Enantioselective Catalysis, 111[◇]

New Chiral Expanded Phosphanes Derived from Substituted Deltacyclenes

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Received April 28, 1997

Keywords: Deltacyclenes / Deltacyclanes / P−H addition reactions / Chiral phosphanes / Enantioselective catalysis

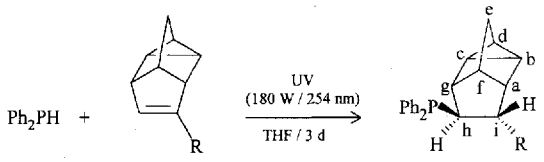
The suitability of enantiomerically pure deltacyclenes as building blocks in the synthesis of expanded phosphanes was examined. Different substituted deltacyclenes were irradiated with diphenylphosphane and three bisphosphanyl derivatives. With these P−H addition reactions, new chiral deltacyclane-derived phosphorus ligands were synthesized. They were tested in the Rh-catalyzed asymmetric hydrogenation of (*Z*)-(α)-*N*-acetamidocinnamic acid and in the Pd-catalyzed asymmetric allylation of 1,5-dimethylbarbituric acid.

Introduction

In the last decades many optically active phosphanes where synthesized, mainly for application as ligands in enantioselective catalysis with transition metal compounds[2][3]. Most of them contain a chiral skeleton bearing two diphenylphosphane groups. The chiral information is transferred from the ligand to the catalytically active metal center via the arrangement of the phenyl rings of the diphenylphosphane groups. In enzymes and receptors, nature uses large molecules, which form chiral pockets around the catalytically active centers. We are working on the synthesis of expanded phosphanes[4][5][6][7][8][9], trying to establish a similar pocket-building architecture in enantioselective catalysts. These expanded phosphanes should contain a chelating system which binds the ligand tightly to the metal atom and several layers attached to the phosphorus atoms to form dendrimeric ligands. The examples known to date consist of an achiral PP chelate backbone, one or two layers of achiral branching units and finally a peripheral layer of chiral units. However, the chirality transfer with these ligands up to now is ineffective as reflected in the low enantioselectivity of catalytic reactions. In a new approach we tried to synthesize expanded phosphanes, in which the first layer, next to the metal center, is built up from chiral units. We resorted to enantioselectively formed deltacyclenes which can be connected to the phosphorus atoms and allow further substitutions[10].

Syntheses

In a previous paper[11] we had described the syntheses of a series of new enantiomerically pure substituted deltacyclenes. These deltacyclenes should be attached to the P-atoms of primary or secondary phosphanes by adding the P−H functions to the C=C bond of the deltacyclene system[12]. For olefins, in which the C=C bond is conjugated to an electron withdrawing group, the addition occurs thermally[13] or in the presence of a catalytic amount of a strong base, such as potassium *tert*-butoxide[14]. For unactivated olefins, e.g. our deltacyclenes, the addition is possible under drastic conditions in a radical reaction. UV light or AIBN have proven to be the best initiators for this kind of reaction[15]. First we tried to react diphenylphosphane with the deltacyclenes **1**−**4** (Scheme 1). 1.1 equivalents of Ph_2PH were irradiated with **1**−**4** in THF in a Schlenk tube for 3 d with a 180 W UV lamp (254 nm). Then the solvent was evaporated and the products were isolated by chromatography on silica gel using petroleum ether/ether mixtures.



R =		yield
1	phenyl	**5** 49 %
2	(o-MeO)phenyl	**6** 51 %
3	(o-$PhCH_2O$)phenyl	**7** 4 %
4	(o-$MeOCH_2CH_2O$)phenyl	**8** 52 %

The addition of Ph_2PH to the double bond in **1** gave the monodentate phosphane **5**. In principle the arrangement of the diphenylphosphane group and the phenyl group can occur in up to six different ways and in fact, the $^{31}P\{^1H\}$-NMR spectrum of the crude product showed three singlets at δ = −5.46, −14.28, and −18.72 in a ratio of about 30:1.5:1. After recrystallization from methanol, the pure compound **5** could be isolated as colorless needles in 49% yield (Scheme 1). Its $^{31}P\{^1H\}$-NMR spectrum exhibited

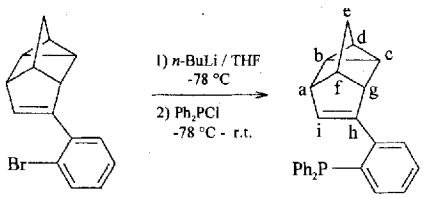
[◇] Part 110: Ref.[1].

  0009−2940/97/1010−1495 $ 17.50+.50/0

only the singlet at $\delta = -5.46$ and **5** could be identified as 8-*exo*-(*S*)-diphenylphosphanyl-9-*endo*-(*R*)-phenyldeltacyclane (spectroscopic characterization see below).

The reaction of the anisole derivative **2** with Ph_2PH gave the desired product **6** after recrystallization from methanol diasteromerically pure in 51% yield. Its $^{31}P\{^1H\}$-NMR spectrum showed only a singlet at $\delta = -6.00$. We also tried the addition of Ph_2PH to the double bond in **3** which should be similarly reactive as **2**. With respect to further derivatization it should be easier to remove the benzyl group in **7**, e.g. by hydrogenolysis, than the methyl group in **6**. After irradiation for 3 d and subsequent chromatography about 65% of the deltacyclene **3** was reisolated. Two products had been formed. The second product eluted in the chromatography was identified as benzyldiphenylphosphane (10% yield). The first eluted product was the desired addition product **7** (4% yield). The $^{31}P\{^1H\}$-NMR spectrum of crude **7** showed three singlets at $\delta = -5.51$, -16.11, and -18.63 in a ratio similar to **5**. After the irradiation of Ph_2PH and **4** the desired product **8** containing a small amount of a side-product was isolated in about 20% yield. Irradiation of a mixture of two equivalents of Ph_2PH and one equivalent of **4** without any solvent for 5 d gave after chromatography and recrystallization from pentane **8** in 52% yield as colorless needles. Its $^{31}P\{^1H\}$-NMR spectrum showed only a singlet at $\delta = -5.85$ (Scheme 1).

Treatment of **9** with 1 equivalent of *n*BuLi in hexane at $-78\,^\circ C$ and subsequent reaction with Ph_2PCl at the same temperature gave **10** as a colorless solid in 56% yield after chromatography on silica gel using a mixture of petroleum ether/toluene (Scheme 2). Because the existing chiral centers can reasonably be expected to maintain their stereochemistry under the given reaction conditions, **10** should have the same optical purity of 98% ee which had been established for **9**[11].



9 **10**

All the new optically active phosphanes **5**, **6**, **8**, and **10** were characterized by mass spectrometry. In the EI mass spectra the molecular ions were detected, followed by the typical fragmentation pattern.

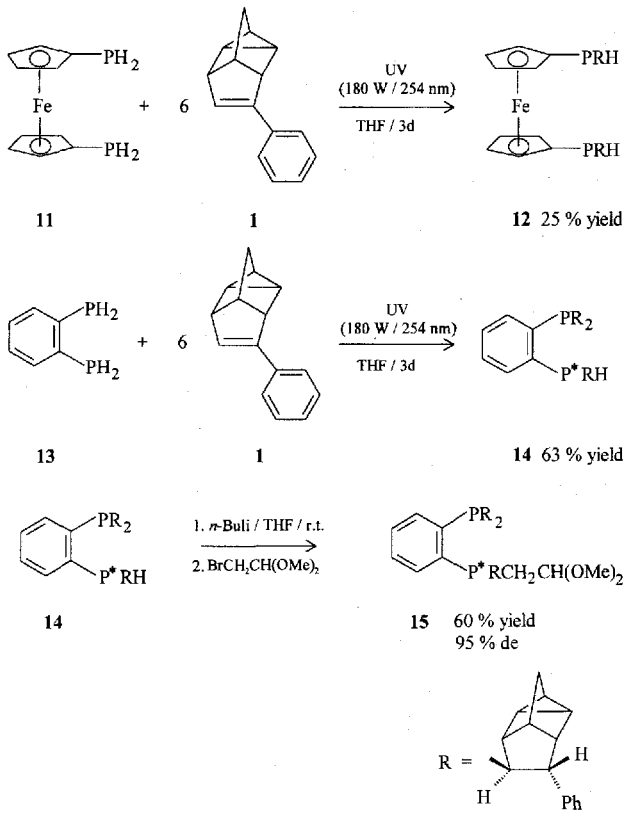
In addition to the successful conversions of **1**–**4** into **5**–**8**, several other deltacyclenes were irradiated with Ph_2PH. These deltacyclenes contained either reactive groups, such as halogens or ester functions which gave untractable mixtures of by-products, or large substituents, such as ferrocene, which did not allow a P–H addition reaction due to steric effects. Further details concerning these reactions are disclosed in ref.[10]

As mentioned above, for compounds **5**, **6**, and **8** up to six different isomers (and their enantiomers) are possible. However, after recrystallization they only show one singlet in the ^{31}P-NMR spectra. In the ^{13}C-NMR spectra of the compounds **5**, **6**, and **8** only one signal of the carbon atoms in the cyclopropane ring ($\delta = 10-20$) shows a strong coupling to the phosphorus atom ($^3J_{PC}$ ca. 16 Hz). This must be the signal of C_c (see Scheme 1). On the basis of a ^{13}C-^1H correlation we assigned the signal at $\delta = 1.22-1.27$ in the ^1H-NMR spectra, which is always a double triplet and the signal at lowest field of the three protons of the cyclopropane ring, to the proton H_c. This exhibits a NOE with the proton, the signal of which appears as a double doublet at $\delta = 1.96-1.97$. This therefore must be H_h and the doublet of doublet of doublet at $\delta = 3.24-3.82$ must be due to H_i. Because H_i exhibits a large NOE with H_f and H_h does not, H_i must be in an *exo* position and H_h in an *endo* position. This is the basis of our structural assignment for the compounds **5**–**8** in Scheme 1.

After irradiation of 1,2-bisphosphanylethane with **1** a mixture of the fourfold, threefold, and twofold addition products (together with a couple of by-products) was obtained, which could not be separated[10]. Reaction of the ferrocenyl phosphane **11** with **1** gave the twofold-adduct **12** as an orange oil in about 25% yield (Scheme 3) and a crystalline orange compound. **12** was characterized by its ^{31}P-NMR spectrum (2 broad signals) and its FD mass spectrum, which showed only the molecular ion at $m/z = 638.2$. The m/z value of the orange solid was 2 units less. Its ^{31}P-NMR spectrum exhibited 2 resonances at $\delta = 21.4$ and 5.9, which formed structured triplets. Its nature remains open (it could be a product with a P–P bond formed by oxidative coupling of 2 P–H bonds in **12**); the same is true for the configuration at the stereogenic P-atoms in **12**. Further irradiation of **11** with **1** only enlarged the yield of the crystalline by-product.

The reaction of 1,2-bisphosphanylbenzene **13** with **1** gave the threefold addition product **14** after recrystallization from ethanol in 63% yield (Scheme 3). Because the phosphorus atom of the PHR group is chiral, **14** exists in two diastereomeric forms. The ^{31}P-NMR spectrum shows two AB systems in a ratio of about 2:1. In the FD mass spectrum there is only the peak of the molecular ion. A larger excess of **1** during the irradiation, a longer reaction time or a further irradiation of **13** with **1** do not lead to the desired fourfold adduct. Obviously, the attachment of a fourth deltacyclene moiety to **14** is sterically hindered.

Substitution of the remaining P–H bond in **14** with a functional group should give a new bidentate phosphorus ligand, which is not C_2-symmetric. We deprotonated **14** with one equivalent of *n*BuLi at room temperature and treated the resulting phosphide anion with bromoacetaldehydedimethylacetal (Scheme 3). After chromatography on silica gel and recrystallization from acetone, **15** was obtained as colorless needles in 60% yield. Compound **15** also has a chiral phosphorus atom and we expected a mixture of two diastereomeres similar to **14**. However, the ^{31}P-NMR spectrum indicated only the four lines of one AB system, revealing its isomeric purity. Before crystallization the crude product contained about 5% of a second diastereomer.



Thus, **15** is formed with a high diastereomeric excess controlled by the three deltacyclane substituents. **15** is a bidentate expanded phosphorus ligand, which is built up of 24 stereogenic carbon atoms and one chiral phosphorus atom. After hydrolysis of the dimethylacetal to give the aldehyde function it should be possible to introduce primary amines into ligand **15** by simple Schiff base condensation.

Catalysis

The new chiral phosphorus ligands **5**, **6**, **8**, **10**, **14**, and **15** were tested in the Rh-catalyzed asymmetric hydrogenation of (*Z*)-(α)-*N*-acetamidocinnamic acid[16][17][18] and/or in the Pd-catalyzed asymmetric allylation of 1.5-dimethylbarbituric acid[19][20].

In the asymmetric hydrogenation reaction, the best results could be obtained with ligand **10** (1.1 bar H_2, 48 h, 60% yield, 27% ee and 20 bar H_2, 16 h, 100% yield, 10% ee, respectively; methanol/toluene solution, room temperature; in situ catalyst $[Rh(cod)Cl]_2$/**10**)[10]. In the asymmetric allylation reaction the monodentate ligands **5**, **6**, and **8** gave fairly good yields of 60–84% and enantioselectivities of 8.0–11.4% ee, which is not bad for this kind of reaction (bases NEt_3, DBU, quinine; Pd/ligand ratio 1:4)[10].

We thank the *Bayerische Forschungsverbund Katalyse (FORKAT)* and the *Fonds der Chemischen Industrie* for support of this work.

Experimental Section

General: All reactions were performed under nitrogen by using standard Schlenk techniques. Solvents were purified and dried by standard procedures. Diphenylphosphane[21], bisphosphanylethane[22], bisphosphanylferrocene **11**[23], and bisphosphanylbenzene **13**[24] were made as described in the literature. – ^{1}H-NMR, ^{31}P-NMR, and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker ARX 400 instrument (T = 21°C) using TMS as internal standard (^{1}H) or H_3PO_4 as external standard (^{31}P). – FD mass spectra were obtained on a Finnigan Mat 95 spectrometer and EI mass spectra on a Finnigan Mat 112 S spectrometer. – Melting points were measured on a Büchi Smp 20 instrument. – The optical rotations were determined on a Perkin-Elmer polarimeter 241 using CH_2Cl_2 Uvasol from Merck.

General Procedure for the Addition of Diphenylphosphane to Deltacyclenes: 1.1 equivalents of Ph_2PH were irradiated with 1 equivalent of **1**–**4** in ca. 2 equivalents of THF in a Schlenk tube externally for 3 d with a 180-W UV lamp (254 nm). Then the solvent was evaporated and the products were isolated by chromatography on silica gel using a mixture of petroleum ether/ether.

8-exo-(S)-Diphenylphosphanyl-9-endo-(R)-phenyldeltacyclane **5**: 2.2 g (11.3 mmol) of **1** were treated as described above. Recrystallization from hot methanol gave 2.1 g (5.5 mmol) of **5** as colorless needles in 49% yield, m.p. 111–112°C. – $[\alpha]^D_{r.t.}$ = −24 (c = 1; CH_2Cl_2). – ^{1}H NMR (400 MHz; $CDCl_3$): δ = 7.52–6.99 (m, 15 H, Ar-H), 3.24 (ddd, $^3J_{PH}$ = 20.4 Hz, ^3J = 3.9 Hz, ^3J = 6.0 Hz, 1 H, H_i), 2.97 (dd, $^2J_{PH}$ = 6.1 Hz, ^3J = 6.0 Hz, 1 H, H_h), 2.29 [s (br), 1 H, H_f], 2.19–2.16 (m, 2 H, $H_{a/g}$), 1.56–1.49 (m, $^2J_{AB}$ = 11.1 Hz, 2 H, H_e), 1.27 (dt, ^3J = 4.9 Hz, ^3J = 1.3 Hz, 1 H, H_c), 1.21 (dt, ^3J = 4.9 Hz, ^3J = 1.4 Hz, 1 H, H_d), 1.01 (dt, ^3J = 4.9 Hz, ^3J = 1.6 Hz, 1 H, H_b). – ^{13}C NMR (100 MHz; $CDCl_3$): δ = 12.2 (CH, C_b), 14.2 (d, $^4J_{PC}$ = 1.0 Hz, CH, C_d), 16.4 (d, $^3J_{PC}$ = 9.6 Hz, CH, C_c), 30.9 (CH_2, C_e), 41.8 (d, $^3J_{PC}$ = 2.8 Hz, CH, C_f), 43.8 (d, $^1J_{PC}$ = 11.4 Hz, CH, C_h), 47.4 (d, $^2J_{PC}$ = 16.8 Hz, CH, C_g), 51.0 (d, $^3J_{PC}$ = 3.9 Hz, CH, C_a), 51.9 (d, $^2J_{PC}$ = 15.5 Hz, CH, C_i); 125.5, 127.5, 127.7, 127.8, 127.9, 128.2, 128.3, 132.8, 134.1 (CH, C_{Ar}); 136.3 (d, $^1J_{PC}$ = 12.6 Hz, quart. C_{Ar}). 139.2 (d, $^1J_{PC}$ = 14.9 Hz, quart. C_{Ar}), 143.9 (d, $^3J_{PC}$ = 3.4 Hz, quart. C_{Ar}). – ^{31}P NMR (162 MHz; $CDCl_3$): δ = −5.5 (s). – $C_{27}H_{25}P$ (380.47): calcd. C 85.24, H 6.62; found C 85.60, H 6.28.

8-exo-(S)-Diphenylphosphanyl-9-endo-(R)-(2'-methoxyphenyl)-deltacyclane **6**: 3.9 g (17.4 mmol) of **2** were treated as described above. Recrystallization from hot methanol gave **6** (3.6 g; 8.9 mmol) as colorless needles in 51% yield, m.p. 75–76°C. – $[\alpha]^D_{r.t.}$ = −92 (c = 1; CH_2Cl_2). – ^{1}H NMR (400 MHz; $CDCl_3$): δ = 7.51–6.55 (m, 14 H, Ar-H), 3.81 (ddd, $^3J_{PH}$ = 20.9 Hz, ^3J = 3.8 Hz, ^3J = 6.3 Hz, 1 H, H_i), 3.52 (s, 3 H, MeO), 2.96 (dd, $^2J_{PH}$ = 6.6 Hz, ^3J = 6.3 Hz, 1 H, H_h), 2.36 (s (br), 1 H, H_f), 2.18–2.14 (m, 2 H, $H_{a/g}$), 1.55–1.49 (m, $^2J_{AB}$ = 15.2 Hz, 2 H, H_e), 1.26 (dt, ^3J = 5.1 Hz, ^3J = 2.0 Hz, 1 H, H_c), 1.19 (dt, ^3J = 5.1 Hz, ^3J = 1.4 Hz, 1 H, H_d), 0.89 (dt, ^3J = 5.1 Hz, ^3J = 1.7 Hz, 1 H, H_b). – ^{31}P NMR (162 MHz; $CDCl_3$): δ = −6.0 (s). – MS (EI); *m/z* (%): 410.3 (41) $[M]^+$, 379.3 (12) $[M - MeO]^+$, 224.1 (100) $[M - Ph_2P]^+$. – $C_{28}H_{27}OP$ (410.49): calcd. C 81.93, H 6.63; found C 81.47, H 6.52.

8-exo-(S)-Diphenylphosphanyl-9-endo-(R)-(2'-benzoxyphenyl)-deltacyclane **7**: 2.68 g (8.92 mmol) of **3** were treated as described above. Chromatography on aluminum oxide with petroleum ether/ether gave three bands. The first contained 65% of the starting material **3** and the third the by-product benzyldiphenylphosphane (10% yield). The second band consisted of a mixture of the desired P–H addition products. **7** (0.17 g; 0.36 mmol) was obtained as a colorless oil in 4% yield. – ^{31}P NMR (162 MHz; $CDCl_3$): δ = −5.5 (s, 88%); −16.1 (s, 6%), −18.63 (s, 6%). – MS (EI); *m/z* (%): 486.4 (25) $[M]^+$, 379.3 (19) $[M - PhCH_2O]^+$, 300.4 (100) $[M - Ph_2P]^+$.

8-exo-(S)-Diphenylphosphanyl-9-endo-(R)-[2'-(2''-methoxy)-ethoxy]phenyldeltacyclane **8**: 1.7 g (6.3 mmol) of **4** were treated as described above (no solvent). A double excess of Ph_2PH was used. The reaction time was 5 d. Recrystallization from pentane gave **8** (1.5 g; 3.3 mmol) as colorless needles in 52% yield, m.p. 52–53°C. – $[\alpha]_{r.t.}^{D} = -87$ (c = 1; CH_2Cl_2). – ^{1}H NMR (400 MHz; $CDCl_3$): δ = 7.49–6.56 (m, 14 H, Ar-H), 3.94–3.89 (m, 1 H, CH_2O), 3.82 (ddd, $^3J_{PH}$ = 21.0 Hz, ^3J = 3.8 Hz, ^3J = 6.3 Hz, 1 H, H_i), 3.62–3.49 (m, 3 H, CH_2O/H_m), 3.42 (s, 3 H, H_n), 2.96 (dd, $^2J_{PH}$ = 6.5 Hz, ^3J = 6.3 Hz, 1 H, H_h), 2.32 [s (br), 1 H, H_f], 2.17–2.12 (m, 2 H, $H_{a/g}$), 1.53–1.47 (m, $^2J_{AB}$ = 15.5 Hz, 2 H, H_e), 1.22 (dt, ^3J = 4.9 Hz, ^3J = 1.1 Hz, 1 H, H_c), 1.16 (t, ^3J = 4.9 Hz, 1 H, H_d), 0.86 (dt, ^3J = 4.9 Hz, ^3J = 1.6 Hz, 1 H, H_b). – ^{13}C NMR (100 MHz; $CDCl_3$): δ = 12.1 (CH, C_b), 14.1 (d, $^4J_{PC}$ = 1.0 Hz, CH, C_d), 16.2 (d, $^3J_{PC}$ = 9.9 Hz, CH, C_c), 31.0 (CH_2, C_e), 41.9 (d, $^3J_{PC}$ = 2.9 Hz, CH, C_f), 42.7 (d, $^2J_{PC}$ = 16.4 Hz, CH, C_i), 43.5 (d, $^1J_{PC}$ = 10.5 Hz, CH, C_h), 47.2 (d, $^2J_{PC}$ = 17.6 Hz, CH, C_g), 49.2 (d, $^3J_{PC}$ = 3.8 Hz, CH, C_a), 59.2 (CH_3, CH_3O), 67.6 (CH_2, CH_2OAr), 71.1 (CH_2, CH_2OMe); 111.2, 120.0, 126.3, 127.27, 127.34, 128.0 (CH, C_{Ar}); 128.17 (d, J_{PC} = 3.3 Hz, CH, C_{Ar}), 128.22 (d, J_{PC} = 1.7 Hz, CH, C_{Ar}), 132.4 (d, $^3J_{PC}$ = 3.2 Hz, quart. C_{Ar}), 132.7 (d, J_{PC} = 17.7 Hz, CH, C_{Ar}), 134.2 (d, J_{PC} = 19.3 Hz, CH, C_{Ar}), 136.4 (d, $^1J_{PC}$ = 12.5 Hz, quart. C_{Ar}), 139.5 (d, $^1J_{PC}$ = 5.0 Hz, quart. C_{Ar}), 156.4 (d, quart. C_{Ar-O}). – ^{31}P NMR (162 MHz; $CDCl_3$): δ = –5.9 (s). – MS (EI); *m/z* (%): 454.4 (5) $[M]^+$, 423.4 (5) $[M - MeO]^+$, 396.3 (100) $[M - CH_2{=}CHOMe]^+$, 268.2 (10) $[M - Ph_2P]^+$, 210.0 (37) $[M - CH_2{=}CHOMe - Ph_2P]^+$, 185.9 (18) $[Ph_2P]^+$, 59.1 (51) $[CH_2{=}CHOMe]^+$. – $C_{30}H_{31}O_2P$ (454.55): calcd. C 79.27, H 6.87; found C 79.37, H 7.05.

8-(2'-Diphenylphosphanylphenyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene **10**: 11.0 ml (17.6 mmol) of a 1.6 M solution of *n*BuLi in hexane were slowly added at –78°C to a solution of **9**[11] (4.4 g; 16.1 mmol) in 40 ml of THF. Then, at the same temperature, Ph_2PCl (3.75 g; 17 mmol) dissolved in 10 ml of THF was added. After warming up to room temperature, the solvent was evaporated and the residue was purified by chromatography on silica gel, using petroleum ether/toluene. Removal of the solvent gave **10** (3.4 g; 9.0 mmol) as a colorless solid in 56% yield, m.p. 29–32°C. – ^{1}H NMR (400 MHz; $CDCl_3$): δ = 7.35–6.87 (m, 14 H, Ar-H), 5.92 (dd, 1 H, $^5J_{PH}$ = 1.4 Hz, $^3J_{HH}$ = 3.0 Hz, H_i), 2.84 (s, 1 H, H_g), 2.60 (d, 1 H, ^3J = 3.0 Hz, H_a), 2.02 (s, 1 H, H_f), 1.71–1.68 (m, 1 H, H_d), 1.50 (d, 2 H, ^3J = 4.1 Hz, H_e), 1.47–1.43 (m, 1 H, H_c), 1.31–1.28 (m, 1 H, H_b). – ^{31}P NMR (162 MHz; $CDCl_3$): δ = –11.0 (s). – MS (EI); *m/z* (%): 378.0 (100) $[M]^+$, 300.0 (13) $[M - Ph]^+$, 220.9 (12) $[M - 2\ Ph]^+$, 182.9 (21) $[Ph_2P]^+$. – $C_{27}H_{23}P$ (378.45): calcd. C 85.69, H 6.13; found C 85.64, H 6.30.

P,P'-Bis(9-phenyldeltacyclan-8-yl)-1,1'-bisphosphanylferrocene **12**: A solution of **11** (0.8 g; 3.2 mmol) and **1** (3.7 g; 19.0 mmol) in 5 ml of THF was irradiated as described above. The product was isolated by chromatography on aluminum oxide with petroleum ether/ether. Two orange bands were obtained, the first contained the product **12** and the second a solid by-product. **12** (0.52 g; 0.81 mmol) was obtained as an orange oil in 25% yield. – ^{1}H{^{31}P} NMR (400 MHz; $CDCl_3$): δ = 7.35–7.17 (m, 10 H, H_{Ar}), 4.25 (s, 4 H, Cp), 4.19 (s (br), 4 H, Cp), 4.04 (s (br), 2 H, PH), 3.77–0.43 (m, 20 H, $H_{aliphat}$). – ^{31}P NMR (162 MHz; $CDCl_3$): δ = –56.4 [s (br)]; –79.8 [s (br)]. – MS (FD, CH_2Cl_2); *m/z* (%): 638.2 (100) $[MH]^+$.

P,P,P'-Tris(9-phenyldeltacyclan-8-yl)-1,2-bisphosphanylbenzene **14**: A solution of **13** (1.0 g; 7.0 mmol) and **1** (8.2 g; 42 mmol) in 5 ml of THF was irradiated as described above. Then the solvent was evaporated and the products were isolated by chromatography on silica gel using a mixture of petroleum ether/ether. Recrystallization of the crude product from ethanol gave **14** (3.2 g; 4.4 mmol) as colorless needles in 63% yield, m.p. 105–110°C. – $[\alpha]_{r.t.}^{D} = +85$ (c = 1; CH_2Cl_2). – ^{31}P NMR (162 MHz; $CDCl_3$): δ = –11.3 (d, J_{PP} = 119.0 Hz, 67%, PR_2), –12.4 (d, J_{PP} = 111.1 Hz, 33%, $P'R_2$), –32.3 (dd, J_{PP} = 111.1 Hz, J_{PH} = 213.7 Hz, 33%, P'RH), –38.6 (dd, J_{PP} = 119.0 Hz, J_{PH} = 215.5 Hz, 67%, PRH). – MS (FD, CH_2Cl_2); *m/z* (%): 724.3 (100) $[MH]^+$.

P,P,P'-Tris(9-phenyldeltacyclan-8-yl)-P'-(2',2'-dimethoxyethyl)-1,2-bisphosphanylbenzene **15**: A solution of **14** (3.3 g; 4.55 mmol) in 20 ml of THF is treated with 3.2 ml (5.1 mmol) of a 1.6 M solution of *n*BuLi in hexane. After stirring at room temperature for 1 h, the deep red solution was cooled to –78°C. Then bromoacetaldehydedimethylacetal (0.6 ml; 5.0 mmol) was added. After warming up to room temperature, the solvent was removed and the residue was purified by chromatography on silica gel using petroleum ether/ether. Recrystallization from hot acetone gave **15** (3.2 g; 3.9 mmol) as colorless needles in 87% yield, m.p. 154–156°C. – $[\alpha]_{r.t.}^{D} = +81$ (c = 1; CH_2Cl_2). – ^{1}H NMR (400 MHz; $CDCl_3$): δ = 7.56–6.58 (m, 19 H, H_{Ar}), 4.08 (dt, $^3J_{PH}$ = 3.8 Hz, $^3J_{HH}$ = 6.1 Hz, 1 H, $CH(OMe)_2$), 2.92 (s, 3 H, OCH_3), 2.84 (s, 3 H, OCH_3), 3.77–0.43 (m, 32 H, $H_{aliphat}$). – ^{31}P NMR (162 MHz; $CDCl_3$): δ = –13.5 (d, J_{PP} = 167 Hz); –30.5 (d, J_{PP} = 167 Hz). – MS (FD, CH_2Cl_2); *m/z* (%): 812.3 (100) $[MH]^+$. – $C_{55}H_{58}O_2P_2$ (813.01): calcd. C 81.25, H 7.19; found C 81.41, H 7.84.

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