Molecular Modeling, a Tool for Predicting Structural Effects on the Macrocyclization Reaction between Bis(vinyl or allyl) Dialdehydes and Thiophosphonic Bis(hydrazides)

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The reaction of new phosphorus dialdehydes PhP(O)-$[(CH_2)_nCH{=}CHC_6H_4CHO]_2$ (**4a–c**, **5a**) (n = 0:**4**, n = 1:**5**; **a**:*para*, **b**:*meta*, **c**:*ortho*), with thiophosphonic bis(hydrazide) $PhP(S)[NMeNH_2]_2$ (**6**) yields macrocyclic compounds **9b′**, **c′**, **10a′**, **9a″**, **b″**, **c″**, **10a″** and **9c‴**, arising from the cyclocondensation of one, two, or three equivalents of each reagent, respectively. Molecular modeling of **4a–c**, **5a**, **6** and of the intermediate monocondensation products **7a–c**, **8a** was carried out and points out the importance of the geometry of the starting reagents in the competition between inter- and intramolecular cyclocodensation.

Studies of the synthesis of organic macrocycles from acyclic precursors started in the sixties and gave rise to the enormous development of supramolecular chemistry[1]. However, the factors which influence the macrocyclization processes have not been intensively studied, and a theoretical treatment of the irreversible formation of macrocycles under kinetic control has been reported only recently[2].

We have already described the synthesis of numerous phosphorus containing macrocycles obtained by cyclocondensation reactions of phosphonic bis(hydrazides) $RP(X)[NMeNH_2]_2$ (X = O, S) with dialdehydes[3]. In all cases, we observed the condensation of two equivalents of each reagent which led to the irreversible formation of [2 + 2] cyclocondensation products. However, some [1 + 1][3c,g,i,j,l,q], [3 + 3][3c,i,o,q], and [4 + 4][3o,q] cycloadducts were also isolated. In order to determine the factors which govern the competition between intra- and intermolecular processes ([1 + 1] and [2 + 2] cyclocondensations) in our cyclocondensation reaction, we decided to study the role played by geometry from a qualitative point of view. For this purpose, we synthesized new difunctionalized precursors, the bis(formylstyryl)phenylphosphane oxides $PhP(O)[CH{=}CHC_6H_4CHO$-*p*, -*m*, -*o*$]_2$ (**4a–c**) and bis(*p*-formylcinnamyl)phenylphosphane oxide $PhP(O)[CH_2CH{=}CHC_6H_4CHO$-*p*$]_2$ (**5a**). The presence of aldehyde functions in *para*, *meta*, or *ortho* position on the aromatic ring would lead to different types of cyclocondensations and give phosphorus macrocycles with the α-P-allylic system[4] or the previously unknown α-P-vinylic system. The type and amount of macrocycles obtained in each case by reaction with phosphonic bis(hydrazide) were determined by Fast Atom Bombardment Mass Spectrometry (FAB MS) and tentatively explained by molecular modeling of the phosphonic bis(hydrazide) **6**, the dialdehydes **4a–c**, **5a**, and the monocondensation products **7a–c**, **8a**.

Results and Discussion

The dialdehydes **4a–c** and **5a** were synthesized by condensation of phenyldivinylphosphane oxide (**1**) or diallyl(phenyl)phosphane oxide (**2**) with two equivalents of bromobenzaldehyde in the presence of triethylamine with palladium acetate/tris(*o*-tolylphosphane) as a catalyst (Scheme). Purification by column chromatography allows the dialdehydes to be isolated in moderate to good yields (35–72%). The high value obtained for the $^3J_{HH}$ coupling constant of the vinylic systems (ca. 17.4 Hz) indicates a *trans* configuration in each case.

The reaction of dialdehydes **4a–c**, **5a** with the thiophosphonic bis(hydrazide) $PhP(S)[NMeNH_2]_2$ (**6**) proceeds smoothly at room temperature for 2 h to 12 d, depending on the dialdehyde used. The reaction was monitored by ^{31}P-NMR spectroscopy, which indicates the disappearance of the signal corresponding to **6** (δ = 84) due to the formation of the intermediates **7a–c**, **8a** [δ(P=S) = 81] from which finally macrocyclic products arise [δ(P=S) = 79] (Scheme). The ^{31}P-NMR spectra of the crude reaction products indicate in all cases, excepted for **4a**, the formation of several species. Traces of the intermediates **7a–c**, **8a** were eliminated by washing with methanol. However, all attempts to

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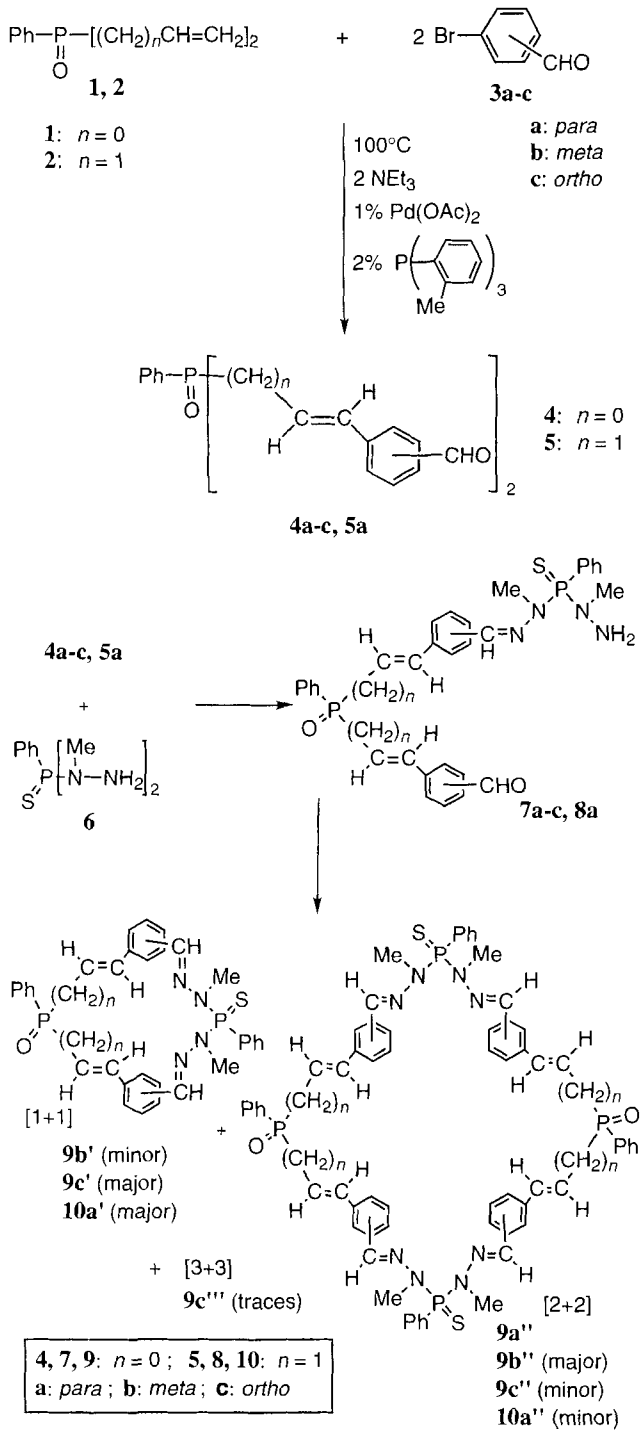


separate the different types of macrocycles by washing or by column chromatography failed. Studies of these mixtures by FAB MS showed that only bis(*p*-formylstyryl)phenylphosphane oxide (**4a**) gives a single compound, the [2 + 2] cyclocondensation product **9a**''. With the aldehyde functions in *meta* position (**4b**) the main reaction product is again a tetraphosphorus macrocycle, **9b**'', but the [1 + 1] cycloadduct **9b**' is also obtained as the minor product. The compound with aldehyde functions in *ortho* position (**4c**) behaves differently since the major product is the [1 + 1] cycloadduct **9c**' and the minor product the [2 + 2] cycloadduct **9c**''; a small amount of a [3 + 3] cyclocondensation product was also obtained. Unexpectedly, the allyl compound with aldehyde functions in *para* position (**5a**) does not behave like the corresponding vinyl compound **4a**: in this case, the major product is not the [2 + 2] but the [1 + 1] cycloadduct (Table 1).

Table 1. Relative amount of [1 + 1], [2 + 2], and [3 + 3] cyclocondensation products measured by FAB MS

Comp.	[1+1]	[2+2]	[3+3]
9a	0	100	0
9b	35	100	0
9c	100	38	8
10a	100	25	0

In order to explain such a different behavior, we decided to study the dialdehydes **4a–c**, **5a** and the bis(hydrazide) **6** by molecular modeling (MM2 parameters, CAChe™ system). The lowest-energy conformers of these compounds [with the carbon-hydrogen backbone in black and the other atoms (N, O, P, S) in grey], are depicted on Figure 1. The C···C distance between the aldehyde groups of **4a–c**, **5a** and the N···N distance between the NH_2 *groups of* ***6*** *for* these lowest-energy conformers are compiled in Table 2, together with the corresponding maximum and minimum distances. However, it must be noticed that the latter are simply obtained by rotation around single bonds and do not take into account the value of the energy of the corresponding conformers.

Figure 1. Molecular modeling of compounds **4a–c**, **5a** and **6**

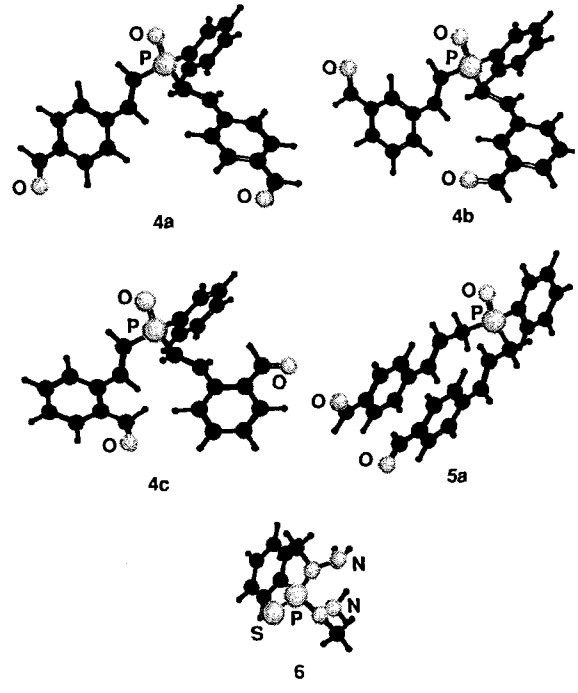


Table 2 allows some conclusions to be drawn concerning the type of cyclocondensation expected for dialdehydes **4a–c**, **5a**. First of all, it is obvious that bis(*p*-formylstyryl)-

phenylphosphane oxide (**4a**) is unable to undergo a [1 + 1] cyclocondensation; indeed, the lowest value for the CHO···CHO distance (11 Å) is much larger than the highest $NH_2 \cdots NH_2$ value for **6** (5 Å). Furthermore, since the longest and shortest CHO···CHO distances for **4a** are not extremely different, one may expect only one type of cyclocondensation, presumably [2 + 2] cyclocondensation reactions; this is in agreement with experiment. For dialdehyde **4b**, most of the CHO···CHO distances lie in the same range as for **4a** so that mainly [2 + 2] cyclocondensations are expected; [1 + 1] cyclocondensations are less likely, but could be possible. For dialdehyde **4c**, the shortest CHO···CHO distance (3 Å) will unambiguously lead to a [1 + 1] cyclocondensation product, presumably the major compound, but [2 + 2] cyclocondensation is also expected, according to the highest value (10 Å). For dialdehyde **5a** (aldehyde functions in *para* position) one would expect the same results as for **4a**. However, molecular modeling shows a very different behavior which was not obvious from examination of Dreiding models. The stacking effect observed for the aromatic groups of **5a** brings the aldehyde groups closer to each other. Thus the CHO···CHO distance for the lowest-energy conformer (3.4 Å) perfectly fits in with the $NH_2 \cdots NH_2$ distance (3.0 Å) of the thiophosphonic bis(hydrazide) **6**. Consequently, the major compound is supposed to arise from [1 + 1] cyclocondensation, even if the longest CHO···CHO distance for **5a** (18 Å) could lead to a [3 + 3] cyclocondensation or an oligomerization.

Table 2. Calculated CHO···CHO and $NH_2 \cdots NH_2$ distances d [Å] for compounds **4a–c**, **5a**, **6**

	$d_{CHO \cdots CHO}$					$d_{NH_2 \cdots NH_2}$				
	d_{mini}		$d_{conformer\ of\ Figure\ 1}$		d_{maxi}	d_{mini}		$d_{conformer\ of\ Figure\ 1}$		d_{maxi}
4a	11	<	12.9	<	15	-		-		-
4b	8	<	11.1	<	14	-		-		-
4c	3	<	7.7	<	10	-		-		-
5a	2	<	3.4	<	18	-		-		-
6	-		-		-	2	<	3.0	<	5

The type of cyclocondensation which can be deduced from molecular modeling of dialdehydes **4a**, **b** perfectly fits in with reality. However, for dialdehydes **4c** and **5a**, the type and amount of each type of cyclocondensation are not entirely predictable. Thus, in order to confirm our results we decided to study the key intermediates **7a–c**, **8a** by molecular modeling also. In fact, four stereoisomers are expected for each compound due to the presence of two chiral phosphorus atoms. The lowest-energy conformers of the (*r*,*r*), (*r*,*s*), (*s*,*r*), and (*s*,*s*)[5] stereoisomers of compounds **7a**, **7b**, **7c**, and **8a** are depicted in Figures 2, 3, 4, and 5, respectively. Figure 2 confirms that it is impossible to realize an intramolecular condensation of the intermediate **7a** due to a long CHO···NH_2 distance. Figure 3 shows that, for some conformers of **7b**, the CHO···NH_2 distance is short and would lead to intramolecular condensation, whereas for other conformers, as long CHO...NH_2 distance implies an intermolecular condensation. The compactness of most of the conformers of **7c** confirms that the [1 + 1] cyclocondensation proceeds readily (Figure 4). The same behavior is observed for **8a**; in this case, the stacking effect of the aro-

Figure 2. Molecular modeling of (*r*-P=O, *r*-P=S), (*r*-P=O, *s*-P=S), (*s*-P=O, *r*-P=S), and (*s*-P=O, *s*-P=S) diastereoisomers of compound **7a**

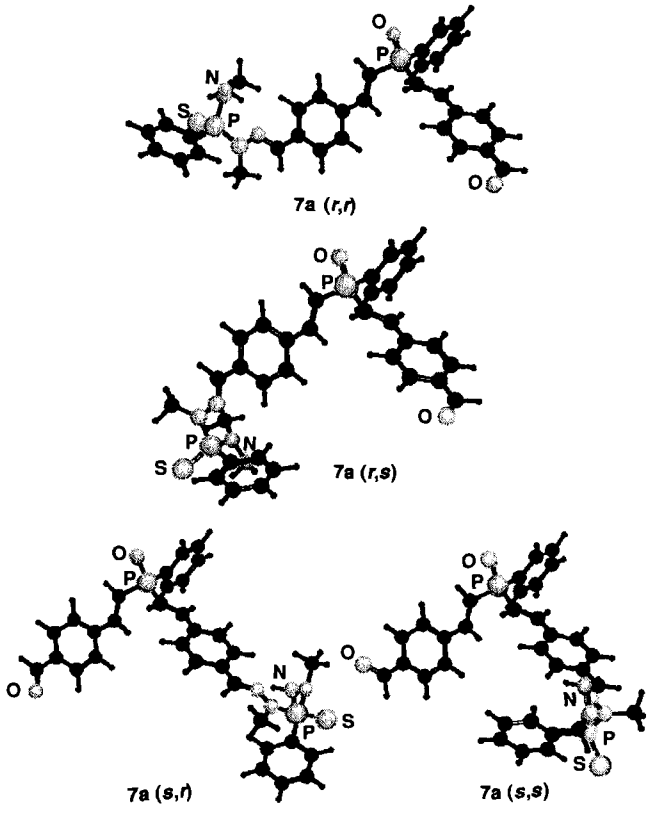


Figure 3. Molecular modeling of (*r*-P=O, *r*-P=S), (*r*-P=O, *s*-P=S), (*s*-P=O, *r*-P=S), and (*s*-P=O, *s*-P=S) diastereoisomers of compound **7b**

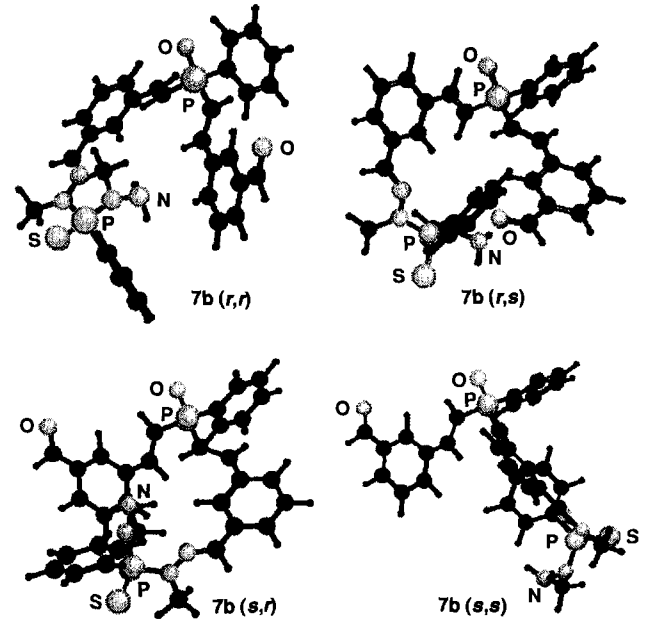


Figure 4. Molecular modeling of (*r*-P=O, *r*-P=S), (*r*-P=O, *s*-P=S), (*s*-P=O, *r*-P=S), and (*s*-P=O, *s*-P=S) diastereoisomers of compound **7c**

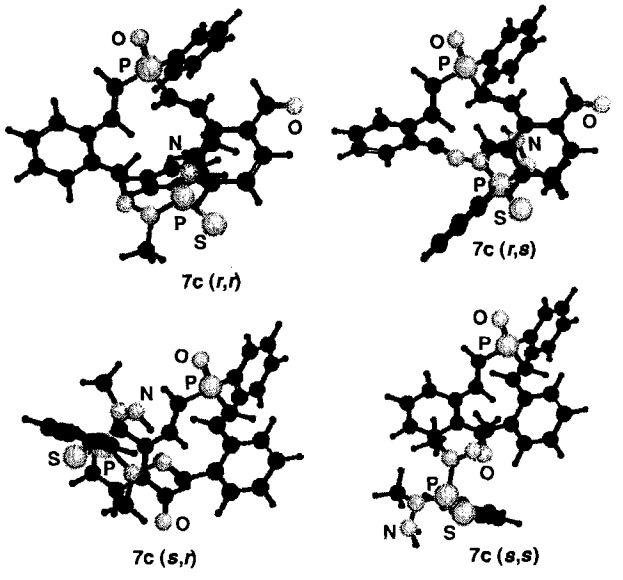
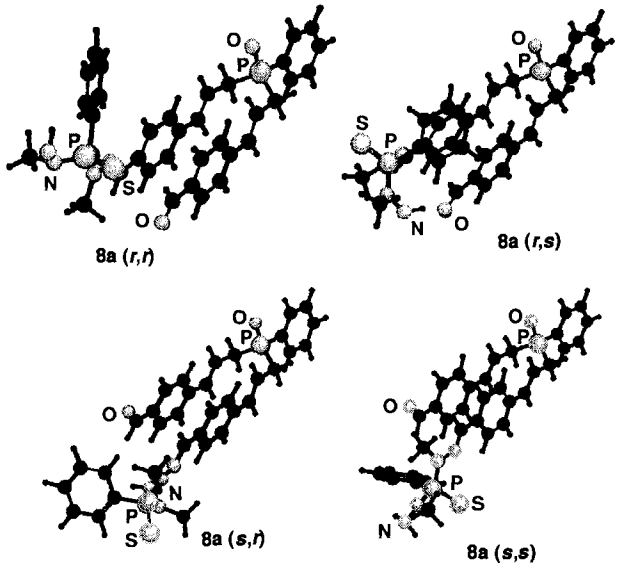


Figure 5. Molecular modeling of (*r*-P=O, *r*-P=S), (*r*-P=O, *s*-P=S), (*s*-P=O, *r*-P=S), and (*s*-P=O, *s*-P=S) diastereoisomers of compound **8a**



matic groups already noted for the dialdehyde **5a** favors the [1 + 1] cyclocondensation, and the competition between inter- and intramolecular condensation processes depends on the orientation of the free NH_2 group relative to the aldehyde function.

In conclusion, this study confirms the importance of the geometry of the starting reagents in the competition between inter- and intramolecular cyclocondensation processes and shows that the type of cyclocondensation experimentally observed can be fairly well predicted by molecular modeling.

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Experimental

All manipulations were carried out in high vacuo or under dry argon. – ^1H, ^{31}P, and ^{13}C NMR: Bruker AC 80 and AC 200. ^{31}P-NMR chemicals shifts are reported relative to 85% H_3PO_4. – MS (EI or FAB): Finnigan Mat 95.

General Procedure for the Synthesis of the Dialdehydes **4a–c** *and* **5a**: Divinylphenylphosphane oxide (**1**) (700 mg, 3.93 mmol) or diallylphenylphosphane oxide (**2**) (810 mg, 3.93 mmol), bromobenzaldehyde **3a**, **3b**, or **3c** (1454 mg, 7.86 mmol), triethylamine (1.095 ml, 7.86 mmol), palladium acetate (18 mg, 0.08 mmol), and tris(*o*-tolyl)phosphane (48 mg, 0.158 mmol) in acetonitrile (5 ml) are heated at 100°C under Ar in a tube sealed with a Rotaflo stopcock. The course of the reaction is monitored by TLC. After heating for 22 h (**4a**, **c** and **5a**) or 36 h (**4b**), the solvent is evaporated, the residue is dissolved in chloroform, the solution washed with water and the aqueous layer extracted several times with a small amount of chloroform. The combined organic layers are dried with magnesium sulfate, and the solvent is evaporated.

Bis(p-formylstyryl)phenylphosphane Oxide (**4a**) is purified by column chromatography on silica gel with tetrachloromethane/acetone (3:1). It is isolated as a white powder (yield 1.092 g, 72%) which can be recrystallized from benzene/acetone. M.p. 172–174°C. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.63. – ^1H NMR ($CDCl_3$): δ = 6.87 (dd, $^3J_{HH}$ = 17.43, $^2J_{HP}$ = 22.42 Hz, 2H, PCH=), 7.51–7.86 (m, 7H, C_6H_5 and PCH=C*H*), 7.69 (d, $^3J_{HH}$ = 8.24 Hz, 4H, C_6H_4), 7.90 (d, $^3J_{HH}$ = 8.24 Hz, 4H, C_6H_4), 10.03 (s, 2H, CHO). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 122.8 (d, $^1J_{CP}$ = 103.4 Hz, PCH=), 128.0 (s), 128.7 (d, J_{CP} = 12.3 Hz), 129.9 (s), 130.5 (d, J_{CP} = 9.7 Hz), 131.9 (d, $^1J_{CP}$ = 108.6 Hz, *i*-C_6H_5), 132.1 (s), 136.8 (s), 140.3 (d, J_{CP} = 17.9 Hz), 145.2 (d, J_{CP} = 2.8 Hz), 191.2 (s, CHO). – MS (70 eV), *m/z*: 386 [M^+]. – $C_{24}H_{19}PO_3$ (386.4): calcd. C 74.60, H 4.96, P 8.02; found C 74.41, H 5.02, P 7.87.

Bis(m-formylstyryl)phenylphosphane Oxide (**4b**) is purified by column chromatography on silica gel with ethyl acetate/acetone (400:1). It is isolated as a pale yellow oil (yield 728 mg, 48%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 21.02. – ^1H NMR ($CDCl_3$): δ = 6.85 (dd, $^3J_{HH}$ = 17.44, $^2J_{HP}$ = 22.18 Hz, 2H, PCH=), 7.50–7.90 (m, 13H, C_6H_5, C_6H_4, and PCH=C*H*), 8.05 (s, 2H, C_6H_4), 10.04 (s, 2H, CHO). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 121.5 (d, $^1J_{CP}$ = 104.5 Hz, PCH=), 127.9 (s), 128.9 (d, $^3J_{CP}$ = 12.4 Hz), 129.6 (s), 130.6 (d, $^2J_{CP}$ = 10.3 Hz), 131.1 (s), 132.2 (s), 133.5 (s), 136.0 (d, $^3J_{CP}$ = 17.8 Hz), 136.8 (s), 145.3 (d, $^2J_{CP}$ = 3.1 Hz), 191.6 (s, CHO). – MS (70 eV), *m/z*: 386 [M^+].

Bis(o-formylstyryl)phenylphosphane Oxide (**4c**) is purified by column chromatography on silica gel with ethyl acetate/acetone (400:1). It is isolated as a white powder (35% yield) which is recrystallized from benzene/acetone (5:1). M.p. 179.5–180.5°C. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 22.24. – ^1H NMR ($CDCl_3$): δ = 6.75 (dd, $^3J_{HH}$ = 17.47, $^2J_{HP}$ = 19.64 Hz, 2H, PCH=), 7.62–7.98 (m, 13H, C_6H_5 and C_6H_4), 8.29 (dd, $^3J_{HH}$ = 17.47, $^3J_{HP}$ = 19.89 Hz, 2H, PCH=C*H*), 10.27 (s, 2H, CHO). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 125.2 (d, $^1J_{CP}$ = 103.2 Hz, PCH=), 127.7 (s), 128.7 (d, $^3J_{CP}$ = 12.2 Hz), 129.6 (s), 130.9 (d, $^2J_{CP}$ = 10.1 Hz), 132.0 (s), 132.1 (s), 133.3 (s), 133.8 (s), 137.3 (d, $^3J_{CP}$ = 19.0 Hz), 144.0 (d, $^2J_{CP}$ = 5.4 Hz), 191.7 (s, CHO). – MS (15 eV), *m/z*: 386 [M^+]. – $C_{24}H_{19}PO_3$ (386.4): calcd. C 74.60, H 4.96, P 8.02; found C 74.45, H 5.05, P 7.93.

Bis(p-formylcinnamyl)phenylphosphane Oxide (**5a**) is purified by column chromatography on silica gel with tetrachloromethane/acetone (2:1). It is isolated as a pale yellow oil (yield 634 mg, 39%).

– $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 35.20. – ^1H NMR ($CDCl_3$): δ = 3.03–3.16 (m, 4H, CH_2), 6.19–6.59 (m, 4H, CH=), 7.42 (d, $^3J_{HH}$ = 8.19 Hz, 4H, C_6H_4), 7.47–7.76 (m, 5H, C_6H_5), 7.79 (d, $^3J_{HH}$ = 8.19 Hz, 4H, C_6H_4), 9.96 (s, 2H, CHO). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 35.0 (d, $^1J_{CP}$ = 64.6 Hz, CH_2), 122.2 (d, $^2J_{CP}$ = 9.5 Hz, PCH=), 126.3 (s), 128.5 (d, $^3J_{CP}$ = 11.5 Hz), 129.7 (s), 130.2 (d, $^2J_{CP}$ = 8.7 Hz), 131.9 (s), 134.1 (d, $^3J_{CP}$ = 11.9 Hz), 135.0 (s), 142.1 (s), 191.2 (s, CHO). – MS (15 eV), *m/z*: 414 [M^+].

General Procedure for the Synthesis of Macrocycles: A solution of thiophosphonic bis(hydrazide) **6** (120 mg, 0.52 mmol) in chloroform (15 ml) and a solution of dialdehyde **4a–c** (201 mg, 0.52 mmol) or **5a** (215 mg, 0.52 mmol) in chloroform (15 ml) are added dropwise and simultaneously to 10 ml of chloroform. The course of the reaction is monitored by ^{31}P-NMR spectroscopy. After 2 h (**4a**), 1 d (**5a**), 8 d (**4b**), or 12 d (**4c**) the solvent is evaporated in vacuo, and the resulting powder is washed several times with methanol. All attempts to purify further the products by column chromatography have failed.

Macrocycle **9a″**: White powder (yield 286 mg, 95%). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 79.5 (s, P=S), 21.1 (s, P=O). – ^1H NMR ($CDCl_3$): δ = 3.22 (d, $^3J_{HP}$ = 8.2 Hz, 12H, NCH_3), 6.63 (dd, $^2J_{HP}$ = 17.9, $^3J_{HH}$ = 22.3 Hz, 4H, PCH=), 7.24–8.12 (m, 44H, C_6H_5, C_6H_4, HC=N, PCH=C*H*). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.7 (d, $^2J_{CP}$ = 9.8 Hz, NCH_3), 119.0 (d, $^1J_{CP}$ = 105.1 Hz, PCH=), 126.2–136.7 (m, C_6H_5, C_6H_4, HC=N), 145.5 (d, $^2J_{CP}$ = 3.6 Hz, PCH=*C*H). – MS (FAB), *m/z* (%): 1161 [M^+ + H] (100). – $C_{64}H_{60}N_8O_2P_4S_2$ (1161.2): calcd. C 66.19, H 5.21, N 9.65; found C 66.09, H 5.11, N 9.69.

Macrocycles **9b′, b″**: White powder (overall yield 273 mg). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 79.5 (br. s, P=S), 21.3 (br. s, P=O). – ^1H NMR ($CDCl_3$): δ = 3.22 (d, $^3J_{HP}$ = 8.5 Hz, 3H, NCH_3), 6.58 (dd, $^2J_{HH}$ = 19.7, $^3J_{HH}$ = 20.0 Hz, 1H, CH=CH), 7.31–8.04 (m, 11H, C_6H_5, C_6H_4, HC=N, PCH=C*H*). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.6 (d, $^2J_{CP}$ = 9.9 Hz, NCH_3), 119.3 (d, $^1J_{CP}$ = 105.0 Hz, PCH=), 124.9–135.7 (m, C_6H_5, C_6H_4, HC=N), 146.0 (d, $^2J_{CP}$ = 3.5 Hz, PCH=*C*H). – MS (FAB), *m/z* (%): 1161 [**9b″**$^+$ + H] (100), 581 [**9b′**$^{++}$ + H] (35). –$(C_{32}H_{30}N_4OP_2S)_x$ (580.6)$_x$: calcd. C 66.19, H 5.21, N 9.65; found C 66.05, H 5.09, N 9.73.

Macrocycles **9c′**, **c″**, **c‴**: White powder (overall yield 261 mg). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 79.2 (br. s, P=S), 21.0–20.0 (m, P=O). – ^1H NMR ($CDCl_3$): δ = 3.15 (d, $^3J_{HP}$ = 8.6 Hz, 3H, NCH_3), 6.61 (d, $^2J_{HP}$ = 18.9, $^3J_{HH}$ = 21.2 Hz, 1H, CH=CH), 7.11–8.02 (m, 11H, C_6H_5, C_6H_4, HC=N, PCH=C*H*). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.2 (d, $^2J_{CP}$ = 8.8 Hz, NCH_3), 122.8 (d, $^1J_{CP}$ = 97.2 Hz, PCH=), 126.1–133.7 (m, C_6H_5, C_6H_4, HC=N), 143.3 (d, $^2J_{CP}$ = 3.5 Hz, PCH=*C*H). – MS (FAB), *m/z* (%): 581 [**9c′**$^{++}$ + H] (100), 1161 [**9c″**$^+$ + H] (38), 1742 [**9c‴**$^+$ + H] (8). – $(C_{32}H_{30}N_4OP_2S)_x$ (580.6)$_x$: calcd. C 66.19, H 5.21, N 9.65; found C 66.11, H 5.13, N 9.69.

Macrocycles **10a′,a″**: White powder (overall yield 285 mg). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 79.2 (br. s, P=S), 35.3 (br. s, P=O). – ^1H NMR ($CDCl_3$): δ = 3.22 (d, $^3J_{HP}$ = 9.5 Hz, 3H, NCH_3), 3.01 (m, 2H, PCH_2), 6.13–6.49 (m, 2H, CH=CH), 7.04–8.10 (m, 10H, C_6H_5, C_6H_4 and HC=N). – MS (FAB), *m/z* (%): 609 [**10a′**$^{++}$ + H] (100), 1217 [**10a″**$^+$ + H] (25). – $(C_{34}H_{34}N_4OP_2S)_x$ (608.65): calcd. C 67.09, H 5.63, N 9.21; found C 67.05, H 5.49, N 9.31.

Molecular modeling calculations are conducted on a Cache™ system (version 3.5) by using standard MM2 parameters (Mechanics software), except for the P–N bond lengths which are locked at 1.69 Å (value obtained from several X-ray structures of related compounds[3c,3j,3o,6]). The calculation is done first on "arms" $CH_3-(CH_2)_n-CH=CH-C_6H_4-CHO$ then $CH_3(CH_2)_n-CH=CH-C_6H_4-CH=N-N(Me)H$ by repetitive exhaustive search of the lowest energy conformer around 3 dihedral angles, followed by optimization (conjugate gradient method). The optimized "arms" are then connected to a P^{IV} atom. The result of a reiterative search of angles of bonds and dihedral angles around phosphorus followed by optimization is depicted on Figures.

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[5] In all cases, the first letter refers to the chirality of the phosphorus atom of the phosphoryl group (P=O), the second letter concerns the chirality of the phosphorus atom of the thiophosphoryl group (P=S).

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