 120.10 (*q*), 120.15 (br s), 126.76, 127.27, 127.78 (d, ^1J(C,P)=96.2 Hz; *i*C–PhP), 128.76 (d, ^3J(C,P)=11.6 Hz; *m*C–PhP), 128.84, 129.16 (d, ^3J(C,P)=12.2 Hz; *m*C–PhP), 129.81 (d, ^1J(C,P)=82.4 Hz; *i*C–PhP), 131.51 (d, ^2J(C,P)=8.7 Hz; *o*C–PhP), 131.89 (br s; *p*C–PhP), 131.02 (br s; *p*C–PhP), 133.09 (d, ^2J(C,P)=7.5 Hz; *o*C–PhP), 133.64, 134.59 (*q*), 139.85 (*q*), 149.91 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2): δ=7.50 (br s, $\Delta\nu_{1/2}$=639 Hz); IR (Nujol): ν=1465 (CP), 1105 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%) 1334 (6) [M$^+$+4], 1332 (9) [M$^+$+2], 1330 (4) [M$^+$], 700 (47), 154 (100); $C_{67}H_{56}Br_3N_{10}P_3$ (1333.86): calcd C 60.33, H 4.23, N 10.50; found C 60.25, H 4.11, N 10.55.

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

A solution of the corresponding triphosphazide **6** (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.

4.4.1. Tri-λ^5-phosphazene 7a. Yield: 62%; mp (decomp.) 277–279 °C (colorless prisms from chloroform/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.89 (d, J(H,H)=12.0 Hz, 3H; CH_AH$_B$N), 3.48 (d, J(H,H)=12.0 Hz, 3H; CH$_A$$H_B$N), 4.05 (pseudoquint, J(H,H),(H,P)=7.5 Hz, 3H; CH_AH$_B$P), 4.26 (pseudot, J(H,H),(H,P)=15.0 Hz, 3H; CH$_A$$H_B$P), 5.77 (t, J(H,H)=8.0 Hz, 2H; H$_{arom}$), 6.17 (d, J(H,H)=8.0 Hz, 2H; H$_{arom}$), 6.19 (t, J(H,H)=6.0 Hz, 1H; H$_{arom}$), 6.44–6.48 (m, 6H; H$_{arom}$), 7.05–7.16 (m, 15H; H$_{arom}$), 7.26–7.37 (m, 9H; H$_{arom}$), 7.50–7.63 (m, 12H; H$_{arom}$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ=37.66 (ddd, ^1J(C,P)=46.4 Hz, ^3J(C,P)=8.8, 7.6 Hz; CH_2P), 47.47 (q, ^2J(C,P)=4.6 Hz; CPh), 57.86 (CH_2N), 118.48, 122.77 (d, ^3J(C,P)=12.8 Hz; *s-cis-C*H=C–N=P), 125.46, 125.60 (d, ^3J(C,P)=27.8 Hz; *s-trans-C*H=C–N=P), 126.12, 127.42, 128.14 (d, ^4J(C,P)=4.1 Hz), 128.76 (d, ^3J(C,P)=10.4 Hz; *m*C–PhP), 130.91 (br s; *p*C–PhP), 130.98 (d, ^1J(C,P)=91.0 Hz; *i*C–PhP), 131.52 (d, ^2J(C,P)=8.1 Hz; *o*C–PhP), 131.68 (br s; *p*C–PhP), 131.85 (d, ^1J(C,P)=87.2 Hz; *i*C–PhP), 131.92 (d, ^2J(C,P)=9.5 Hz; *o*C–PhP), 139.20 (*q*), 141.76 (*q*), 151.13 (*q*); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=4.32; IR (Nujol): ν=1446 (CP), 1110 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%)=1036 (18) [M$^+$+Na], 1014 (62) [M$^+$+1], 1013 (100) [M$^+$]; $C_{67}H_{59}N_4P_3$ (1013.13): calcd C 79.43, H 5.87, N 5.53; found C 79.30, H 5.92, N 5.66.

4.4.2. Tri-λ^5-phosphazene 7b. Yield: 87%; mp (decomp.) 291–293 °C (colorless prisms from dichloromethane/diethyl ether); ^{1}H NMR (300 MHz, CD_2Cl_2): δ=3.37 (d, J(H,H)=14.2 Hz, 3H; CH_AH$_B$N), 3.47 (d, J(H,H)=14.2 Hz, 3H; CH$_A$$H_B$N), 4.01 (pseudoquint, J(H,H),(H,P)=7.7 Hz, 3H; CH_AH$_B$P), 4.23 (pseudot, J(H,H),(H,P)=15.1 Hz, 3H; CH$_A$$H_B$P), 5.84 (t, J(H,H)=8.4 Hz, 2H; H$_{arom}$), 6.18 (d, J(H,H)=7.9 Hz, 2H; H$_{arom}$), 6.26 (t, J(H,H)=7.5 Hz, 1H; H$_{arom}$), 6.71 (t, J(H,H)=2.6 Hz, 3H; H$_{arom}$), 6.98 (dd, J(H,H)=8.7, 2.9 Hz, 3H; H$_{arom}$), 7.15 (dt, J(H,H)=7.3, 3.5 Hz, 6H; H$_{arom}$), 7.24–7.29 (m, 12H; H$_{arom}$), 7.37–7.45 (m, 9H; H$_{arom}$), 7.59–7.66 (m, 6H; H$_{arom}$); ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ=39.03 (ddd, ^1J(C,P)=46.1 Hz, ^3J(C,P)=11.2, 4.1 Hz; CH_2P), 47.95 (br s; Ph*C*), 56.94 (CH_2N), 111.40 (*q*), 123.35 (d, ^3J(C,P)=11.6 Hz; *s-cis-C*H=C–N=P), 126.11, 126.66, 127.44 (d, ^3J(C,P)=27.3 Hz), 127.55, 128.58 (d, ^3J(C,P)=12.8 Hz; *m*C–PhP), 129.18 (d, ^3J(C,P)=10.4 Hz; *m*C–PhP), 130.66 (d, ^1J(C,P)=65.5 Hz; *i*C–PhP), 131.36 (d, ^2J(C,P)=8.7 Hz; *o*C–PhP), 131.48 (br s; *p*C–PhP), 131.67 (br s; *p*C–PhP), 132.04 (d, ^2J(C,P)=9.3 Hz; *o*C–PhP), 133.12 (d, ^4J(C,P)=2.9 Hz), 139.34 (*q*), 139.50 (*q*), 151.32 (*q*), the resonance of one *i*C–PhP was not observed; ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ=3.91; IR (Nujol): ν=1457 (CP), 1105 (NP) cm^{-1}; MS (FAB$^+$): *m*/*z* (%)=1250 (89) [M$^+$+4], 1248 (100) [M$^+$+2], 1246 (25) [M$^+$]; $C_{67}H_{56}Br_3N_4P_3$ (1249.82): calcd C 64.39, H 4.52, N 4.48; found C 64.27, H 4.65, N 4.53.

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7. 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.
8. 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 three-fold axis from the side of the tribenzylamine fragment.
9. X-ray crystal data for **7b**·$3CH_2Cl_2$: $C_{70}H_{62}Br_3Cl_6N_4P_3$, M=1504.58, colorless block, $0.30\times0.20\times0.20$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), a=24.8734(14), b=23.4692(16), c=23.6959(12) Å, β=108.255(3)°, V=13,136.5(13) Å^3, Z=8, D_c=1.522 g/cm^3, F_{000}=6096, KappaCCD, Mo Kα radiation, λ=0.71073 Å, T=200(2) K, $2\theta_{max}$=50.0°, 43,196 reflections collected, 19,345 unique (R_{int}=0.1164). Final *GooF*=1.023, $R1$=0.1055, $wR2$=0.2010, R indices based on 10,772 reflections with $I>2$sigma(I) (refinement on F^2), 1441 parameters, 936 restraints. Lp and absorption corrections applied, μ=2.206 mm^{-1}. Detailed X-ray crystallographic data can be obtained, free of charge, on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK or via www.ccdc.cam.ac.uk/data_request/cif. (CCDC No. 613199).
10. Semiempirical calculations were carried out using the MNDO method as implemented in the Gaussian 98 set of programs. The geometries of both stationary points were optimized, and harmonic frequency calculations were performed in order to characterize both structures as minima.
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