Staudinger Reaction at *in*-Bridgehead Positions of Phosphorus Macrobicyclic Compounds

Ingmar Bauer,* Margit Gruner, Sigrid Goutal, and Wolf D. Habicher*[a]

Dedicated to Professor Edward E. Nifantyev on the occasion of his 70th birthday

Abstract: Reaction of *in*,*in*-phosphite **1** with thiophosphoryl azide **2** affords *in*,*in*-dithiophosphate **3**, *in*,*in*-thiophosphate–imidophosphate **4**, and *in*,*in*-phosphite–imidophosphate **5**. Compounds **4** and **5** are the first examples of the modification of *in*-bridgehead positions in macrobicyclic compounds with groups larger than methyl. The benzaldehyde arms of the *in*-substituent in **4** and **5** jut out of the cage bars. In **4** they are trapped between the macrocyclic arms to give the NMR spectra of a C_s-symmetric solution-state structure. In contrast, in **5** the benzaldehyde arms can move between the gaps of the cage. This results in ^{1}H and ^{13}C NMR spectra which are consistent for a compound with C_{3v} symmetry. *In*,*out*-diimidophosphate **7** is obtained in moderate yield by reaction of *in*,*out*-phosphite **6** with thiophosphoryl azide **2**. Its *in*-benzaldehyde moieties are not fixed between the cage arms, but can freely move from one gap to the next as is indicated by NMR measurements.

Keywords: atropisomerism · cage compounds · macrocycles · phosphorus · Staudinger reaction

Introduction

Macrobicyclic and other cage compounds play an important role in supramolecular chemistry. They are used for the complexation of cations and anions and also for the molecular recognition of neutral substrates.[1] The largest number of those compounds is represented by azacryptands. Phosphorus-containing macrobicyclic compounds, however, have been investigated much less.[2]

Macrobicyclic compounds with configurationally stable bridgehead atoms with at least one exocyclic moiety show the interesting feature of *in*,*out*-isomerism.[3] The *in*-positioned groups are of special interest due to their exceptional location inside a cavity; this can lead to different properties as compared to *out*-groups or to those which are attached to "normal" open chain skeletons.

Up to now a number of stable *in*-isomers have been isolated. Bridgehead functions in those compounds are mostly amines and ammonium ions,[1] rarely also methines[4], phosphanes, and phosphane oxides.[5] Stabilization of the *in*-position of azacryptands is mainly achieved by interaction of the nitrogen atom lone pairs with metal ions complexed in the cavity. The largest *in*-substituent described so far is a methyl group at an sp^3-carbon bridgehead atom, reported by Vögtle et al.[6] Pascal, Jr. et al.[7] described an *in*-fluorosilaphane of, however, rather small size. In almost all cases the *in*-position of the exocyclic groups was obtained in the course of the cyclization reaction, and not introduced by subsequent reaction inside the molecule.

Of special interest is the different reactivity of *in*- and *out*-positions of chemically equivalent functionalities. Studies on the reactivity of *in*-positioned groups have been carried out on a few examples. Thus, the intramolecular proton transfer in partially protonated azabicyclic compounds has been investigated.[8] Pascal, Jr. et al.[9] showed the low reactivity of an *in*-phosphane bicyclic compound towards oxidation and hydrobromination. Whitlock et al.[5] oxidized *in*-P^{III} atoms in larger phosphorus cryptands. We have already shown the different reactivity of *in*- and *out*-P^{III} atoms of flexible phosphite cage compounds.[2h–k]

The work presented here concerns itself with reactions at *in*-phosphorus macrobicyclic compounds, which allow, in combination with an appropriate-size cavity, the introduction of various groups into the cavity in a covalent manner. One could thus envision tailoring the cavity for applications such as molecular recognition of various substrates or complexation of metal ions with further regard to the design of ligands for metal-catalyzed reactions.

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Results and Discussion

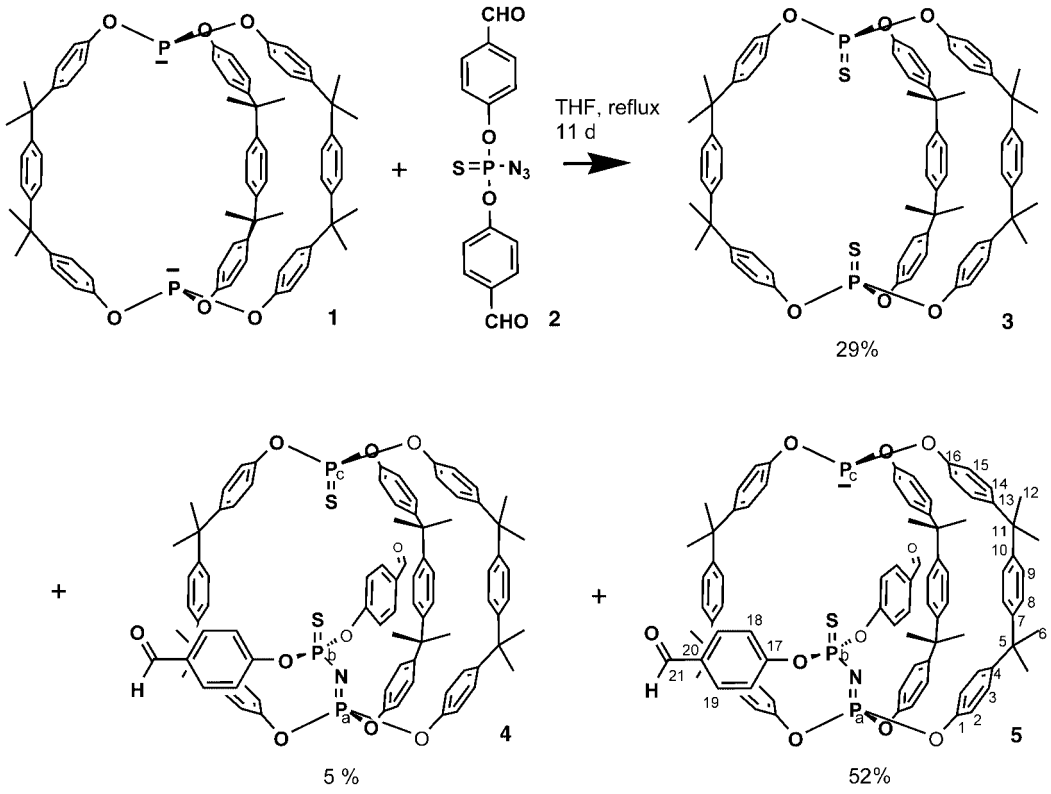
We previously reported a one-step procedure to obtain three homeomorphic *in*,*out*-isomers of phosphite macrobicycles according to a *double-capping* method.[2j,k] The objective of the present paper was to find out whether *in*,*in*-phosphite **1** or *in*,*out*-phosphite **6** could be functionalized with large groups at their *in*-positions. For that reason we treated *in*,*in*-isomer **1**[2j] with an excess of thiophosphoryl azide **2**[10] (ratio 1:3) in THF (Scheme 1). The type of P=N−P=S compounds obtained has been used by Majoral et al. for the synthesis of macrocyclic[2b,11] and dendritic[12] structures. Though Staudinger reactions[13,14] are usually carried out in THF at room temperature, we observed no conversion under such conditions. Consequently, the mixture was heated to reflux. The course of the reaction was followed by ^{31}P NMR spectroscopy and MALDI-TOF mass spectrometry. A slow decrease of the intensity of the *in*-phosphite NMR peak at 142.3 ppm was accompanied by the appearance of new signals characteristic of imidophosphates and thiophosphates. After eleven days the reaction was stopped when the starting phosphite **1** was no longer detectable by MALDI-TOF mass spectrometry.

Chromatographic separation of the product mixture led to the isolation of three structurally interesting *in*,*in*-compounds. The *in*,*in*-thiophosphate **3** was obtained in 29% yield, presumably by thiolation of *in*,*in*-phosphite **1** by thiophosphoryl azide **2**. Whether the reaction of **2** with the bridgehead P atoms occurs inside the cavity or outside the cavity (through a higher energy twisted conformation with an outward-pointing P atom) is unclear.

In the ^{31}P NMR spectrum the *in*-phosphorus atom in **3** shows a downfield shifted signal at 52.2 ppm. We have previously observed this effect with other P-bridgehead atoms in macrobicyclic *in*-phosphites and *in*-phosphates.[2h–k] The proton and ^{13}C NMR spectra of compound **3** reflect the D_{3h} symmetry of the molecule in solution. The two halves of the molecule around the phosphorus bridgeheads are magnetically equivalent, as are the arms of the macrocycle.

As an additional fraction, the monosubstituted product **4** was chromatographically isolated from the reaction mixture in 5% yield. We believed that the cavity size would allow only monosubstitution of the *in*,*in*-phosphite, and so were surprised to find that the second phosphite was oxidized to the corresponding thiophosphate. The structure of **4** was unambiguously established by two-dimensional NMR spectroscopy, mass spectrometry, and X-ray analysis.

The crystal structure of **4** is presented in two views in Figure 1.[15] In the top illustration the *in*-position of the P-bridgehead atoms is clearly visible. The thiophosphoryl sulfur at P_c points almost vertically into the cavity with an angle θ (S-P_c–P_a) of 7.07(6)° representing an almost ideal *in*-substituent.[3] The bottom view shows that the benzaldehyde moieties are positioned between the arms of the macrobicycle and jut out between the bars of the cage. The cage itself almost retains a C_3 symmetry, with its arms equidistant to each other. This is surprising when one considers that a benzaldehyde group is located between two of the arms (arms A and B, Scheme 2, structure **I**). The remaining space between cage arms A (Scheme 2, structure **I**) stays empty. The distance between the P-bridgehead atoms is 8.764(2) Å, which is slightly larger than in the free phosphite **1** with 8.5



Scheme 1. Staudinger reaction of the macrobicyclic *in*,*in*-phosphite **1** with thiophosphoryl azide **2** to give *in*-substituted macrobicyclic compounds.

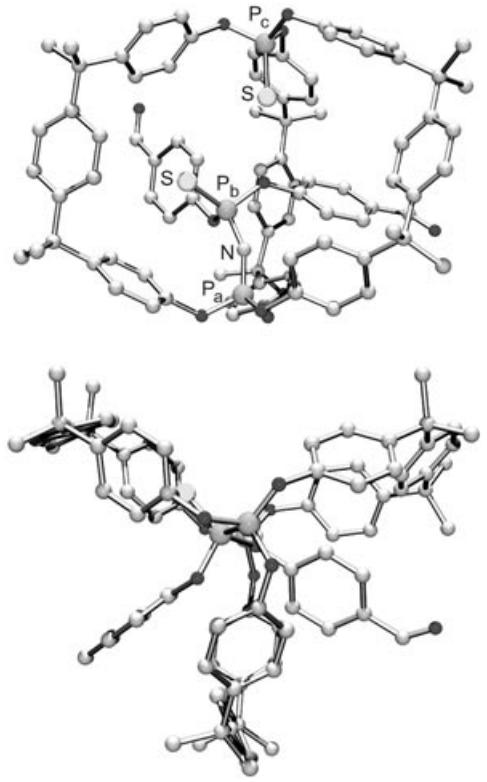
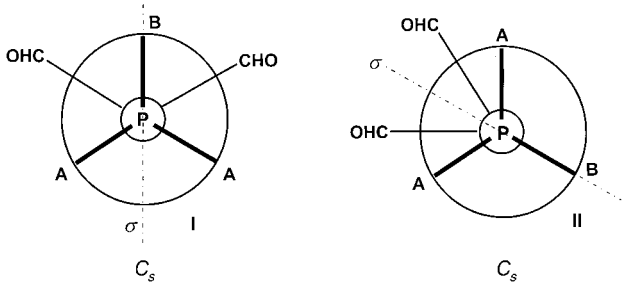


Figure 1. Crystal structure of *in*,*in*-compound **4**. Hydrogen atoms and solvent molecules are omitted for clarity. Top: View into the cavity. Bottom: View along the P_a–P_c axis of the macrobicycle.



Scheme 2. Schematic representation of two possible atropisomers **I** and **II** of the monosubstituted *in*,*in*-macrobicyclic compound **4**. (P represents any of the phosphorus atoms.)

and 8.3 Å, respectively (two conformers).[2j] The P_a-N-P_b angle of 153.4(3)° is very much distorted towards a linear geometry.

The ^{31}P NMR spectrum of compound **4** shows three doublets at 62.2 (P_c), 37.6 (P_b) and −20.0 ppm (P_a). The signal for the thiophosphate phosphorus atom (P_c) is shifted strongly downfield; this, in analogy to compound **3**, gives an indication of the *in*-position of the bridgehead atom. The signal for thiophosphate P_b is shifted upfield inside the cavity. Phosphorus atoms P_a and P_b give a ^2J(P,P) coupling of 66.3 Hz, which is in the normal region for coupling constants of such P=N−P compounds.[12a] Compound **4** was investigated by various two-dimensional NMR techniques (COSY, ^{1}H/^{13}C HSQC, ^{1}H/^{13}C HMBC, ^{1}H/^{31}P HMBC, NOESY, ROESY) for full assignment of all ^{1}H, ^{13}C, und ^{31}P signals. Due to the mechanical fixation of the benzaldehyde moieties between the cage arms the molecule has a C_s symmetry in solution. For this reason two of the arms of the macrocycle are magnetically equivalent, whereas the third gives additional signals (Scheme 2, structure **I**, arms A and B). The location of the two benzaldehyde functions inside the cage is indicated by NOE and ROE interactions of their protons with those of the macrocyclic arms especially with the protons of the central and the opposite phenylene rings (e.g., 18/14, 18/14′, 18/8′, 18/9, 18/9′, Figure 2). These correlations could not occur with an *out*-position at P_a and, thus, *out*-positioned benzaldehyde groups.

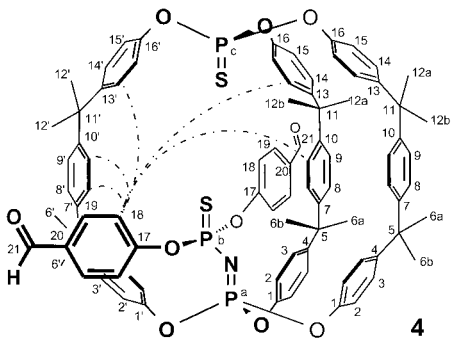


Figure 2. Selected important NOE interactions in compound **4**. Protons are omitted for clarity.

Moreover, the 18-H protons are exposed to a ring current effect inside the cage, formed by the aromatic moieties, resulting in an upfield shift of their ^{1}H signals to 6.02 ppm.

The fixation of the benzaldehyde groups between the cage arms opens the possibility for the formation of two C_s symmetric atropisomers (Scheme 2). The benzaldehyde groups can either be positioned between the same (structure **II**) or different arms of the macrobicycle (structure **I**).

The possible atropisomers **I** and **II** (Scheme 2) can be distinguished by their different NOE correlations. In case of the presence of isomer **II**, one of the macrocyclic cage arms has no benzaldehyde group in the neighborhood (arm B). However, because all three cage arms give NOE interactions with the inner benzaldehydes, we ruled out structure **II**. This was supported by single-crystal X-ray analysis (Figure 1).

The NOESY and ROESY cross peaks between the benzaldehyde protons and the protons of the macrobicyclic arms appear as exchange signals. The same is true for corresponding protons in nonequivalent macrocyclic arms. This suggests that the position of the inner benzaldehyde moieties is not completely fixed between two particular cage arms. Instead, a slow rotation around the P–N-bond (and/or the configurationally unstable P=N-bond) moves the benzaldehyde groups from one gap to the next underneath the arms of the macrocycle. In this way the position of each arm relative to the symmetry plane of the molecule changes and the signals of the corresponding positions (2′/2, 3′/3, 8′/8, 9′/9, 14′/14, 15′/15) exchange. Only further lengthening of

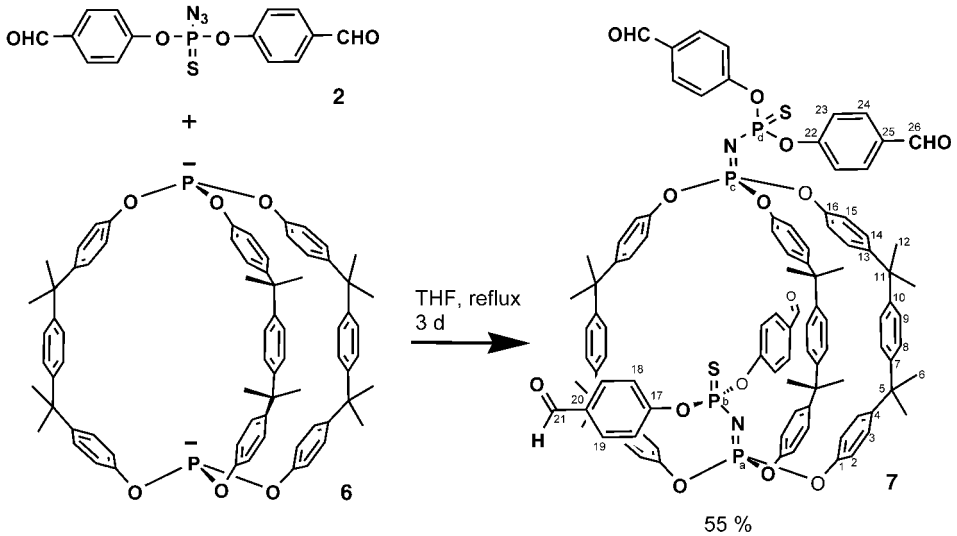
the *in*-groups would firmly (mechanically) fix the substituents between the cage bars.

The main product of the reaction of phosphoryl azide **2** with *in*,*in*-phosphite **1** was the monosubstituted *in*,*in*-compound **5**, which was obtained in 52% yield. The cavity of **1** proves to be too small to react a second time with azide **2**. The ^{31}P NMR spectrum of **5** shows a chemical shift for the *in*-phosphite phosphorus atom (P_c) at 142.5 ppm, which is similar to that of the starting material **1**. For the positions P_a and P_b doublets at 39.2 (P_b) and −22.5 ppm (P_a) with a coupling constant of $^2J(P,P) = 62$ Hz are obtained. All signals of the ^{1}H and ^{13}C NMR spectra could be unambiguously assigned using two-dimensional NMR techniques. In contrast to *in*,*in*-compound **4**, the ^{1}H and ^{13}C spectra of **5** reflect a C_{3v} symmetry. This proves that the energy barrier for the movement of the benzaldehyde groups from one gap of the cage to the next in **5** is lower than in **4**. This process presumably does not proceed through a horizontal rotation of these groups, because the arms of the macrocycle certainly hinder this movement. Instead it seems only possible by means of a process in which one benzaldehyde group is lifted up in the direction to the opposite bridgehead atom. Once in this position it might move over to the next gap. This process is fast enough on the NMR timescale to provide the C_{3v}-symmetric solution structure. This also explains why such a movement is not observed in *in*,*in*-macrobicycle **4**. The inward pointing sulfur atom prevents a passage of the benzaldehyde group near the bridgehead atom. Similar to **4**, the benzaldehyde protons in **5** show NOE correlations with the protons of the central and opposite phenylene groups of the cage arms (18/8, 18/9, 18/14); this proves the arrangement of the former inside the cage. This is also confirmed by an upfield shifted ^{1}H signal of the 18-H protons at 5.94 ppm, due to a ring current effect inside the cage of aromatic moieties.

The reaction of *in*,*out* phosphite **6**[2j] with thiophosphoryl azide **2** proceeded much faster than that of phosphite **1** and was completed after three days (Scheme 3). Because the *out*-position leads to a larger cavity, the *in*-position in **6** is more accessible than in **1**. The ^{31}P NMR spectrum of the crude product shows almost exclusively the formation of *in*,*out*-isomer **7**. This product could be isolated by chromatographic separation in 55% yield.

As in starting material **6** the two halves of the molecule with the corresponding bridgehead positions are not equivalent in compound **7**. This is reflected in the ^{31}P NMR spectrum by the presence of two doublets each at 46.0 (*out*) and −20.3 (*out*) or 39.2 (*in*) and −22.0 ppm (*in*), respectively. Corresponding ^{1}H and ^{13}C positions in the opposite halves of the molecule also give different signals. The inner protons (18-H) of the *in*-benzaldehyde groups show NOE interactions with the phenylene protons of the macrocycle, especially with those of the central and opposite phenylene groups (18/9, 18/8, 18/14), as described for compounds **4** and **5**. For the *out*-positioned benzaldehyde groups such interactions are completely missing. In compound **7** the 18-H protons show an upfield shift to 5.83 ppm due to the ring current effect inside the cage. The corresponding protons and ^{13}C positions are magnetically equivalent; this is in agreement with *in*,*in*-phosphite–imidophosphate **5**, but contrary to *in*,*in*-thiophosphate–imidophosphate **4**. This leads to the suggestion that the inner benzaldehyde arms, just like in the case of macrobicycle **5**, freely rotate between the cage bars and therefore give the averaged picture of a C_{3v} symmetric structure. The free movement of the *in*-substituent is supported by the opposite *out*-position which in comparison to **5** gives even more space for the change of the benzaldehyde groups to the next gap in the macrobicyclic compound.

The synthesis of compounds **4**, **5**, and **7** includes the first reaction of macrobicyclic cage compounds with large groups at *in*-bridgehead positions. This provides access to specific modification of the cavity of macrobicyclic compounds in order to adapt macrobicyclic hosts to special substrates for molecular recognition or to design novel ligands for metal-catalyzed reactions with a defined microenvironment.



Scheme 3. Staudinger reaction of the macrobicyclic *in*,*out*-phosphite **6** with thiophosphoryl azide **2** for formation of *in*,*out*-imidophosphate **7**.

Experimental Section

The melting points were determined on a Boëtius melting point apparatus. ^{1}H NMR (TMS internal reference), ^{13}C NMR (TMS internal reference), and ^{31}P NMR spectra (85% H_3PO_4 external reference) were recorded on a Bruker DRX-500 spectrometer at the frequencies indicated. Exact assignment of ^{1}H and ^{13}C NMR spectra was carried out by two-dimensional NMR techniques (COSY, ^{1}H/^{13}C correlated HSQC, ^{1}H/^{13}C correlated HMBC, ^{1}H/^{31}P correlated HMBC, NOESY, ROESY). MALDI-TOF mass spectra were measured on a Kratos Kompact MALDI II (Shimadzu Europa GmbH, Duisburg, Germany) with an N_2-laser source ($\lambda = 337$ nm), a positive polarity, and 20 kV acceleration voltage. The microanalyses were recorded on a CHN-S analyzer (Carlo Erba). Thin-layer chromatography (TLC) was carried out on aluminum sheets coated

with silica gel 60F254 (Merck, 1.05549). Plates were developed by UV irradiation. Column chromatography was performed using silica gel (Merck, 60A, 230–400 Mesh).

Tetrahydrofuran was dried immediately prior to use by distillation under N_2 over Na. Compounds **1**,[2j] **6**,[2j] and **2**[10] were synthesized according to literature procedures.

Reaction of 1 with 2: Compounds **1** (537 mg, 0.490 mmol) and **2** (511 mg, 1.47 mmol) were placed in a 25 mL flask and dissolved in dry THF (5 mL) under argon atmosphere. The reaction mixture was refluxed for eleven days. After removal of the solvent under reduced pressure, a yellow viscous oil was obtained, containing compounds **3**, **4**, and **5** and small amounts of other byproducts. Chromatographic separation on silica gel with CH_2Cl_2 led to the isolation of *in*,*in*-thiophosphoryl macrobicycle **3** (164 mg, 29%), *in*,*in*-thiophosphate–imidophosphate **4** (34 mg, 5%) and *in*,*in*-phosphite–imidophosphate **5** (358 mg, 52%) as colorless solids.

***in*,*in*-Dithiophosphate 3**: M.p. >360°C; ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 59.2$ ppm; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 7.15$ (d, $^3J(H,H) = 8.8$ Hz, 12H; H-2 or H-3), 7.06 (d, $^3J(H,H) = 8.8$ Hz, 12H; H-2 or H-3), 6.95 (s, 12H; H-8), 1.65 ppm (s, 36H; H-6); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 148.68$ (d, $^2J(P,C) = 6.6$ Hz; C-1), 147.77 (C-4, C-7), 127.95 (C-3), 126.10 (C-8), 120.87 (d, $^3J(P,C) = 4.7$ Hz; C-2), 42.06 (C-5), 30.31 ppm (C-6); MALDI-TOF-MS (matrix: 1,8,9-trihydroxyanthracene): *m*/*z*: 1159 $[M+H]^+$; elemental analysis calcd (%) for $C_{72}H_{72}O_6P_2S_2$ (1159.42): C 74.58, H 6.26, S 5.53; found C 73.63, H 6.03, S 5.21.

***in*,*in*-Thiophosphate–imidophosphate 4**: M.p. 335–337°C; ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 62.5$ (s; P_c), 37.9 (d, $^2J(P,P) = 66.3$ Hz; P_b), −20.0 ppm (d, $^2J(P,P) = 66.3$ Hz; P_a); ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta =$ 9.77 (s, 2H; H-21), 7.13 (d, 4H; H-14)*, 7.12 (d, 4H; H-3)*, 7.00 (d, 2H; H-3′)*, 6.99 (d, 4H; H-8)*, 6.98 (d, 4H; H-2)*, 6.98 (d, 4H; H-19)*, 6.97 (d, 4H; H-15)*, 6.92 (d, $^3J(H,H) = 8.3$ Hz, 2H; H-14′), 6.89 (d, $^3J(H,H) =$ 8.3 Hz, 4H; H-9), 6.80 (d, $^3J(H,H) = 8.2$ Hz, 2H; H-8′), 6.72 (d, $^3J(H,H) =$ 7.9 Hz, 2H; H-15′), 6.68 (d, $^3J(H,H) = 8.2$ Hz, 2H; H-9′), 6.54 (d, $^3J(H,H) = 7.8$ Hz, 2H; H-2′), 6.02 (d, $^3J(H,H) = 7.9$ Hz, 4H; H-18), 1.64 (s, 6H; H-12a), 1.64–1.62 (m, 24H; H-6a, H-6b, H-6′, H-12b), 1.52 ppm (s, 6H; H-12′) (*: signals were overlaid; coupling constant could not be determined); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 191.05$ (C-21), 155.94 (d, $^2J(P,C) = 11.0$ Hz; C-17), 149.05 (d, C-16′), 149.02 (d, C-1), 148.55 (C-10), 148.38 (C-10′), 148.13 (C-4′), 148.12 (C-4), 148.04 (C-1′), 147.52 (C-7′), 147.43 (C-7), 147.35 (C-16), 147.32 (C-13), 146.84 (C-13′), 132.07 (C-20), 130.37 (C-19), 128.51 (C-14), 127.85 (C-3′), 127.77 (C-3), 127.56 (C-14′), 126.36 (C-8), 126.10 (C-9, C-9′), 125.95 (C-8′), 122.66 (d, $^3J(P,C) = 4.7$ Hz; C-18), 121.56 (C-15), 121.08 (C-15′), 120.60 (C-2), 120.01 (C-2′), 42.23 (C-5, C-11, C-11′), 41.94 (C-5′), 31.23 (C-12b), 31.08 (C-6a), 30.82 (C-12′), 30.59 (C-6b), 30.23 (C-12a), 30.18 ppm (C-6′); MALDI-TOF-MS (matrix: 1,8,9-trihydroxyanthracene): *m*/*z*: 1446 $[M+H]^+$; elemental analysis calcd (%) for $C_{86}H_{82}NO_{10}P_3S_2$ (1446.66): C 71.40 H 5.71 N 0.97 S 4.43; found C 71.17 H 5.52 N 0.91 S 4.12. .

***in*,*in*-Phosphite–imidophosphate 5**: M.p. 175–180°C; ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 142.5$ (P_c), 39.2 (d, $^2J(P,P) = 61.8$ Hz; P_b), −22.5 ppm (d, $^2J(P,P) = 63.4$ Hz; P_a); ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta =$ 9.70 (s, 2H; H-21), 7.13 (brd, $^3J(H,H) = 5.7$ Hz, 6H; H-3), 6.97 (brd, 6H; H-8), 6.95–6.85 (br, overlaid; H-2), 6.94 (d, $^3J(H,H) = 8.5$ Hz, 4H; H-19), 6.92 (d, $^3J(H,H) = 8.6$ Hz, 6H; H-14), 6.88 (brm, 6H; H-9), 6.73 (brs, 6H; H-15), 5.94 (d, $^3J(H,H) = 7.5$ Hz, 4H; H-18), 1.68 (s, 18H; H-6), 1.57 ppm (s, 18H; H-12); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 190.79$ (C-21), 155.73 (d, $^2J(P,C) = 10.7$ Hz; C-17), 149.44 (d, $^2J(P,C) = 9.9$ Hz; C-16), 148.76 (C-4), 148.02 (C-10), 147.32 (C-7), 147.29 (d, $^2J(P,C) = 8.2$ Hz; C-1), 146.29 (C-13), 131.97 (C-20), 130.58 (C-19), 128.04 (C-3), 127.98 (C-14), 126.31 (C-9), 125.95 (C-8), 121.69 (d, $^3J(P,C) = 4.8$ Hz; C-18), 120.03 (br, C-2), 119.33 (d, $^3J(P,C) = 8.7$ Hz, C-15), 42.01 (C-11), 41.84 (C-5), 30.50 (br, C-12), 29.82 ppm (br, C-6); MALDI-TOF-MS (matrix: 1,8,9-trihydroxyanthracene): *m*/*z*: 1415 $[M+H]^+$; elemental analysis calcd (%) for $C_{86}H_{82}NO_{10}P_3S$ (1414.56): C 73.01 H 5.84 N 0.99 S 2.27; found C 73.01 H 6.03 N 1.08 S 2.18.

Reaction of 6 with 2: Compound **6** (252 mg, 0.230 mmol) was refluxed with compound **2** (167 mg, 0.481 mmol) for 3 d in dry THF (5 mL). Removal of the solvent under reduced pressure afforded a yellow viscous oil. After column chromatographic separation (silica gel, CH_2Cl_2/EtOAc 100:1), *in*,*out*-diimidophosphate **7** (218 mg,55%) was isolated as a colorless solid.

***in*,*out*-Diimidophosphate 7**: M.p. 127–130°C; ^{31}P NMR (202.46 MHz, $CDCl_3$): $\delta = 46.0$ (d, $^2J(P,P) = 65.4$ Hz; P_d), 39.2 (d, $^2J(P,P) = 59.6$ Hz; P_b), −20.3 (d, $^2J(P,P) = 65.6$ Hz; P_c), −22.0 ppm (d, $^2J(P,P) = 59.6$ Hz; P_a); ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 9.90$ (s, 2H; H-26), 9.76 (s, 2H; H-21), 7.68 (d, $^3J(H,H) = 8.5$ Hz; 4H, H-24), 7.14 (m, 6H; H-3), 7.09 (d, 4H; H-23)*, 7.06 (d, 6H; H-8)*, 7.00 (d, $^3J(H,H) = 8.5$ Hz, 4H; H-19), 6.94 (d, $^3J(H,H) = 8.2$ Hz, 6H; H-9), 6.88 (d, $^3J(H,H) = 8.3$ Hz, 6H; H-14), 6.93–6.84 (br, 6H; H-2), 6.82 (brs, 6H; H-15), 5.83 (d, $^3J(H,H) = 8.2$ Hz, 4H; H-18), 1.71 (s, 18H; H-6), 1.56 ppm (s, 18H; H-12) (*: signals are overlaid. Coupling constant could not be determined); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 190.88$ (C-26), 190.57 (C-21), 156.25 (d, $^2J(P,C) = 8.5$ Hz; C-22), 155.46 (d, $^2J(P,C) = 10.7$ Hz; C-17), 148.80 (C-4), 148.70 (C-13), 147.65 (d, $^2J(P,C) = 9.7$ Hz; C-16), 147.39 (C-7), 147.32 (C-10), 147.17 (d, $^2J(P,C) = 8.5$ Hz; C-1), 132.76 (C-25), 132.21 (C-20), 131.08 (C-24), 130.48 (C-19), 128.10 (C-14), 127.90 (C-3), 126.49 (C-9), 125.95 (C-8), 121.83 (d, $^3J(P,C) = 5.1$ Hz; C-23), 121.70 (d, $^3J(P,C) = 5.1$ Hz, C-18), 120.03 (br, C-2), 119.47 (d, $^3J(P,C) = 4.8$ Hz; C-15), 42.28 (C-11), 41.71 (C-5), 30.63 (br, C-12), 29.48 ppm (br, C-6); MALDI-TOF-MS (matrix: 1,8,9-trihydroxyanthracene): *m*/*z*: 1735 $[M+H]^+$; elemental analysis calcd (%) for $C_{100}H_{92}N_2O_{14}P_4S_2$ (1733.88): C 69.27 H 5.35 N 1.62 S 3.70; found C 69.16 H 5.38 N 1.59 S 3.62.

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[15] X-ray analysis of **4**: Kappa-CCD diffractometer (Bruker-Nonius), $T=198(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å), θ-range for data collection: 3.54 to 22.00°, index range: $-16\le h\le 16$, $-16\le k\le 16$, $-19\le l\le 20$, collected reflections: 47114, independent reflections: 10368 [$R_{int}=0.0565$], absorption correction: semi-empirical from equivalents, $\mu=0.384\ mm^{-1}$, max/min transmission: 0.8975/0.8092, triclinic, space group $P\bar{1}$, unit cell dimensions: $a=15.3210(12)$, $b=15.898(2)$, $c=19.2700(13)$ Å, $\alpha=104.929(8)°$, $\beta=97.425(6)°$, $\gamma=103.700(10)°$, $V=4314.8(7)$ Å^3, $Z=2$, $\rho_{calcd}=1.322\ g\,cm^{-3}$, $F(000)$: 1785, structure solution with direct methods, refinement method F^2, relation data/parameters: 10368/1049, Goof refined against F^2: 1.089, R values [$I>2\sigma(I)$]: $R_1=0.0677$, w$R_2=0.2160$ (all data), disordered $CDCl_3$ solvent outside the cavity, used programs: Collect (Nonius BV, 1997–2000), Dirax/lsq (Duisenberg & Schreurs, 1989–2000), EvalCCD (Duisenberg & Schreurs), DABS Version 2.03. (Sheldrick, Bruker AXS Inc, 2000), Schakal-99 (E. Keller 1999). CCDC 224854 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk).

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