The First Helical-Chiral Phosphane Ligands: *rac*-[5]- and *rac*-[6]-Heliphos

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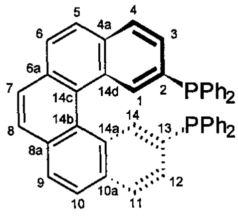
The syntheses of two helical, chiral phosphanes in their racemic forms are described. Their helicene backbone was built up using an improved photocyclization approach. The phosphorus functionalities were introduced in the last step. Up to now, separation of the enantiomers of the helicene phosphanes could be achieved analytically but not on a preparative scale.

Since the discovery of transition-metal-catalyzed asymmetric synthesis in the presence of chiral (phosphane) ligands, a large number of ligands has been described in the literature.[1] All of these carry only three of the four elements of asymmetry (central, planar, and axial asymmetry): no helical phosphane ligand was known until today.

In this work two of the simplest members of this class will be presented, both having an all-benzene backbone: [5]-Heliphos (**1**) and [6]-Heliphos (**2**). These phosphanes are both bidentate ligands with phosphorus atoms positioned in a way that chelation of metal atoms should be possible. Thus, the pentahelicene derivative has a 2,13-substitution and the hexahelicene derivative a 2,15-substitution (according to the Newman nomenclature).[2] The remaining valences of the phosphorus atoms were substituted by phenyl groups to give bis(triarylphosphanes) having the advantage of increased tendency for crystallization and decreased affinity for oxygen. Forcefield calculations[3] performed before the syntheses revealed P-P distances of 4.9 Å ([5]-Heliphos, **1**) and 4.6 Å ([6]-Heliphos, **2**), respectively; the complexation of larger transition metal atoms such as rhodium seemed to be possible.



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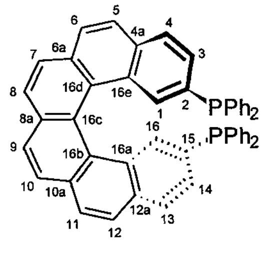

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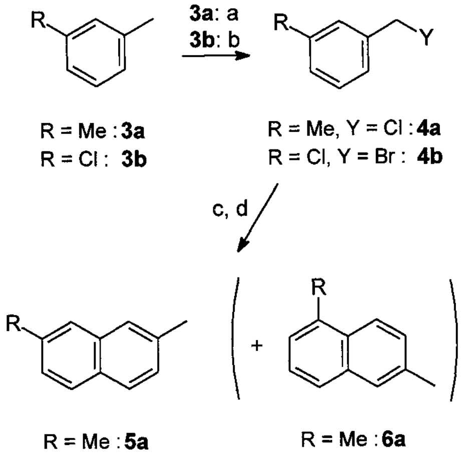
For the assembly of the helicene frame the common photocyclization of mono- and bisstilbenes in the presence of iodine was utilized.[4] This technique was recently improved by Katz, who introduced methyloxirane as scavenger for the evolving hydrogen iodide which causes side reaction.[5] Further improvement, particularly in yield, could be achieved by us upon working at elevated temperatures and using ethyloxirane.

For reasons of simplification the syntheses of C_2-symmetric helicenes usually start from symmetric stilbenes, thus leading to a clear synthetic strategy for hexahelicenes: the double cyclization of 2,7-bis(styryl)naphthalene derivatives. These should have a suitable substitution which is easily transformed to the phosphane groups but which does not interfere with the construction of the carbon backbone. Halogens, preferably bromine, proved to be applicable.

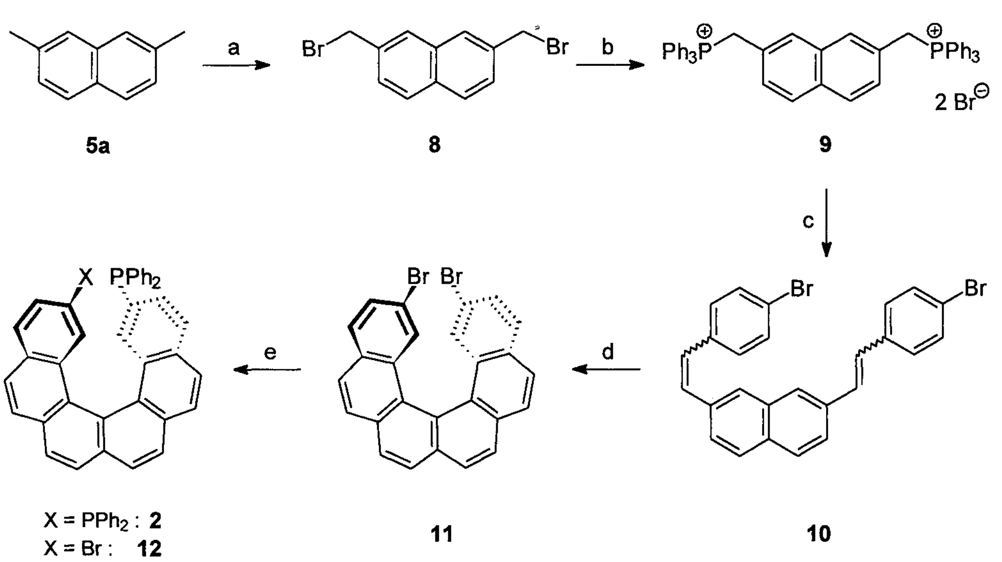
Though 2,15-dibromohexahelicene (**11**) has already been described,[6,7] several improvements in the synthesis and the first complete characterization of this material justify a detailed description. Starting from *m*-xylene (**3a**), 3-methylbenzyl chloride (**4a**) was obtained by monochlorination with sulfuryl chloride (Scheme 1).[8] In a modification of a literature procedure, **4a** was transformed into the Grignard reagent and reacted with 4,4-dimethoxybutan-2-one [$(MeO)_2CHCH_2COCH_3$, **7**].[9] The crude intermediate product obtained by hydrolysis of the reaction mixture was directly cyclized to the naphthalene derivative using hydrobromic acid. Since the ring closure is not completely regioselective, a mixture of 2,7-dimethylnaphthalene (**5a**, solid) and its 1,6-isomer **6a** (liquid) was obtained, which could be separated by crystallization from ethanol (74–81 % yield of **5a**).



(a) ref 8: 68 %; (b) ref 13: 63 %; (c) 1. Mg Et_2O, reflux, 2. CH_3CO CH_2CH $(OCH_3)_2$ (**7**), r.t. →reflux, 3. aq NH_4Cl; (d) HBr, AcOH, 90–100 °C, 74–81 % for **5a**, 11–20 % for **5b**.

Scheme 1

2,7-Dimethylnaphthalene (**5a**) was converted into **8** by means of *N*-bromosuccinimide (Scheme 2). Since the Wohl–Ziegler technique gave only unsatisfactory results, a new method has been chosen, which has proven its efficacy particularly with dimethylnaphthalenes; by photobromination in acetone nearly quantitative yields of bis(bromomethyl)naphthalenes could be obtained.[10] In our case, the only losses of **8** occurred during recrystallization, which had to be carried out to get rid of impurities (such as only monobrominated naphthalenes)



(a) NBS, acetone, hν, 64%; (b) PPh_3, DMF, r.t., 94–99%; (c) 1. NaOMe, MeOH, r.t., 2. 4-BrC_6H_4CHO, r.t., 70%; (d) I_2, ethyloxirane, C_6H_6, 60 °C, hν, 67–73%; (e) 1. BuLi, THF, −70 °C, 2. $ClPPh_2$, −50 °C, 28% of **2**, 34% of **12**. If the halogen–metal exchange in step e was performed with *t*-BuLi, the yields of **2** and **12** were 14% and 71%, respectively.

Scheme 2

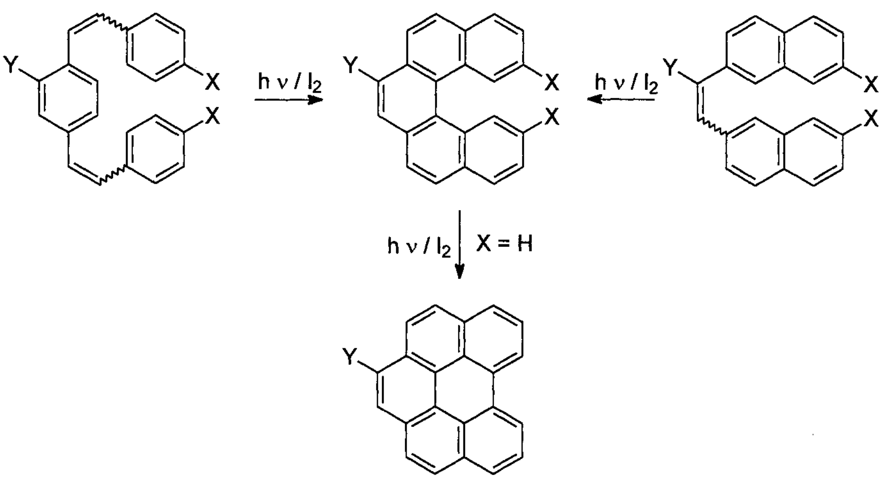
which would complicate the purification of the products of the following reactions by formation of products with very similar properties.

For the quaternation of **8** with triphenylphosphane, DMF was used rather than the nonpolar solvents recommended in the literature,[11] resulting in a faster reaction and quantitative yield of **9**. This was converted via a Wittig reaction into the mixture of isomers of 2,7-bis(4-bromostyryl)naphthalene (**10**) following the literature procedure.[7] The photocyclization of **10** to 2,15-dibromohexahelicene (**11**) was performed as a 1.5–2 M solution in benzene in the presence of a 70-fold excess of ethyloxirane, resulting in a 67% isolated yield of **11**. Halving the concentration during photocyclization raised the yield to 73%, but was not usually performed due to practical reasons.

Since the metalation of **11** via Grignard reaction failed due to its low solubility in diethyl ether or THF, metalation was achieved by metal–halogen exchange using butyllithium at −60 °C. At higher temperatures Wurtz-like reactions occurred yielding mono- or dibutylated helicene-species, at lower temperatures the halogen–metal exchange proceeded too slowly. Since both the dibromo- and the dilithio-species are little soluble in THF at this temperature, the starting material had to be finely ground prior to reaction. Addition of excess chlorodiphenylphosphane resulted in the formation of 2,15-bis(diphenylphosphanyl)hexahelicene (**2**, [6]-Heliphos) which could be isolated by chromatography, besides varying amounts of substrate and 2-bromo-15-(diphenylphosphanyl)hexahelicene (**12**), which could also be isolated but was not characterized in detail. The use of *tert*-butyllithium helped to get around the problems with the Wurtz-coupling, but did result in a preferred formation of monolithiated helicene probably due to steric reasons (the yield of **12** rose up to 71%, while [6]-Heliphos (**2**) was formed in only 14% yield). [6]-Heliphos (**2**) crystallizes from toluene in the form of pale yellow crystals, which are sensitive to air and light, particularly in solution. In the absence of both, the solid is storable for prolonged periods at ambient temperature.

For the synthesis of [5]-Heliphos (**1**) two ring-closure strategies were possible, as shown in Scheme 3. Both ways have been used for the synthesis of pentahelicene derivatives, but in most cases only low yields of helicenes were obtained since usually a second ring closure takes place under the reaction conditions resulting in the formation of benzoperylenes. Liu and Katz[12] reported that an introduction of bromine atoms into the three aromatic rings of the bis(styryl)benzene derivative at the designated places (X,Y = Br) led to a significant increase of the helicene yield (92%), whereas with Y = H a 68% yield in the crude product was detected (by ^{1}H NMR), but only minor amounts of the helicene could be actually isolated. In our hands, a complex reaction mixture formed under the conditions described, which contained only minor amounts of the desired product. Experiments with the monochlorinated derivative (X = Br, Y = Cl, to enable differentiation at later stages of the synthesis) were equally unsuccessful.

Therefore, the second reaction path, the cyclization of the dinaphthylethene derivative, was investigated. Since no suitable naphthalene derivatives (with a halogen substitution at the 2-position and a carbon functionality at the 7-position) were commercially available, 2-chloro-7-methylnaphthalene (**5b**) was synthesized according to the synthesis of 2,7-dimethylnaphthalene (**5a**): 3-chlorotol-



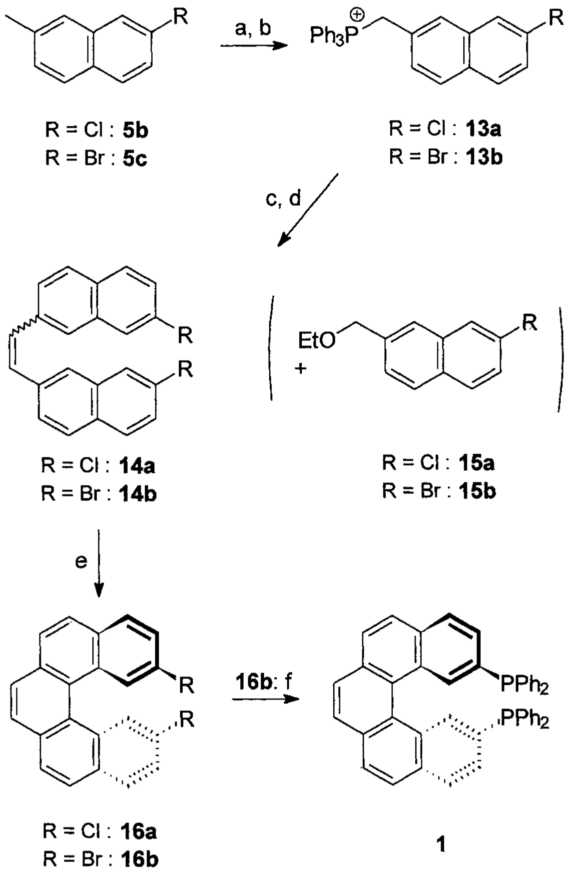
Scheme 3

uene (**3b**) was brominated at the methyl group,[13] transformed to the Grignard reagent and reacted with ketone **7**. The acid-catalyzed ring closure of the crude intermediate resulted in the usual mixture of the 2,7- and 1,6-isomer, **5b** and **6b**, respectively, which could be separated by crystallization from ethanol (Scheme 1). The yield of **5b** was significantly lower than that of **5a**, probably because of the more difficult intramolecular attack at the electron-deficient chloro-substituted arene ring.

To get the dinaphthylethene a reaction sequence published by Bestmann was utilized, the oxidative coupling of two phosphonium salts.[14–16] For this purpose **5b** was monobrominated in its side chain using the approved photoreaction and, after removal of the succinimide, directly quaternized with triphenylphosphane (Scheme 4). The pure phosphonium bromide **13a** was transformed into the corresponding periodate which couples to the dinaphthylethene derivative **14a** upon treatment with sodium ethoxide. A side product (5–10%) of this reaction is the ethyl ether **15a**, which is not mentioned by Bestmann.

The *E*/*Z*-mixture of bis(7-chloronaphthyl)ethene **14a** can be photocyclized under the conditions described above, yielding 2,13-dichloropentahelicene (**16a**) in the form of a pale yellow crystalline powder (35%). However, no conditions could be found to attain a metal–halogen exchange. Even treatment with sodium dust in toluene left the substance unchanged.

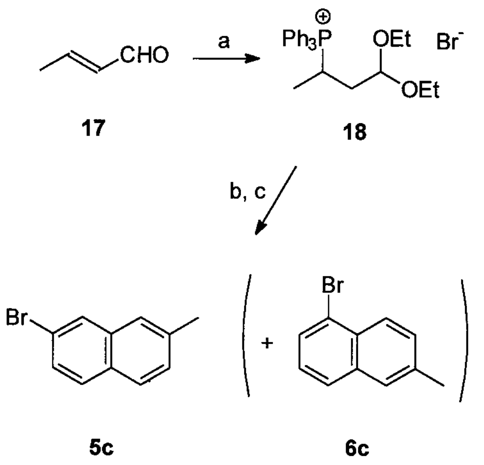
For this reason, 2,13-dibromopentahelicene (**16b**) was synthesized. This required a different access to the naphthyl system since the Grignard reaction of 3-bromobenzyl bromide was expected to yield a considerable amount of species metalated on the nucleus. Thus, the enaldehyde system needed for the ring closure was introduced by a Wittig reaction. Initial studies proved that the reaction of benzylidenephosphorane with ketone **7** proceeds too slowly and with yields too low to be useful. The inverse reaction of an aromatic aldehyde with the appropriate alkylidenephosphane proceeded more smoothly. The required phosphonium salt **18** was easily accessible in a one-pot reaction of but-2-enal (**17**) with triphenylphosphonium bromide and an orthoformate (Scheme 5).[17]



(a) NBS, acetone, hν; (b) PPh_3, DMF, r.t., 74% for **13a**, 87% for **13b**; (c) $NaIO_4$. $MeOH/H_2O$; (d) NaOEt, EtOH, reflux, 50% for **14a**, 59% for **14b**; (e) ethyloxirane, C_6H_6, 60 °C, hν, 32% for **16a**, 51% for **16b**; (f) 1. BuLi, THF, −70 °C, 2. $ClPPh_2$, −50 °C, 37%.

Scheme 4

Using this strategy, the Wittig reaction proceeded smoothly and the resulting β,γ-unsaturated acetal was directly cyclized without purification to yield 2-bromo-7-methylnaphthalene (**5c**, 22% after two crystallizations relative to but-2-enal (**17**), some 1-bromo-6-methylnaphthalene (**6c**) remained in the mother liquor). The forma-



(a) 1. PPh_3. HBr, CH_2Cl_2, EtOH, −10 °C − r.t., 2. $CH(OEt)_3$, 0 °C − r.t., 95 %; (b) 1. BuLi, THF, 2. $3\text{-}BrC_6H_4CHO$, −75 °C →r.t.; (c) HBr, AcOH, 90–100 °C, 22 %

Scheme 5

tion of 2,13-dibromopentahelicene (**16b**) from this product was performed analogously to that of 2,13-dichloropentahelicene (**16a**) (Scheme 4) facilitated by the fact that the yields in the photocyclization step were higher (51 % versus 32 %). In contrast to 2,15-dibromohexahelicene (**11**), **16b** is quite soluble in THF making the halogen–metal exchange with butyllithium easier than in the former case. Reaction of the bislithiated species with chlorodiphenylphosphane yielded the desired 2,13-bis-(diphenylphosphanyl)pentahelicene (**1**, [5]-Heliphos) in 38 % yield after chromatography under nitrogen. Compound **1** forms crystals from toluene, which are paler than the [6]-Heliphos crystals. The solid is stable towards short air-exposure and the light sensitivity seems to be lower than that of **2**.

Small crystals of **1** with X-ray quality could be grown from toluene and were measured at −90 °C. The substance crystallizes in the form of a racemate. The actual P-P distance (5.03 Å) is a little larger than the calculated one, but still should be appropriate for complexation (Figure).

Since no crystal of **2** suitable for X-ray analysis could be obtained, the only structure information is derived from the NMR spectra. These clearly reveal the expected C_2-symmetry of the molecule. But both the ^1H and the ^{13}C spectra show a double set of signals for the atoms of the phenyl rings at the phosphorus atoms. From COSY spectra it could be deduced that these sets represent not two different sides of the phenyl rings, but the two different diastereotopic rings. In contrast to this, the protons of the diphenylphosphanyl groups of **1** appear as a complex multiplet with only few elements of symmetry.

Neither of these two phosphanes **1** and **2** could yet be resolved into its enantiomers on a preparative scale. Attempts to achieve resolution by complexation with chiral palladium complexes according to Otsuka[18] resulted in the formation of gels, which was reversible upon heating/cooling. This suggests that an intermolecular complexation occurs, forming polymeric species, which break up on heating. The classic reagent for the resolution of helicenes, α-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)-propionic acid (TAPA),[19] seemed to cause decomposition of the phosphanes indicated by an irreversible color change to brown. The resolution at the stage of the dibromohelicenes did not succeed because of too weak interactions between the resolving agent and the helicenes. Separation on an analytical scale was achieved by HPLC (Chiralpak OT, methanol, 0 °C) and will be used in the future to screen the success of to-be-developed resolution procedures.

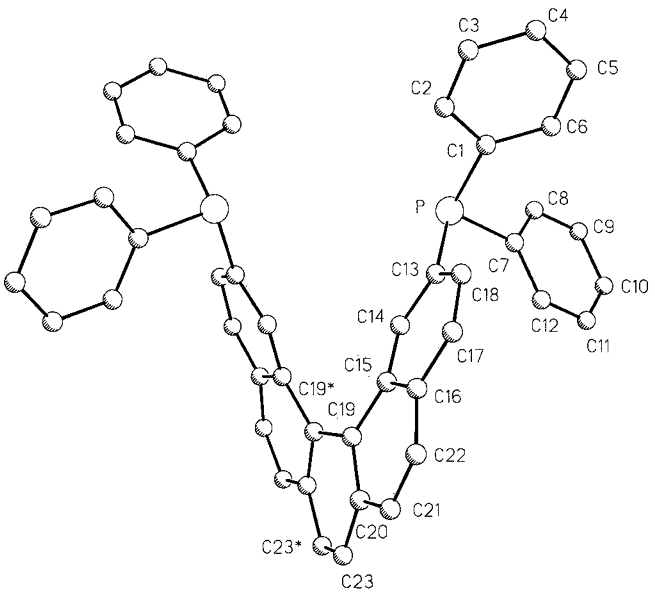


Figure: X-ray structure of **1**. H-Atoms are omitted for clarity. The distance between the phosphorus atoms amounted to 5.03 Å, the distortion of the helicene ring is 31.4° (dihedral angle C15-C19-C19*-C15*).

All procedures involving phosphanes were performed under exclusion of air using purified N_2. If organometallic reagents were involved, water was also excluded. Solvents used for preparative purposes were dried and deaerated according to standard procedures. Water and solvents for chromatography were deaerated by bubbling N_2 through the fluids for at least 12 h. Two acronyms will be used successively: EE for ethyl acetate and PE for petroleum ether (bp 40–60 °C). Liquid starting materials were distilled under N_2 prior to use. Chromatographic materials (silica 60 (65–200 μm), Merck), and alumina (basic, Super I, Woelm) were heated in vacuo for 24 h and then saturated with N_2.

Melting points were determined using a SMP-20 (Büchi) and were not corrected. Vibrational spectra were recorded on a Beckman spectrometer IR 4240 or a Bruker FTIR IFS 25 either as films between NaCl windows (film) or as KBr pellets (KBr). For MS, the MAT 112 S (electron impact ionization, 70 eV) and the MAT 95 (field desorption) apparatus (both Finnigan) were used. The intensities are relative to the basic peak (I = 100 %), possible interpretations are given within brackets. Elemental analysis were performed at the Mikroanalytisches Labor of the Universität Regensburg. ^1H NMR spectra were recorded using the following spectrometers: EM 360L (60 MHz, Varian), FT 80 A (80 MHz, Varian), AC 250 (250 MHz, Bruker), ARX 400 (400 MHz, Bruker), and VXR 500 (500 MHz, Varian). The chemical shifts are given in units of the δ scale relative to internal TMS, J values are given in Hz.

The same standard was used for the ^{13}C NMR spectra (including DEPT and APT sequences), performed on AC 250 (63 MHz), ARX 400 (101 MHz), and VXR 500 (126 MHz). Exact peak assignments were possible after two-dimensional experiments, recorded on the ARX 400 and the VXR 500 spectrometers. For the ^{31}P NMR spectra (^1H-decoupled), the AC 200 (81 MHz, Bruker, internal standard PPh_3) and the ARX 400 (162 MHz, external standard H_3PO_4) were used.

2-Substituted 7-Methylnaphthalenes 5; General Procedure 1:[9]

A solution of the Grignard reagent was prepared in the usual manner by treatment of the respective benzyl halide **4a**[8] or **4b**[13] (0.5 mol) with Mg (0.50–0.65 mol) in Et_2O (300–400 mL). To the cooled solution 4,4-dimethoxybutan-2-one (**7**, 63 g, 0.48 mol) in dry Et_2O (100 mL) was added dropwise, resulting in an exothermic reaction accompanied by a color change to green and the formation of a large amount of precipitate complicating efficient stirring. The mixture was heated to reflux for 16 h, then cooled and cautiously poured onto a mixture of ice (200 g) and aq sat. NH_4Cl (300 mL). The organic phase was separated, the aqueous layer extracted with Et_2O (3 x 200 mL) and the combined organic extracts concentrated in vacuo. The residual oil was dissolved in HOAc (500 mL), then 48 % HBr in H_2O (400 mL, 3.5 mol) was added, causing an exothermic reaction and color change to black. After the mixture was heated to 90–100 °C for 2 h, most of the solvent was removed in vacuo and the residue was poured onto ice-water (500 mL). The mixture was extracted with CH_2Cl_2 (3 x 400 mL) and the black solution was evaporated in the presence of silica gel (~400 mL) by means of a rotary evaporator. The silica gel prepared in this way was brought on top of a pad of silica gel (10 cm ∅ × 8 cm) and the naphthalenes were eluted by PE. After removal of the solvent, the residue was crystallized twice from EtOH (250–300 mL, –30 °C) and dried in vacuo.

Side-Chain Bromination of Methylarenes 5; General Procedure 2:[10]

The methylarene **5a–c** (100 mmol) and NBS (14.5 g, 110 mmol per methyl group) were dissolved in acetone (1.9 L) and a weak stream of N_2 was bubbled through the solution for 0.5–1 h. Maintaining the stream of N_2, the mixture was irradiated by a water-cooled mercury vapor lamp (180 W), until the product formation was completed (4–6 h, monitored by TLC). Then, the solvent was removed immediately using a vacuum rotary evaporator (*Caution!* Traces of bromoacetone (lachrymator) may have formed!) and the residue was partitioned between CH_2Cl_2 (250 mL) and H_2O (500 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 200 mL) and the combined organic phases were dried ($MgSO_4$).

Quaternization of Triphenylphosphane; General Procedure 3:

The alkyl halides **8**, **5b**, **5c** or **17** (0.10 mol, 0.05 mol for dihalides) were dissolved in a solution of 1.2 N PPh_3 in DMF (100 mL, 0.12 mol) and stirred at r.t. for 1–3 d, in the course of which the product might already precipitate. The mixture was poured into toluene (500 mL) under stirring precipitating the product as a solid or an oil. After stirring for 30 min, the toluene was decanted, fresh toluene (500 mL) was added and stirring was continued, until a fine crystalline material resulted. This was filtered off, washed with toluene and dried in vacuo.

Formation of Helicenes 11 and 16a,b by Photocyclization; General Procedure 4:

The stilbene **10** or **14a,b** (5.5–7.0 mmol), I_2 (1.1–1.3 equiv per stilbene double bond) and ethyloxirane (40 mL, 0.46 mol) were dissolved in dry C_6H_6 (3.5 L) and the mixture was heated to 60 °C by circulating water of this temperature through the cooling jacket of the immersed mercury vapor lamp (a reflux condenser is required to minimize solvent losses). Before the mixture was irradiated, N_2 was bubbled through for 1–2 h. Maintaining the stream of N_2, the mixture was irradiated for 16 h, before the solvent was evaporated in vacuum (reuse of the benzene was possible after distillation from Na). The iodobutanol formed was removed by a stream of N_2. Three more preparations were run similarly and the combined crude products were taken up in warm toluene (90 °C, 300 mL). This solution was quickly filtered through silica gel (10 cm ∅ × 5 cm), topped with a 2 cm layer of alumina (basic, Super I) and concentrated to 50 mL. After crystallization under N_2, the solid was crystallized a second time from a minimum amount of toluene yielding the pure helicene.

Conversion of Aryl Bromides 11 and 16b to Diphenylphosphanylarenes 2 and 1; General Procedure 5:

Air had to be excluded in every part of this procedure. To a mixture of the dibromohelicene **11** or **16b** (5 mmol) and dry THF (50 mL) under N_2, 1.6 M BuLi in hexane, (7.5 mL, 12 mmol) was added at – 70 °C. The mixture was stirred at – 60 to – 50 °C for 1 h, before $ClPPh_2$ (2.5 mL, 14 mmol) in dry THF (10 mL) was slowly added maintaining a temperature below – 50 °C. The mixture was allowed to warm up to r.t., stirred for another hour and then was directly evaporated onto silica gel (50 mL, deaerated before use). This silica gel was brought onto a column (3.5 cm ∅ × 16 cm) and chromatography was performed with a gradient (PE → toluene).

Silbenes 14a,b by Oxidative Coupling of Phosphonium Salts 13a,b; General Procedure 6:[14–16]

Formation of the Phosphonium Periodate: A solution of the phosphonium bromide **13a,b** (100 mmol) in MeOH (150 mL for **13a**, 250 mL for **13b**) was added to a solution of $NaIO_4$ (25 g, 120 mmol) in H_2O (300 mL). Crystallization of the precipitating oil was achieved by cautious addition of MeOH (100–300 mL) under stirring, then all MeOH was removed in vacuo at r.t. The solid was filtered off, washed with H_2O and dried (P_4O_{10}); yielding white to yellowish crystals (95–100 %) which were directly used for the next step.

Formation of the Stilbenes: A solution of Na (3.3 g, 140 mmol) in anhyd EtOH (200 mL) was added dropwise to a suspension of the phosphonium periodate (100 mmol) in anhyd EtOH (750 mL) under N_2 at reflux temperature, resulting in a color change to yellowish orange. After completion of the addition, the resulting mixture was heated to reflux for 3 h, then silica gel (~300 mL) was added and the solvent was removed in vacuo. The silica gel prepared in this way was brought on top of a column filled with silica gel (~800 mL) and eluted with toluene. Evaporation of the solvent and drying in vacuo resulted in colorless solids, which represented a mixture of the *E*/*Z* isomers.

2,13-Bis(diphenylphosphanyl)pentahelicene (1, [5]-Heliphos):

Prepared according to General Procedure 5. The product was recrystallized from toluene (10 mL) at – 30 °C yielding light yellow crystals (39 %); R_f (silica gel, cyclohexane/toluene 1:1) = 0.43; mp 235–237 °C.

^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.02–7.16 (m, 10 H, phenyl rings A), 7.20–7.27 (m, 10 H, phenyl rings B), 7.36 (ddd, J = 8.3 Hz, J_{PH} = 6.2 Hz, ^4J = 1.5 Hz, 2 H, 3-H, 12-H), 7.79 (s, 2 H, 7-H, 8-H), 7.81 (d, J = 8.7 Hz, 2 H, 6-H, 9-H), 7.84 (d, J = 8.7 Hz, 2 H, 5-H, 10-H), 7.86 (dd, J = 8.3 Hz, J_{PH} = 1.6 Hz, 2 H, 4-H, 11-H), 8.29 (dd, J_{PH} = 9.0 Hz, ^4J = 1.5 Hz, 2 H, 1-H, 14-H).

^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ = 126.9 (C-14b, C-14c), 127.0 (C-6, C-9), 127.5 (C-7, C-8), 127.5 (C-5, C-10), 128.3 (d, J_{PC} = 6.2 Hz, C-4, C-11), 128.6–128.8 (m, C-3′A, C-4′A, C-3′B), 129.1 (C-4′B), 130.7 (d, J_{PH} = 16.3 Hz, C-3, C-12), 131.0 (d, J_{PC} = 7.8 Hz, C-2, C-13), 132.7 (C-6a, C-8a), 132.8 (C-4a, C-10a), 133.9 (d, J_{PC} = 23.2 Hz, C-1, C-14), 133.9 (d, J_{PC} = 20.5 Hz, C-2′A), 134.2 (d, J_{PC} = 11.5 Hz, C-14a, C-14d), 134.8 (d, J_{PC} = 20.4 Hz, C-2′B), 136.9 (d, J_{PC} = 11.8 Hz, C-1′A), 137.6 (d, J_{PC} = 11.2 Hz, C-1′B).

^{31}P NMR (CD_2Cl_2, 162 MHz): δ = –3.39 (s).

MS (EI, 70 eV): *m*/*z* (%) = 646 (54, M^+), 569 (9, $[M-C_6H_5]^+$), 537 (4, $[M-C_6H_6P]^+$), 459 (29, $[537-C_6H_6]^+$), 381 (22, $[459-C_6H_6]^+$), 350 (26, $[459-C_6H_6P]^+$), 305 (100), 276 (40, $[M-2Ph_2P]^+$), 183 (52, $C_{12}H_8P^+$).

IR (KBr): ν = 3030 (ar. C—H), 2990, 1570 (ar. C—C), 1460, 1420, 1280, 1070 (ar. C—H ip), 830 (ar. C—H oop), 720 (P—C), 670 cm^{-1}.

$C_{46}H_{32}P_2$ calc.	C	85.43	H 4.99
found		85.20	4.80

2,15-Bis(diphenylphosphanyl)hexahelicene (2, [6]-Heliphos):

Prepared according to General Procedure 5. The starting material **11** had to be finely ground to achieve maximum transformation.

Phosphane **2** was crystallized from toluene by cautious addition of cyclohexane. The yellowish, light- and air-sensitive crystals (28 %) obtained contained one mol equiv of toluene, which was easily lost under vacuum resulting in a yellow powder; R_f (silica gel, cyclohexane/toluene 1:1) = 0.37; mp 207–208 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 6.82$ (ddd, $J = 8.2$ Hz, $J_{PH} = 7.6$ Hz, $^4J = 1.3$ Hz, 4 H, 2′A-H), 6.93 (ddd, $J = 8.2$ Hz, $J_{PH} = 7.6$ Hz, $^4J = 1.3$ Hz, 4 H, 2′B-H), 7.03 (ddd, $J = 8.2$ Hz, $J = 7.4$ Hz, $J_{PH} = 1.5$ Hz, 4 H, 3′A-H), 7.10 (ddd, $J = 8.2$ Hz, $J = 7.4$ Hz, $J_{PH} = 1.5$ Hz, 4 H, 3′B-H), 7.14 (dd, $J = 8.1$ Hz, $J_{PH} = 4.7$ Hz, $^4J = 1.8$ Hz, 2 H, 3-H, 14-H), 7.14 (dtt, $J_{PH} = 1$ Hz, $J = 7.4$ Hz, $^4J = 1.3$ Hz, 2 H, 4′A-H), 7.21 (dtt, $J_{PH} = 1$ Hz, $J = 7.4$ Hz, $^4J = 1.3$ Hz, 2 H, 4′B-H), 7.66 [d (br), $J = 8.1$ Hz, 2 H, 4-H, 13-H], 7.79 (d, $J = 8.6$ Hz, 2 H, 5-H, 12-H), 7.81 (md, $J_{PH} = 11.2$ Hz, 2 H, 1-H, 16-H), 7.84 (d, $J = 8.6$ Hz, 2 H, 6-H, 11-H), 7.85 (d, $J = 8.3$ Hz, 2 H, 7-H, 10-H), 7.88 (d, $J = 8.3$ Hz, 2 H, 8-H, 9-H).

^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 123.6$ (C-16c), 126.7 (C-8, C-9), 127.1 (C-7, C-10), 127.1 (C-6, C-11), 127.7 (C-5, C-12), 127.7 (C-16b, C-16d), 127.8 (d, $J_{PC} = 5.1$ Hz, C-4, C-13), 128.1 (C-4′A), 128.2 (C-4′B), 128.2 (d, $J_{PC} = 6.7$ Hz, C-3′A), 128.3 (d, $J_{PC} = 6.9$ Hz, C-3′B), 129.6 (d, $J_{PC} = 11.3$ Hz, C-16a, C-16e), 130.1 (d, $J_{PC} = 10.7$ Hz, C-3, C-14), 131.2 (C-6a, C-10a), 132.0 (C-4a, C-12a), 132.9 (d, $J_{PC} = 6.6$ Hz, C-2, C-15), 133.0 (C-8a), 133.3 (d, $J_{PC} = 19.0$ Hz, C-2′A), 133.5 (d, $J_{PC} = 19.4$ Hz, C-2′B), 134.6 (d, $J_{PC} = 33.8$ Hz, C-1, C-16), 137.0 (d, $J_{PC} = 11.0$ Hz, C-1′B), 137.1 (d, $J_{PC} = 11.3$ Hz, C-1′A).

^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = -3.39$ (s).

MS (FD, toluene): $m/z = 696$ (M^+).

IR (KBr): $\nu = 3030$ (ar. C–H), 1570 (ar. C–C), 1460, 1420, 1170, 1075 (ar. C–H ip), 980, 830 (ar. C–H oop), 720 (P-C), 670 cm^{-1}.

$C_{50}H_{34}P_2$	calc.	C 86.19	H 4.92
	found	86.11	5.05

2,7-Dimethylnaphthalene (5a):

According to General Procedure 1. Colorless, nacreous, blade-shaped crystals (74–81 %); R_f (silica gel, PE) = 0.41; R_f (silica gel, CH_2Cl_2) = 0.85; R_f (silica gel, CCl_4) = 0.56; mp 95–96 °C (Lit.[9] 95 °C).

^{1}H NMR ($CDCl_3$, 80 MHz): $\delta = 2.45$ (s, 6 H, CH_3), 7.16 (dd, $J = 8$ Hz, $^4J = 2$ Hz, 2 H, H-3, H-6), 7.44 (s, (br), 2 H, H-1, H-8), 7.62 (d, $J = 8$ Hz, 2 H, H-4, H-5).

2-Chloro-7-methylnaphthalene (5b):

From **4b** following General Procedure 1. Colorless, nacreous, blade-shaped crystals (11–20 %); R_f (silica gel, PE) = 0.44; R_f (silica gel, CCl_4) = 0.53; mp 125–126 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 2.47$ (s, 3 H, CH_3), 7.29 (dd, $J = 8.5$ Hz, $^4J = 1.5$ Hz, 1 H, H-6), 7.32 (dd, $J = 8.5$ Hz, $^4J = 2.0$ Hz, 1 H, H-3), 7.50 (s br, 1 H, H-8), 7.70 (d, $J = 8.5$ Hz, 1 H, H-5), 7.71 (dd, $J = 8.5$ Hz, 1 H, H-4), 7.71 (d, $^4J = 2.0$ Hz, 1 H, H-1).

$C_{11}H_9Cl$	calc.	C 74.79	H 5.13
	found	74.78	5.15

From the mother liquors of the crystallization the isomeric *1-chloro-6-methylnaphthalene* (**6b**) could be isolated in the form of a colorless oil.

^{1}H NMR ($CDCl_3$, 60 MHz): $\delta = 2.30$ (s, 3 H, CH_3), 6.9–7.6 (m, 5 H, arom. H), 8.10 (d, $J = 8$ Hz, 1 H, H-8).

2-Bromo-7-methylnaphthalene (5c):

To a suspension of **18** (170 g, 0.30 mol) in anhyd THF (1.0 L) under N_2 1.6 M BuLi in hexane (200 mL, 0.32 mol) was added slowly maintaining a temperature of less then −60 °C. The mixture was warmed up to 0 °C for 30 min causing the formation of a deep red colored solution, which was cooled to −75 °C again. At this temperature, a solution of 3-bromobenzaldehyde (65 g, 0.35 mol) in THF (100 mL) was added dropwise. The mixture was stirred at r.t. for 16 h, then NEt_3 (5 mL) was added and the mixture was evaporated onto silica gel (~ 600 mL). This was brought onto a pad of silica gel (~ 300 mL) and the product was eluted with toluene. The solvent was removed in vacuo, then HOAc (2 × 250 mL) was added and evaporated again (to remove traces of toluene which interfere with the following reaction), before the cyclization was performed as described in General Procedure 1. Colorless crystals (15.6 g, 22 %); R_f (silica gel, CCl_4) = 0.60; mp 136–137 °C.

^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 2.50$ (s, 3 H, CH_3), 7.31 (dd, $J = 8.4$ Hz, $^4J = 1.6$ Hz, 1 H, H-6), 7.46 (dd, $J = 8.7$ Hz, $^4J = 1.9$ Hz, 1 H, H-3), 7.50 (s br, 1 H, H-8), 7.65 (d, $J = 8.7$ Hz, 1 H, H-4), 7.69 (d, $J = 8.4$ Hz, 1 H, H-5), 7.90 (d, $^4J = 1.9$ Hz, 1 H, H-1).

^{13}C NMR ($CDCl_3$, 62.9 MHz): $\delta = 21.7$ (CH_3), 119.9 (C-2), 126.0 (C-8), 127.6 (C-5), 128.3 (C-3), 128.6 (C-6), 129.3 (C-1 + C-4), 130.2 (C-4a), 134.8 (C-8a), 136.7 (C-7).

IR (KBr): $\nu = 3050$ (ar. C–H), 2910, 2840 (al. C–H), 1615, 1580 (ar. C–C), 1500, 1050, 895, 825, 700 (arom.).

$C_{11}H_9Br$	calc.	C 59.76	H 4.10
	found	59.75	4.10

2,7-Bis(bromomethyl)naphthalene (8):[11]

Prepared from **5a** according to General Procedure 2. After removal of the CH_2Cl_2 in vacuo, the residue was taken up in a minimum amount of benzene (~ 100 mL) and the same amount of cyclohexane was added. After completion of the crystallization it was filtered and dried in vacuo. Crystallization was repeated until the ^{1}H NMR showed no CH_3 peak ($\delta = 2.45$). Colorless blades (64 %); R_f (silica gel, PE) = 0.00; R_f (silica gel, CH_2Cl_2) = 0.83; R_f (silica gel, CCl_4) = 0.40; mp 147 °C (lit.[11] 147 °C).

^{1}H NMR ($CDCl_3$, 80 MHz): $\delta = 4.60$ (s, 4 H, CH_2Br), 7.43 (dd, $J = 9$ Hz, $^4J = 2$ Hz, 2 H, H-3, H-6), 7.71 (s br, 2 H, H-1, H-8), 7.74 (d, $J = 9$ Hz, 2 H, H-4, H-5).

2,7-Bis(triphenylphosphoniomethyl)naphthalene Dibromide (9):

Prepared from **8** following General Procedure 5. Colorless powder (94–99 %).

^{1}H NMR (DMSO-d_6, 80 MHz): $\delta = 5.36$ (d br, $J = 16$ Hz, 4 H, CH_2P^+), 6.9–8.1 (m, 36 H, arom. H).

2,7-Bis(4-bromostyryl)naphthalene (10):

To a solution of Na (1.0 g, 43 mmol) in dry MeOH (150 mL) under N_2 2,7-bis(triphenylphosphoniomethyl)naphthalene dibromide (**9**, 27 g, 33 mmol) was added in small portions, resulting in an orange solution. A solution of freshly distilled 4-bromobenzaldehyde (13 g, 70 mmol) in dry MeOH (50 mL) was added dropwise resulting in decolorization and the formation of a precipitate. After stirring at r.t. was continued for 16 h, the mixture was slightly acidified by addition of conc. HCl and concentrated to dryness. The residue was distributed between H_2O and toluene, the aqueous layer was extracted several times with toluene (some undissolved material remained) and the combined organic extracts were filtered through alumina (100 mL) after drying (Na_2SO_4). The solvent of the eluate was removed and the remainder was taken up in warm THF (100 mL), filtered and crystallized by slow addition of PE (final temperature: −30 °C). After drying in vacuo, a colorless powder (11.2 g, 70 %) was obtained, which melted around 155 °C, forming a very high melting product.

^{1}H NMR ($CDCl_3$, 60 MHz): $\delta = 6.1–6.3$ (m, 4 H, CH=CH), 7.0–7.9 (m, 14 H, arom. H).

MS (EI, 70 eV): m/z (%) = 490 (100, M^+), 408 (8, $[M-HBr]^+$), 330 (28, $[M-Br_2]^+$), 253 (28, $[330-C_6H_5]^+$), 228 (92, $[253-C_2H_2]^+$).

2,15-Dibromohexahelicene (11):

Photocyclization of **10** according to General Procedure 4 yielded yellow crystals (67 %), halving of the initial concentration increased the yield to 73 %; R_f (silica gel, cyclohexane/toluene 1:1) = 0.79.

^{1}H NMR (CS_2/CD_2Cl_2 9:1, 400 MHz): $\delta = 7.30$ (dd, $J = 8.5$ Hz, $^4J = 1.9$ Hz, 2 H, 3-H, 14-H), 7.59 (ddd, $^4J = 1.9$ Hz, $^nJ = 0.7$ Hz, $^nJ = 0.4$ Hz, 2 H, 1-H, 16-H), 7.67 (d, $J = 8.5$ Hz, 2 H, 4-H, 13-H), 7.85 (d br, $J = 8.5$ Hz, 2 H, 5-H, 12-H), 7.91 (d, $J = 8.5$ Hz, 2 H, 6-H, 11-H), 7.93 (d, $J = 8.2$ Hz, 2 H, 7-H, 10-H), 7.97 (d, $J = 8.2$ Hz, 2 H, 8-H, 9-H).

^{13}C NMR (CS_2/CD_2Cl_2 9 : 1, 100.6 MHz): $\delta = 119.9$ (C-2, C-15), 124.0 (C-16c), 126.6 (C-16b, C-16d), 127.0 (C-6, C-11), 127.8 (C-7, C-10), 127.9 (C-5, C-12), 128.0 (C-8, C-9), 129.2 (C-3, C-14), 129.5 (C-4, C-13), 130.1 (C-1, C-16), 130.7 (C-4a, C-12a), 130.9 (C-16a, C-16e), 132.1 (C-6a, C-10a), 133.5 (C-8a).

IR (KBr): $\nu = 3030$ (ar. C—H), 1580 (C—C), 1455, 1060 (ar. C—H ip), 980, 830 (ar. C—H oop), 810, 795 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 486 (100, M^+ (^{81}Br)), 484 (49, M^+), 404 (4, [M-HBr]$^+$), 324 (98, [M-2Br]$^+$), 300 (40), 163 (27).

$C_{26}H_{14}Br_2$	calc.	C 64.23	H 2.90
	found	64.19	3.09

2-Bromo-15-(diphenylphosphanyl)hexahelicene (12):
This product formed in 34% yield during the synthesis of **2**. The use of 1.7 M *t*-BuLi in pentane increased the yield of **12** (yellowish crystals) to 71%; R_f (silica gel, cyclohexane/toluene 1 : 1) = 0.59.

MS (FD, toluene): $m/z = 592$ (M^+).

[(7-Chloro-2-naphthyl)methyl]triphenylphosphonium Bromide (13a):
2-Chloro-7-methylnaphthalene (**5b**, 10 g, 57 mmol) was photobrominated according to General Procedure 2. After evaporation of the solvent the remainder was taken up in CH_2Cl_2, washed several times with H_2O and column filtered (silica gel, 60 mmØ × 80 mm). The product containing fractions were evaporated to dryness and the solid was reacted with PPh_3 according to General Procedure 3 (stirring for 3 d). The resulting colorless powder (23.7 g) contained ~9% of toluene even after prolonged drying, thus the yield was 74%.

^{1}H NMR ($CDCl_3$, 60 MHz): $\delta = 5.90$ (d, $J_{PH} = 15$ Hz, 2 H, CH_2P), 7.0–8.0 (m, 21 H, arom. H).

[(7-Bromo-2-naphthyl)methyl]triphenylphosphonium Bromide (13b):
Analogous to **13a** following General Procedures 2 and 3. Colorless powder (87%).

^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 5.73$ (d, $J = 15$ Hz, 2 H, CH_2), 7.20 (td, $^4J = 1.8$ Hz, $J = 8.5$ Hz, 1 H, H-3), 7.36 (d br, $J \approx 8.5$ Hz, 1 H, H-4), 7.37 (ddd, $J = 8.8$ Hz, $^4J = 1.9$ Hz, $J_{PH} = 1.0$ Hz, 1 H, H-6), 7.42 (d, $J = 8.8$ Hz, 1 H, H-5), 7.47 (md, $J \approx 3.5$ Hz, 1 H, H-1), 7.54–7.60 (m, 7 H, H-8, 3 × H-3′, 3 × H-5′), 7.70–7.75 (m, 3 H, 3 × H-4′), 7.75–7.81 (m, 6 H, 3 × H-2′, 3 × H-6′).

^{13}C NMR ($CDCl_3$, 62.8 MHz): $\delta = 30.5$ (d, $J = 46$ Hz, CH_2), 117.9 (d, $J = 86$ Hz, C-1′), 120.1 (d, $J = 2$ Hz, C-2), 126.2 (d, $J = 9$ Hz), 127.9 (d, $J = 3$ Hz), 129.0 (d, $J = 2$ Hz), 129.3 (d, $J = 4$ Hz), 129.6 (s br, C-4′), 130.1 (d, $J = 13$ Hz, C-3′, C-5′), 130.2 (d, $J = 7$ Hz), 130.8 (d, $J = 3$ Hz, C-4a), 133.7 (d, $J = 4$ Hz, C-8a), 134.6 (d, $J = 10$ Hz, C-2′, C-6′), 134.8 (d, $J = 3$ Hz).

^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = +24.1$ (s).

IR (KBr): $\nu = 3040$, 3005 (ar. C—H), 2890, 2820, 2770 (al. C—H), 1630, 1590 (ar. C—C), 1440 (CH_2 asymm.), 1115, 840, 755, 735, 690 (arom.) cm^{-1}.

(*E*/*Z*)-1,2-Bis(7-chloro-2-naphthyl)ethene (14a):
Oxidative coupling of **13a** according to General Procedure 6 yielded a yellowish powder (50%); R_f (silica gel, cyclohexane/toluene 4 : 1) = 0.60; R_f (silica gel, cyclohexane/toluene 1 : 1) = 0.88; mp ~155 °C.

^{1}H NMR ($CDCl_3$, 60 MHz): $\delta = 5.50$ and 5.80 (2 s, 2 H, CH=CH, $E/Z \approx 2:1$), 7.1–7.8 (m, 12 H, arom. H).

MS (EI, 70 eV): m/z (%) = 348 (100, M^+), 312 (37, [M-HCl]$^+$), 276 (27, [312-HCl]$^+$).

From the mother liquor of the crystallization *2-chloro-7-(ethoxymethyl)naphthalene* (**15a**); mp 45 °C, may be obtained by chromatography with toluene.

^{1}H NMR ($CDCl_3$, 60 MHz): $\delta = 1.20$ (t, $J = 7$ Hz, 3 H, CH_2CH_3), 3.50 (q, $J = 7$ Hz, 2 H, CH_2CH_3), 4.50 (s, 2 H, CH_2OEt), 7.1–7.7 (m, 6 H, arom. H).

MS (EI, 70 eV): m/z (%) = 220 (100, M^+), 176 (93, [M-C_2H_4O]), 175 (96, [M-C_2H_5O]).

(*E*)-1,2-Bis(7-bromo-2-naphthyl)ethene (14b):
Starting from **13b**, General Procedure 3 yields a light yellow solid (59%); R_f (silica gel, cyclohexane/toluene 1 : 1) = 0.77.

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 6.83$ (s, 2 H, –CH=), 7.33 (dd, $J = 8.5$ Hz, $^4J = 1.6$ Hz, 2 H, H-3), 7.50 (dd, $J = 8.8$ Hz, $^4J = 1.9$ Hz, 2 H, H-6), 7.58–7.64 (m, 6 H, H-1,5,4), 7.90 (d, $^4J = 1.8$ Hz, 2 H, H-8).

IR (KBr): $\nu = 3040$ (ar. C—H), 2900, 2830 (al. C—H), 1605, 1570 (ar. C—C), 1480, 1045, 895, 885, 825, 815, 795 cm^{-1}.

$C_{22}H_{14}Br_2$	calc.	C 60.31	H 3.22
	found	60.45	3.47

2,13-Dichloropentahelicen (16a):
According to General Procedure 4. Yellowish, air-sensitive crystals (32%); R_f (silica gel, cyclohexane/toluene 4 : 1) = 0.53; R_f (silica gel, cyclohexane/toluene 1 : 1) = 0.71; mp 165–170 °C.

^{1}H NMR (CS_2/CD_2Cl_2 9 : 1, 400 MHz): $\delta = 7.40$ (dd, $J = 8.6$, $^4J = 2.0$ Hz, 2 H, 3-H, 12-H), 7.75 (d, $J = 8.5$ Hz, 2 H, 6-H, 9-H), 7.78 (s, 2 H, 7-H, 8-H), 7.80* (d, $J = 8.5$ Hz, 2 H, 5-H, 10-H), 7.81 (d, $J = 8.6$ Hz, 2 H, 4-H, 11-H), 8.36* (d, $^4J = 2.0$ Hz, 2 H, 1-H, 14-H).

*These signals were broadened due to their long range coupling.

^{13}C NMR (CS_2/CD_2Cl_2 9 : 1, 100.6 MHz): $\delta = 126.2$ (C-14b, C-14c), 127.0 (C-6, C-9), 127.4 (C-3, C-12), 127.7 (C-5, C-10), 127.1 (C-1, C-14), 128.1 (C-7, C-8), 129.7 (C-4, C-11), 131.1 (C-4a, C-10a), 131.4 (C-2, C-13), 131.5† (C-14a, C-14d), 133.1† (C-6a, C-8a).

†These signals suffered a high field shift (approx. 0.1 ppm) when the CD_2Cl_2 concentration was raised.

MS (EI, 70 eV): m/z (%) = 346 (61, M^+), 310 (26, M^+-HCl), 276 (100, M^+-2 Cl), 175 (4, $C_{11}H_8Cl$).

IR (KBr): $\nu = 3030$ (ar. C—H), 2910, 1585 (ar. C—C), 1490, 1460, 1415, 1080 (ar. C—H ip), 930, 885, 835 (ar. C—H oop), 805 cm^{-1}.

$C_{22}H_{12}Cl_2$	calc.	C 76.10	H 3.43
	found	76.22	3.74

2,13-Dibromopentahelicene (16b):
According to General Procedure 4. Yellowish crystals (37%); R_f (silica gel, cyclohexane/toluene 1 : 1) = 0.76; mp 235–240 °C. Workup of the mother liquors increased the yield to 51%.

^{1}H NMR (CS_2/CD_2Cl_2 9 : 1, 400 MHz): $\delta = 7.55$ (dd, $J = 8.5$ Hz, $^4J = 1.9$ Hz, 2 H, 3-H, 12-H), 7.76 (td, $^nJ = 0.4$ Hz, $J = 8.5$ Hz, 2 H, 4-H, 11-H), 7.79 (d, $J = 8.6$ Hz, 2 H, 6-H, 9-H), 7.80 (s, 2 H, 7-H, 8-H), 7.82 (td, $^nJ = 0.5$ Hz, $J = 8.6$ Hz, 2 H, 5-H, 10-H), 8.55 (qd, $^nJ = 0.7$ Hz, $^4J = 2.0$ Hz, 2 H, 1-H, 14-H).

The long range coupling constants ^nJ were determined after line sharpening using a Gaussian algorithm.

^{13}C NMR (CS_2/CD_2Cl_2 9 : 1, 100.6 MHz): $\delta = 119.7$ (C-2, C-13), 126.1 (C-14b, C-14c), 127.1 (C-6, C-9), 127.8 (C-5, C-10), 128.2 (C-7, C-8), 129.7 (C-4, C-11), 130.1 (C-3, C-12), 131.1 (C-1, C-14), 131.3 (C-4a, C-10a), 131.7 (C-14a, C-14d), 133.1 (C-6a, C-8a).

MS (EI, 70 eV): m/z (%) = 436 [21, M^+(^{81}Br)], 434 (11, M^+), 276 (100, M^+-2 Br), 219 (17, $C_{11}H_8Br$), 139 (25, $C_{11}H_8$).

IR (KBr): $\nu = 3030$ (ar. C—H), 2910, 1590 (ar. C—C), 1500, 1475, 1425, 1085 (ar. C—H ip), 940, 905, 835 (ar. C—H oop), 820 cm^{-1}.

$C_{22}H_{12}Br_2$	calc.	C 60.84	H 2.79
	found	60.84	2.93

(1,1-Diethoxy-3-butyl)triphenylphosphonium Bromide (18):
A solution of but-2-enal (**17**, 45 mL, 0.54 mol) in CH_2Cl_2 (500 mL) was added to a mixture of PPh_3 (130 g, 0.50 mol), 48% HBr in H_2O (70 mL, 0.62 mol), EtOH (100 mL), and CH_2Cl_2 (100 mL) at −10 °C in the course of 12 h. After completion of the addition, stirring was continued for 3–4 h at r.t. Then, the aqueous layer was removed and the mixture was cooled to 0 °C, before $CH(OEt)_3$ (350 mL, 2.1 mol) was added. The temperature was raised to r.t. over 3 h, then NEt_3 (28 mL, 0.20 mol) was added and all volatiles were removed in vacuo. The oily residue was stirred with a mixture of toluene (200 mL) and cyclohexane (1.5 L), then the solvent was decanted and replaced by dry Et_2O (1.0 L) and stirring was continued until the oil solidified. The supernatant solvent was replaced

by a fresh portion of Et_2O (1.0 L) and stirring was continued for 1–3 h until a fine powder resulted, which was filtered off and dried in vacuo. White powder (267 g), melting at ~110 °C. The compound contained approximately stoichiometric amounts of Et_2O, which could not be removed in vacuo, implying that the compound crystallized with 1 mol of Et_2O. The yield calculated for an etherate was 95 %.

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.20$ and 1.27 (2 t, $J = 7.0$ Hz, 6 H, 2 × CH_2CH_3), 1.37–1.51 (m, 1 H, H-2), 1.52 (dd, $J_{PH} = 20.0$ Hz, $J = 6.9$ Hz, 3 H, H_3-4), 1.81 [s br, 1 H, 0.5 H_2O], 2.14 (ddd, $J_{PH} = 14.4$ Hz, $^2J = 13.9$ Hz, $J = 4.9$ Hz, 1 H, H-2), 3.65–3.83 (m, 4 H, 2 × CH_2CH_3), 4.83–4.90 (m, 1 H, H-3), 5.09 (t, $J = 4.9$ Hz, 1 H, H-1), 7.69–7.74 (m, 6 H, H-3′, H-5′), 7.77–7.82 (m, 3 H, H-4′), 7.91–7.97 (m, 6 H, H-2′, H-6′).

^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = +31.9$ (s).

Crystal Structure Analysis of 1:

Crystal data: $C_{46}H_{32}P_2$, colorless; dimensions: 0.40 × 0.38 × 0.36 mm^3, $M = 646.66\ g\,mol^{-1}$, monoclinic, space group C2/c, $a = 13.781$ (3), $b = 12.447$ (2), $c = 20.512$ (4) Å, $\beta = 105.10$ (3)°, $V = 3397$ (1) $Å^3$, $Z = 4$, $D_c = 1.264\ g\,cm^{-1}$, Mo-Kα radiation, $\lambda = 0.71069$ Å (graphite monochromator), $\mu = 1.61\ cm^{-1}$.

Data collection: The intensity data for the compound were collected on an Enraf-Nonius CAD4 diffractometer, using the $\omega - 2\theta$ scan technique at −90 °C. 9179 reflections were measured, of which 4588 were independent reflections with θ in the range of 1–27.4°, 2599 reflections having $I > 2\sigma(I)$. The data were corrected for Lorentz and polarization effects but not for absorption.[20]

Structure Solution and Refinement: The structure was solved by direct methods (SHELXS-86)[21] and refined with the full-matrix least-squares procedures against Fo^2 (SHELXL-93)[22] with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with fixed thermal parameters. The refinement converged at $R1 = 0.056$ and $wR2 = 0.131$. The difference Fourier synthesis on the basis of the final structural model showed[23] a maximum of 0.58 $eÅ^{-1}$ and a minimum of −0.45 $eÅ^{-1}$.

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