Chiral Phosphabarrelene Ligands: Synthesis and Evaluation in Rhodium-Catalyzed Asymmetric Hydrogenation

Bernhard Breit,* Evelyn Fuchs

Institut für Organische Chemie und Biochemie, Albert-Ludwigs-Universität Freiburg, Albertstr. 21, 79104 Freiburg i. Brsg., Germany
Fax +49(761)2038715; E-mail: bernhard.breit@organik.chemie.uni-freiburg.de

Received 25 April 2006

Abstract: The first chiral and enantiomerically pure monodentate and bidentate phosphabarrelene ligands have been prepared and their potential in rhodium-catalyzed asymmetric hydrogenation has been evaluated.

Key words: asymmetric catalysis, hydrogenation, ligands, phosphorus, rhodium

Phosphabarrelenes **1** have been introduced recently by us as a new class of modifying ligands for homogeneous metal complex catalysis.[1] The strong pyramidalization at the phosphorus atom forced by incorporation in a [2.2.2] bicyclic framework increases the s-character of the lone pair at phosphorus.[1–3] Additionally, σ* orbitals of the P–C bonds are lowered in energy, rendering phosphabarrelenes interesting π-acceptor ligands for homogeneous catalysis.

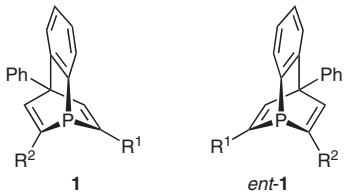
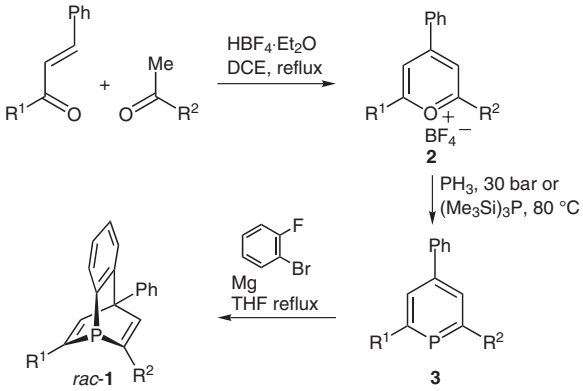


Figure 1 Chiral phosphabarrelenes

In fact, monodentate phosphabarrelenes furnished rhodium catalysts that enabled the hydroformylation of generally poorly reactive internal alkenes with extremely high catalytic activity and with surprisingly low alkene isomerization.[1]

These properties render these catalysts a unique choice for the position-selective hydroformylation of internal alkenes. Interestingly, phosphabarrelenes equipped with two different substituents R^1 and R^2, as shown in Figure 1, are chiral. Considering the unique electronic properties of this ligand system combined with an unusual and, so far unexplored, asymmetric geometry, induced us to synthesize and investigate the potential of these systems in asymmetric catalysis, which is the subject of this report.

Preparation of chiral phosphabarrelenes **1** commenced from pyrylium salts **2a–c**, which were obtained by Brønsted acid mediated condensation of chalcones with acetophenones (Scheme 1, Table 1).[4,5] Transformation to the corresponding phosphabenzenes (alternatively known as phosphinines or phosphorins) **3a–c** was accomplished by treatment of **2** with either phosphine at elevated pressure or with tris(trimethylsilyl)phosphine.[5]



Scheme 1 Synthesis of chiral phosphabarrelenes

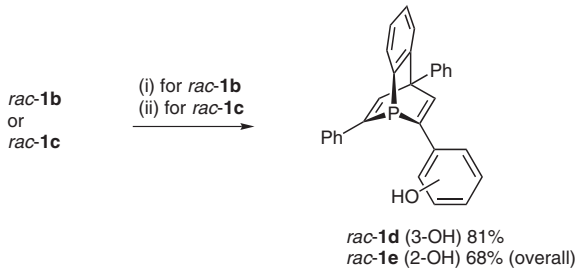
Table 1 Preparation of Chiral Phosphabarrelenes

Compound	R^1	R^2	Yield (%)		
			2	**3**	*rac*-**1**
a	Ph	2-Naphthyl	57	70	24
b	Ph	3-$MeOC_6H_4$	62	81	31
c	Ph	2-$MeOC_6H_4$	47	56	29

Reaction of benzyne, generated from 1-bromo-2-fluorobenzene and magnesium, with the phosphabenzenes **3a–c** in a Diels–Alder reaction furnished the desired chiral phosphabarrelenes **1a–c** in racemic form as air-stable, colorless solids in moderate yield.[1,6] With the goal of preparing bidentate phosphabarrelene ligands, liberation of the hydroxy function of **1b**,**c** as a handle for the attachment of a second binding site was addressed (Scheme 2).

In case of the 3-methoxyphenyl system *rac*-**1b**, ether cleavage occurred cleanly upon treatment with boron triiodide to give the 3-hydroxyphenyl-substituted barrelene *rac*-**1d**. The 2-methoxyphenyl derivative *rac*-**1c** proved more sensitive, and required protection of the phosphine as the phosphine oxide prior to ether cleavage with boron tribromide. Reduction back to the phosphine stage was

SYNTHESIS 2006, No. 13, pp 2121–2128
Advanced online publication: 12.06.2006
DOI: 10.1055/s-2006-942425; Art ID: C01606SS



Scheme 2 Preparation of phenol-substituted phosphabarrelene derivatives *rac*-**1d** and *rac*-**1e**: *Reagents and conditions*: (i) BI_3, CH_2Cl_2, –8 °C; (ii) (a) H_2O_2, CH_2Cl_2, r.t.; (b) $BBr_3 \cdot SMe_2$, DCE, 80 °C; (c) Cl_3SiH, toluene, 110 °C.

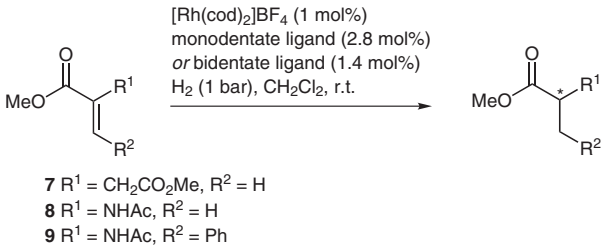
achieved with trichlorosilane to furnish 2-hydroxyphenyl-functionalized *rac*-**1e** in good overall yield.

The racemic mixtures of *rac*-**1a–e** were each resolved by preparative chiral HPLC. In all cases clean baseline separation was achieved employing Chiralpak AD-H as the stationary phase to give enantiomerically pure barrelenes (+)-**1a–e** and (–)-**1a–e**. The absolute configuration of the enantiomerically pure phosphabarrelenes (+)-**1a–e** and (–)-**1a–e** is, as yet, unknown. Transformation of the phenolic phosphabarrelenes into bidentate ligands was readily accomplished upon reaction with (*S*)-(1,1′-binaphthyl-2,2′-dioxy)chlorophosphine (**4**)[7] to give the diastereomeric 3- and 2-substituted ligands **5a**,**b** and **6a**,**b**, respectively (Scheme 3). Note as the absolute configurations of (+)- and (–)-**1d** and (+)- and (–)-**1e** are unknown, the structures given for the diastereomers (+)-**5a**/(+)-**5b** and (+)-**6a**/(+)-**6b** in Scheme 3 may be exchanged.

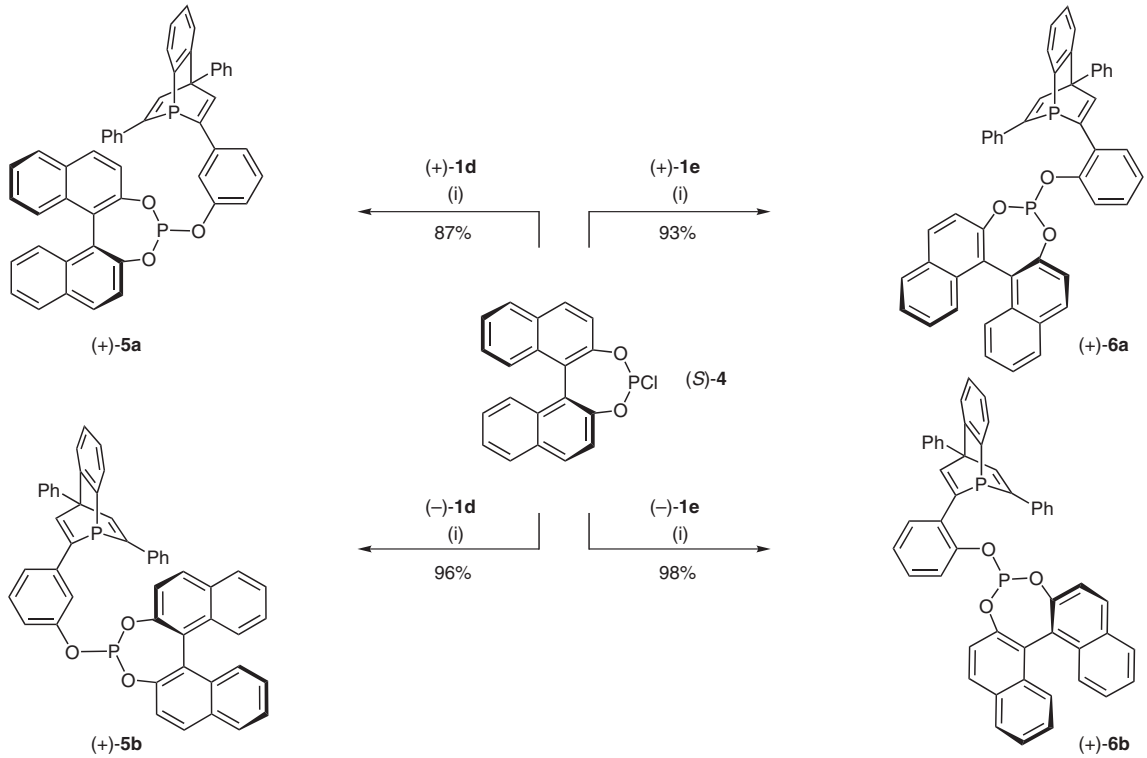
In order to learn about the coordination properties of these ligands, the stoichiometric reaction of **6a** with bis(η^4-cycloocta-1,5-diene)rhodium(I) tetrafluoroborate was studied. NMR spectroscopy showed the quantitative formation of the complex (η^4-cycloocta-1,5-diene)rhodium(I)–**6a** tetrafluoroborate. Furthermore, chemical shift and signal splitting in the ^{31}P NMR proved that both phosphorus atoms of **6a** are bound to the same metal center.[8]

With chiral monodentate and bidentate phosphabarrelene ligands in hand, we turned to rhodium-catalyzed asymmetric hydrogenation. As substrates itaconic ester **7**, and the acetamidoacrylates **8** and **9** were chosen (Scheme 4). Results of asymmetric hydrogenation are depicted in Table 2. Of the monodentate phosphabarrelenes, derivative **1a** gave the most promising results. Thus, **1a** furnished a rhodium catalyst, which operated with high activity for the hydrogenation of methyl itaconate, albeit enantioselectivity was moderate (Table 2, entries 1 and 2).

In the case of the bidentate ligands (+)-**5a**, (+)-**5b**, and (+)-**6b**, again active hydrogenation catalysts were formed, the



Scheme 4



Scheme 3 Preparation of chiral bidentate phosphabarrelene/phosphite ligands **5a**,**b** and **6a**,**b**: *Reagents and conditions*: (i) Et_3N, toluene, –40 °C to r.t.

asymmetric induction however, was low (Table 2, entries 7–9). Conversely, when the diastereomer (+)-**6a** was employed as a ligand, a dramatic boost in the enantioselectivity was observed and in the case of the acetamidoacrylates **8** and **9** (Table 2, entries 10, 11, and 13) the rhodium-catalyzed hydrogenation occurred with up to 90% ee.

Table 2 Results of Asymmetric Hydrogenation

Entry	Ligand	Substrate	Time (h)	Conversion (%)[a]	ee (%)[b]
1	(+)-**1a**	**7**	6	100	31 (*R*)
2	(–)-**1a**	**7**	4	100	31 (*S*)
3	(–)-**1a**	**8**	19	100	14 (*S*)
4	(–)-**1b**	**7**	16	100	<1 (*S*)
5	(+)-**1c**	**8**	19	100	18 (*R*)
6	(–)-**1e**	**8**	70	44	15 (*R*)
7	(+)-**5a**	**8**	21	100	22 (*S*)
8	(+)-**5b**	**8**	26	100	35 (*S*)
9	(+)-**6b**	**8**	20	100	9 (*R*)
10	(+)-**6a**	**8**	20	100	87 (*S*)
11[c]	(+)-**6a**	**8**	22	100	90 (*S*)
12	(+)-**6a**	**7**	20	100	19 (*S*)
13	(+)-**6a**	**9**	21	100	88 (*S*)

[a] Determined by ^{1}H NMR.
[b] **7**: GC (trifluoroacetyl-γ-cyclodextrin), **8**: GC (hydroxydex-β-TBDAc), **9**: HPLC (Chiralpak-AD).
[c] Reaction run at –3 °C.

In conclusion, the first chiral monodentate and bidentate phosphabarrelene ligands have been prepared in enantiomerically pure form. Both monodentate and bidentate ligands furnished active rhodium catalysts for rhodium-catalyzed asymmetric hydrogenation. Best enantioselectivities were found for the chelating phosphabarrelene/phosphite system (+)-**6a** with up to 90% ee, thus chiral phosphabarrelenes are a promising new ligand class for further studies in asymmetric catalysis including combinatorial approaches employing chiral monodentate ligand libraries.[9]

All reactions were carried out in dried glassware under an argon atmosphere 5.0 (Südwest-Gas). Air and moisture sensitive liquids and solutions were transferred via syringe. All reagents were obtained commercially unless otherwise noted. All solvents were dried and distilled by standard procedures. Organic solutions were concentrated under reduced pressure by rotary evaporation. Chromatographic purification of products was accomplished using flash chromatography[10] on Merck silica gel Si 60 (200–400 mesh). NMR spectra were acquired on a Varian Mercury spectrometer (300 MHz, 121 MHz, and 75 MHz for ^{1}H, ^{31}P, and ^{13}C respectively), on a Bruker AMX 400 (400 MHz, 162 MHz, and 100 MHz for ^{1}H, ^{31}P, and ^{13}C respectively) and on a Bruker DRX 500 (500 MHz, 202 MHz, and 125 MHz for ^{1}H, ^{31}P, and ^{13}C respectively). ^{1}H and ^{13}C NMR spectra are referenced according to residual solvent signals. ^{31}P NMR spectra are referenced with 85% H_3PO_4 as external standart. HRMS were obtained on a Finnigan MAT 8200 instrument. Elementary analysis was performed on an elementar vario (Fa. Elementar Analysensysteme GmbH). Optical rotations were measured on a Perkin Elmer 241 polarimeter. Separation of the enantiomers was achieved on a Chiralpak AD-H column using a Knaur K-2501 UV detector. The enantiomeric excess of the phosphabarrelene ligands was determined by analytical HPLC using a Chiralpak AD-H column. The absolute configuration of the enantiomerically pure phosphabarrelenes **1a–e** is, as yet, unknown. Hydrogenation experiments were performed following the general procedure using hydrogen gas 5.0 (Südwest-Gas). Pyrylium salts **2a–c** were obtained by Brønsted acid mediated condensation of chalcones with acetophenones.[4,5] Phosphabenzenes **3a–c**[5] and (*S*)-(1,1′-binaphthyl-2,2′-dioxy)chlorophosphine (**4**)[7] were prepared by literature procedures.

8,10-Diphenyl-11-(2-naphthyl)-1-phosphatricyclo[6.2.2.0^{2,7}]-dodeca-2(7),3,5,9,11-pentaene (1a)

Mg turnings (1.05 g, 43.21 mmol, 2.7 equiv) were suspended in a soln of phosphabenzene **3a** (5.95 g, 15.90 mmol, 1.0 equiv) in THF (60 mL) and a small amount of 1-bromo-2-fluorobenzene (0.50 mL of a total of 4.34 mL, 6.94 g, 39.68 mmol, 2.5 equiv) was added to start the reaction. Subsequently the remaining 1-bromo-2-fluorobenzene was slowly added, keeping the mixture under gentle reflux. When the addition was complete, the soln was heated to reflux for 4 h, then cooled to r.t. and hydrolyzed by addition of H_2O (5.0 mL). The THF was removed in vacuo and the residue extracted with toluene (400 mL). After washing with H_2O (3 × 200 mL) and reextraction of the aqueous phase with toluene (3 × 100 mL), the combined organic phases were dried (Na_2SO_4). The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 (250 mL) and filtered through a small pad of silica gel (6 × 7 cm). The silica gel was flushed with additional CH_2Cl_2 (200 mL) and the combined filtrates were evaporated to dryness in vacuo. The residue was dissolved in cyclohexane (1 L) and irradiated (150 W, visible light) with cooling (approx. 10 °C) for 48 h to remove an unknown red-colored byproduct. The suspension was concentrated to 100 mL and filtered through a small pad of alumina (4 × 5 cm, activity grade IV). The alumina was flushed with additional cyclohexane (700 mL) and the combined filtrates were evaporated to dryness in vacuo to give analytically pure phosphabarrelene *rac*-**1a** as a pale yellow foam; yield: 1.73 g (24%); mp 144 °C.

Resolution via preparative HPLC (Chiralpak AD-H, *n*-heptane–*i*-PrOH, 95:5):

(–)-**1a**: $[\alpha]_D^{20}$ –18.7 (*c* 1.01, $CHCl_3$).

(+)-**1a**: $[\alpha]_D^{20}$ +18.3 (*c* 0.99, $CHCl_3$).

^{1}H NMR (499.870 MHz, $CDCl_3$): δ = 6.67–6.69 (m, 1 H, H6), 7.06–7.12 (m, 2 H, H4, H5), 7.31 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, H4″), 7.40–7.43 (m, 2 H, H3″), 7.45–7.47 (m, 1 H, H6‴[a]), 7.48–7.52 (m, 1 H, H7‴[a]), 7.57 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, H4′), 7.68–7.71 (m, 2 H, H3′), 7.79–7.83 (m, 5 H, H2″, H2‴, H3‴, H5‴[b]), 7.91 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H2′), 7.94 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, H8‴[b]), 7.95–7.97 (m, 1 H, H3), 8.19 (d, $^3J_{H,P}$ = 6.2 Hz, 1 H, H9), 8.28 (d, $^3J_{H,P}$ = 6.0 Hz, 1 H, H12), 8.36 (br s, 1 H, H10‴) ([a] and [b] interchangeable assignments).

^{13}C NMR (125.692 MHz, $CDCl_3$): δ = 63.8 (C8), 123.8 (d, $^3J_{C,P}$ = 9.1 Hz, C2‴), 124.2 (d, $^3J_{C,P}$ = 13.3 Hz, C4), 124.3 (d, $^3J_{C,P}$ = 0.9 Hz, C6), 125.2 (d, $^3J_{C,P}$ = 18.5 Hz, C10‴), 125.9 (C6‴[a]), 126.0 (d, $^3J_{C,P}$ = 13.0 Hz, 2 C, C2″), 126.2 (C7‴[a]), 127.2 (d, $^4J_{C,P}$ = 1.5 Hz, C5), 127.5 (C3‴), 127.6 (C4′), 127.6 (d, $^5J_{C,P}$ = 1.5 Hz, C4″), 128.1 (d, $^6J_{C,P}$ = 1.2 Hz, C5‴), 128.2 (C8‴), 128.5 (d, $^4J_{C,P}$ = 0.9 Hz, 2 C, C3″), 128.9 (2 C, C2′), 129.1 (2 C, C3′), 131.6 (d, $^2J_{C,P}$ = 39.1 Hz, C3), 132.8 (d, $J_{C,P}$ = 1.5 Hz, C4‴[b]), 133.5 (d,

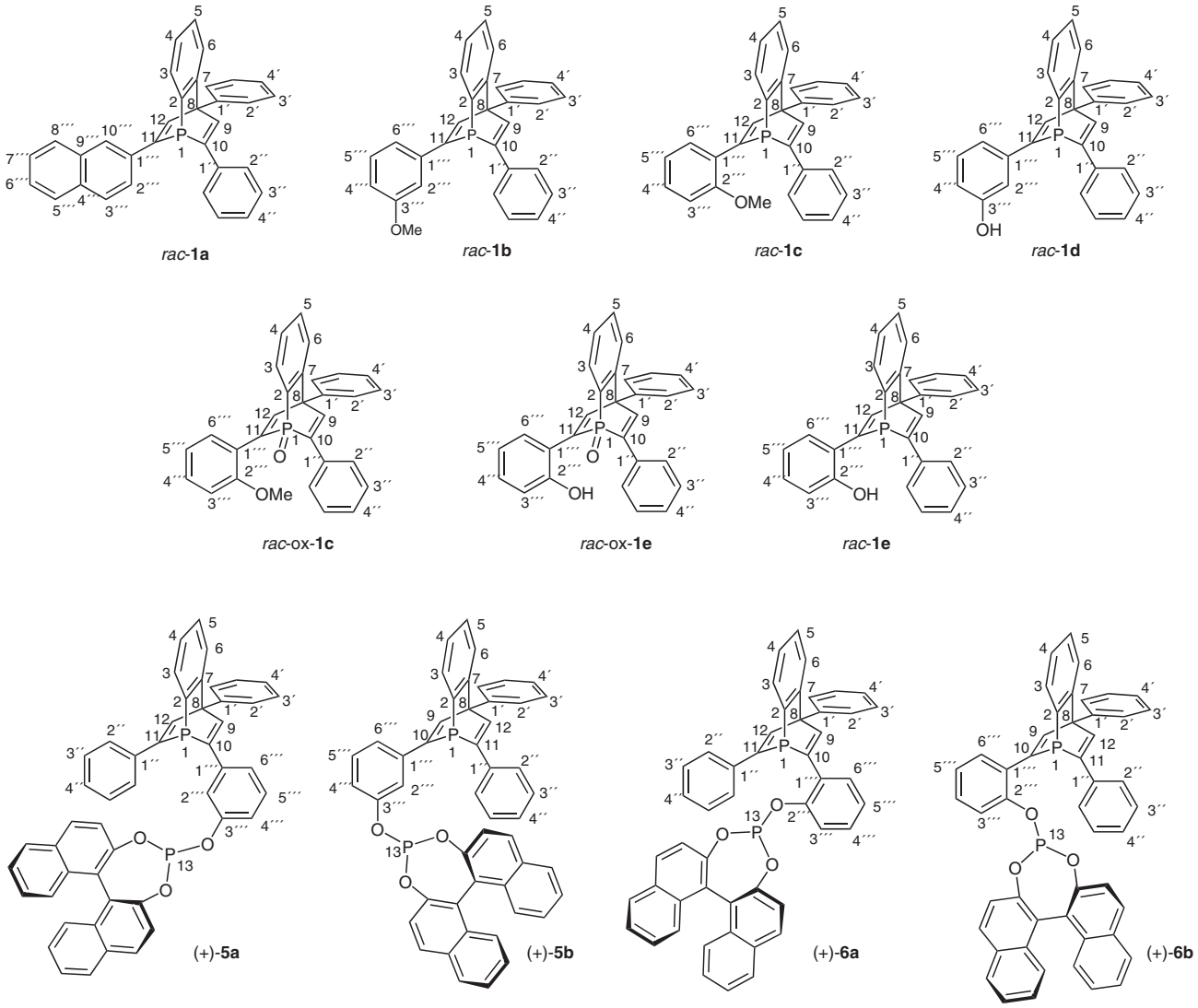


Figure 2

$J_{C,P}$ = 1.2 Hz, C9‴[b]), 135.9 (d, $^2J_{C,P}$ = 24.8 Hz, C1‴), 138.6 (d, $^2J_{C,P}$ = 24.8 Hz, C1″), 141.0 (d, $^1J_{C,P}$ = 11.2 Hz, C2), 141.2 (C1′), 147.3 (d, $^2J_{C,P}$ = 5.1 Hz, C9 or C12), 147.4 (d, $^2J_{C,P}$ = 5.2 Hz, C9 or C12), 152.3 (d, $^1J_{C,P}$ = 16.0 Hz, C10[c]), 152.4 (d, $^1J_{C,P}$ = 15.7 Hz, C11[c]), 155.3 (d, $^2J_{C,P}$ = 3.3 Hz, C7) ([a,b,c] interchangeable assignments).

^{31}P NMR (121.474 MHz, $CDCl_3$): δ = –69.4 (s).

Anal. Calcd for $C_{33}H_{23}P$ (450.51): C, 87.98; H, 5.15. Found: C, 87.68; H 5.29.

11-(3-Methoxyphenyl)-8,10-diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene (1b)

Mg turnings (0.72 g, 29.75 mmol, 2.2 equiv) were suspended in a soln of phosphabenzene **3b** (4.82 g, 13.60 mmol, 1.0 equiv) in THF (70 mL) and a small amount of 1-bromo-2-fluorobenzene (0.50 mL of a total of 3.10 mL, 4.96 g, 28.34 mmol, 2.1 equiv) was added to start the reaction. Subsequently the remaining 1-bromo-2-fluorobenzene was slowly added, keeping the mixture under gentle reflux. When the addition was complete, the soln was heated to reflux for 3.5 h, then cooled to r.t. and hydrolyzed by addition of H_2O (5.0 mL). The THF was removed in vacuo and the residue extracted with Et_2O (600 mL). After washing with 3% aq HCl (4 × 200 mL) and reextraction of the aqueous phase with Et_2O (3 × 100 mL), the combined organic phases were dried (Na_2SO_4) and irradiated (150 W, visible light) with cooling (approx. 10 °C) for 48 h to remove an unknown red-colored byproduct. The suspension was concentrated to 100 mL and filtered through a small pad of silica gel (7 × 7 cm). The silica gel was flushed with additional cyclohexane–EtOAc (5:1, 300 mL) and the combined filtrates were evaporated to dryness in vacuo. The residue was recrystallized (MeOH, 50 mL) to give *rac*-**1b** in analytically pure form (0.80 g, 1.85 mmol). The mother liquor was evaporated to dryness in vacuo, the residue dissolved in CH_2Cl_2 (20 mL) and filtered through a small pad of silica gel (3 × 3 cm). The silica gel was flushed with additional CH_2Cl_2 (100 mL) and the combined filtrates again were irradiated (150 W, visible light) with cooling (approx. 10 °C) for 2 h to remove an unknown red-colored byproduct. The suspension was filtered through a small pad of silica gel (3 × 3 cm) to give, after evaporation, a further 1.01 g (2.35 mmol) *rac*-**1b** in analytically pure form as a colorless solid; total yield: 1.81 g (31%); mp 98–100 °C.

Resolution via preparative HPLC (Chiralpak AD-H, *n*-heptane–*i*-PrOH, 90:10):

(–)-**1b**: $[\alpha]_D^{20}$ –3.3 (*c* 0.98, $CHCl_3$).

(+)-**1b**: $[\alpha]_D^{20}$ +3.1 (*c* 1.00, $CHCl_3$).

^{1}H NMR (499.873 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, OCH_3), 6.57–6.59 (m, 1 H, H6), 6.82 (ddd, $^3J_{H,H}$ = 8.0 Hz, *J* = 2.5 Hz, *J* = 1.1 Hz, 1 H, H4‴), 6.99–7.05 (m, 2 H, H4, H5), 7.25–7.32 (m, 4 H, H4″, H2‴, H5‴, H6‴), 7.34–7.37 (m, 2 H, H3″), 7.51–7.54 (m, 1 H, H4′), 7.62–7.65 (m, 2 H, H3′), 7.69–7.70 (m, 2 H, H2″), 7.82 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H2′), 7.83–7.85 (m, 1 H, H3), 8.09 (d, $^3J_{H,P}$ = 6.1 Hz, 1 H, H9[a]), 8.10 (d, $^3J_{H,P}$ = 6.0 Hz, 1 H, H12[a]) ([a] interchangeable assignments).

^{13}C NMR (125.692 MHz, $CDCl_3$): δ = 55.3 (CH_3), 63.8 (d, $^3J_{C,P}$ = 2.4 Hz, C8), 111.7 (d, $^3J_{C,P}$ = 13.6 Hz, C2‴[a]), 113.0 (d, $^5J_{C,P}$ = 1.2 Hz, C4‴), 118.6 (d, $^3J_{C,P}$ = 13.3 Hz, C6‴[a]), 124.1 (d, $^3J_{C,P}$ = 13.3 Hz, C4), 124.3 (d, $^3J_{C,P}$ = 1.2 Hz, C6), 125.9 (d, $^3J_{C,P}$ = 13.0 Hz, 2 C, C2″), 127.2 (d, $^4J_{C,P}$ = 1.5 Hz, C5), 127.6 (C4′), 127.7 (d, $^5J_{C,P}$ = 1.5 Hz, C4″), 128.5 (d, $^4J_{C,P}$ = 1.2 Hz, 2 C, C3″), 128.9 (2 C, C2′), 129.1 (2 C, C3′), 129.5 (d, $^4J_{C,P}$ = 0.9 Hz, C5‴), 131.7 (d, $^2J_{C,P}$ = 39.1 Hz, C3), 138.6 (d, $^2J_{C,P}$ = 24.8 Hz, C1″), 140.2 (d, $^2J_{C,P}$ = 24.8 Hz, C1‴), 141.1 (d, $^1J_{C,P}$ = 11.5 Hz, C2), 142.2 (C1′), 147.2 (d, $^2J_{C,P}$ = 4.5 Hz, C9), 147.6 (d, $^2J_{C,P}$ = 4.9 Hz, C12), 152.4 (d, $^1J_{C,P}$ = 16.1 Hz, C10[b]), 152.6 (d, $^1J_{C,P}$ = 16.1 Hz, C11[b]), 155.2 (d, $^2J_{C,P}$ = 3.6 Hz, C7), 159.8 (d, $^4J_{C,P}$ = 1.2 Hz, C3‴) ([a] and [b] interchangeable assignments).

^{31}P NMR (121.474 MHz, $CDCl_3$): δ = –68.6 (s).

HRMS: *m*/*z* calcd for $C_{30}H_{23}OP$: 430.1487; found: 430.1479.

11-(2-Methoxyphenyl)-8,10-diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene (1c)

Mg turnings (0.45 g, 18.52 mmol, 2.2 equiv) were suspended in a soln of phosphabenzene **3c** (3.00 g, 8.47 mmol, 1.0 equiv) in THF (50 mL) and a small amount of 1-bromo-2-fluorobenzene (0.20 mL of a total of 1.93 mL, 3.09 g, 17.66 mmol, 2.1 equiv) was added to start the reaction. Subsequently the remaining 1-bromo-1-fluorobenzene was slowly added, keeping the mixture under gentle reflux. When the addition was complete, the soln was heated to reflux for 4 h, then cooled to r.t. and hydrolyzed by addition of H_2O (3.0 mL). The THF was removed in vacuo and the residue extracted with Et_2O (5 × 100 mL). After washing with 3% aq HCl (5 × 100 mL) and reextraction of the aqueous phase with Et_2O (2 × 100 mL), the combined organic phases were dried (Na_2SO_4). The solvent was removed in vacuo, the residue dissolved in cyclohexane (20 mL) and filtered through a small pad of basic alumina (3 × 3 cm, activity grade IV). The alumina was flushed with additional cyclohexane (400 mL) and the combined filtrates were irradiated (150 W, visible light) with cooling (approx. 10 °C) for 20 h to remove an unknown red-colored byproduct. The suspension was concentrated to 100 mL and filtered through a small pad of alumina (4 × 4 cm). The alumina was flushed with additional cyclohexane (400 mL) and the combined filtrates were evaporated to dryness in vacuo. The residue was recrystallized (MeOH, 30 mL) to give analytically pure phosphabarrelene *rac*-**1c** as a colorless solid; yield: 1.04 g (29%); mp 183–185 °C.

Resolution via preparative HPLC (Chiralpak AD-H, *i*-PrOH–MeCN, 60:40):

(–)-**1c**: $[\alpha]_D^{20}$ –31.6 (*c* 0.83, $CHCl_3$).

(+)-**1c**: $[\alpha]_D^{20}$ +31.2 (*c* 1.00, $CHCl_3$).

^{1}H NMR (400.130 MHz, $CDCl_3$): δ = 3.74 (s, 3 H, OCH_3), 6.52–6.53 (m, 1 H, H6), 6.86–6.90 (m, 2 H, H3‴, H5‴), 6.96–7.03 (m, 2 H, H4, H5), 7.15–7.17 (m, 1 H, H6‴), 7.20–7.25 (m, 2 H, H4″, H4‴), 7.31–7.35 (m, 2 H, H3″), 7.47 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, H4′), 7.56–7.60 (m, 2 H, H3′), 7.72–7.74 (m, 2 H, H2″), 7.76–7.79 (m, 3 H, H3, H2′), 7.86 (d, $^3J_{H,P}$ = 6.0 Hz, 1 H, H12), 8.06 (d, $^3J_{H,P}$ = 5.6 Hz, 1 H, H9).

^{13}C NMR (100.620 MHz, $CDCl_3$): δ = 55.4 (CH_3), 63.4 (d, $^3J_{C,P}$ = 2.9 Hz, C8), 110.9 (C3‴), 120.7 (C5‴), 124.0 (C6), 124.1 (d, $^3J_{C,P}$ = 13.1 Hz, C4), 126.0 (d, $^3J_{C,P}$ = 13.1 Hz, 2 C, C2″), 126.9 (C5), 127.4 (2 C, C4′, C4″), 128.4 (2 C, C3″), 128.5 (d, $^3J_{C,P}$ = 8.7 Hz, C6‴), 128.8 (C4‴), 128.9 (2 signals, 4 C, C2′, C3′), 131.5 (d, $^2J_{C,P}$ = 39.2 Hz, C3), 139.0 (d, $^2J_{C,P}$ = 24.7 Hz, C1″), 141.5 (C1′), 142.1 (d, $^1J_{C,P}$ = 13.1 Hz, C2), 147.0 (d, $^2J_{C,P}$ = 4.4 Hz, C9), 148.9 (d, $^2J_{C,P}$ = 4.4 Hz, C12), 152.0 (d, $^1J_{C,P}$ = 17.4 Hz, C10[a]), 153.0 (d, $^1J_{C,P}$ = 17.4 Hz, C11[a]), 155.7 (d, $^2J_{C,P}$ = 2.9 Hz, C7), 156.9 (C2‴) ([a] interchangeable assignments; signal for C1‴ not detectable).

^{31}P NMR (121.474 MHz, $CDCl_3$): δ = –61.9 (s).

HRMS: *m*/*z* calcd for $C_{30}H_{23}OP$: 430.1487; found: 430.1483.

3-{8,10-Diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaen-11-yl}phenol (1d)

To a soln of **1b** (205 mg, 0.477 mmol, 1.0 equiv) in CH_2Cl_2 (9 mL) was added dropwise a soln of BI_3 (224 mg, 0.572 mmol, 1.2 equiv) in CH_2Cl_2 (3 mL) at –8 °C. The reaction was warmed to 0 °C over 1 h and hydrolyzed by the addition of a small amount of ice. The organic phase was washed consecutively with H_2O (3 × 15 mL) and sat. $Na_2S_2O_3$ soln (2 × 10 mL). The aqueous phases were reextracted with CH_2Cl_2 (2 × 15 mL) and the combined organic phases were dried ($MgSO_4$) and evaporated to dryness in vacuo. The residue was purified by flash chromatography (silica gel, cyclohexane–EtOAc, 10:1) to give *rac*-**1d** as a colorless solid in analytically pure form; yield: 161 mg (81%); mp 208 °C.

Resolution via preparative HPLC (Chiralpak AD-H, *n*-heptane–EtOH, 50:50):

(–)-**1d**: $[\alpha]_D^{20}$ –3.3 (*c* 1.01, $CHCl_3$).

(+)-**1d**: $[\alpha]_D^{20}$ +3.1 (*c* 1.00, $CHCl_3$).

^{1}H NMR (499.870 MHz, $CDCl_3$): δ = 5.03 (br, 1 H, OH), 6.54–6.56 (m, 1 H, H6), 6.72 (ddd, $^3J_{H,H}$ = 8.0 Hz, *J* = 2.5 Hz, *J* = 0.8 Hz, 1 H, H4‴), 6.97–7.03 (m, 2 H, H4, H5), 7.17–7.20 (m, 2 H, H2‴[a], H5‴), 7.22–7.26 (m, 2 H, H4″, H6‴[a]), 7.31–7.34 (m, 2 H, H3″), 7.49 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, H4′), 7.59–7.62 (m, 2 H, H3′), 7.66-7.68 (m, 2 H, H2″), 7.79 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H2′), 7.79–7.81 (m, 1 H, H3), 8.05 (d, $^3J_{H,P}$ = 6.2 Hz, 1 H, H9[b]), 8.06 (d, $^3J_{H,P}$ = 6.0 Hz, 1 H, H12‴[b]) ([a] and [b] interchangeable assignments).

^{13}C NMR (125.692 MHz, $CDCl_3$): δ = 63.8 (d, $^3J_{C,P}$ = 2.1 Hz, C8), 112.8 (d, $^3J_{C,P}$ = 13.3 Hz, C2‴[a]), 114.6 (d, $^5J_{C,P}$ = 1.2 Hz, C4‴), 118.5 (d, $^3J_{C,P}$ = 13.3 Hz, C6‴[a]), 124.2 (d, $^3J_{C,P}$ = 13.3 Hz, C4), 124.3 (d, $^3J_{C,P}$ = 0.9 Hz, C6), 125.9 (d, $^3J_{C,P}$ = 13.0 Hz, 2 C, C2″), 127.2 (d, $^4J_{C,P}$ = 1.5 Hz, C5), 127.6 (C4′), 127.7 (d, $^5J_{C,P}$ = 1.5 Hz, C4″), 128.5 (d, $^4J_{C,P}$ = 1.2 Hz, 2 C, C3″), 128.9 (2 C, C2′), 129.1 (2 C, C3′), 129.7 (d, $^4J_{C,P}$ = 1.2 Hz, C5‴), 131.7 (d, $^2J_{C,P}$ = 39.1 Hz, C3), 138.6 (d, $^2J_{C,P}$ = 24.8 Hz, C1″), 140.3 (d, $^2J_{C,P}$ = 25.1 Hz, C1‴), 141.0 (d, $^1J_{C,P}$ = 11.2 Hz, C2), 141.1 (C1′), 147.2 (d, $^2J_{C,P}$ = 4.8 Hz, C9), 147.7 (d, $^2J_{C,P}$ = 4.8 Hz, C12), 152.1 (d, $^1J_{C,P}$ = 16.1 Hz, C10[b]), 152.5 (d, $^1J_{C,P}$ = 16.1 Hz, C11[b]), 155.1 (d, $^2J_{C,P}$ = 3.3 Hz, C7), 155.7 (d, $^4J_{C,P}$ = 1.2 Hz, C3‴) ([a] and [b] interchangeable assignments).

^{31}P NMR (121.474 MHz, $CDCl_3$): δ = –68.9 (s).

HRMS: *m*/*z* calcd for $C_{29}H_{21}OP$: 416.1330; found: 416.1326.

2-{8,10-Diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaen-11-yl}phenol (1e)

Oxidation: To a soln of **1c** (475 mg, 1.10 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was added dropwise 35% H_2O_2 in H_2O (170 μL, 1.99 mmol, 1.8 equiv). After stirring overnight at r.t. the organic phase was washed with H_2O (3 × 7 mL), treated with a small amount MnO_2 to destroy peroxides, dried ($MgSO_4$) and evaporated to dryness in vacuo. The residue was purified by flash chromatography (silica gel, cyclohexane–EtOAc, 1:1) to give 11-(2-methoxyphenyl)-8,10-diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene 1-oxide (*rac*-ox-**1c**) in analytically pure form; yield: 411 mg (84%).

^{1}H NMR (400.130 MHz, $CDCl_3$): δ = 3.74 (s, 3 H, OCH_3), 6.48–6.51 (dd, *J* = 7.7 Hz, *J* = 5.2 Hz, 1 H, H6), 6.90–6.93 (m, 2 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 7.17–7.30 (m, 4 H), 7.35–7.39 (m, 2 H, H3″), 7.49 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, H4′), 7.57–7.61 (m, 2 H, H3′), 7.69–7.74 (m, 2 H, H2″), 7.81–7.84 (m, 2 H, H2′), 7.83 (d, $^3J_{H,P}$ = 32.7 Hz, 1 H, H12[a]), 8.00 (d, $^3J_{H,P}$ = 31.8 Hz, 1 H, H9[a]), 8.03–8.07 (m, 1 H, H3) ([a] interchangeable assignments).

^{31}P NMR (121.468 MHz, $CDCl_3$): δ = 11.1 (s).

Deprotection: Oxide *rac*-ox-**1c** (560 mg, 1.25 mmol, 1.0 equiv) was dissolved in DCE (15 mL) in a pressure vessel at r.t. A suspension of BBr_3·SMe_2 (1.375 g, 4.40 mmol, 3.5 equiv) in DCE (6 mL) was added to the mixture which was then heated to 80 °C overnight. The reaction was cooled to 0 °C and hydrolyzed by cautious addition of ice. The organic phase was washed with H_2O (3 × 10 mL) and the aqueous phases were reextracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were dried ($MgSO_4$) and evaporated to dryness in vacuo. The residue was purified by flash chromatography (silica gel, cyclohexane–EtOAc, 3:1) to give 11-(2-hydroxyphenyl)-8,10-diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene 1-oxide (*rac*-ox-**1e**) in analytically pure form; yield: 508 mg (94%).

^{1}H NMR (300.066 MHz, $CDCl_3$): δ = 6.51–6.56 (dd, *J* = 7.5 Hz, *J* = 5.3 Hz, 1 H, H6), 6.82–6.87 (m, 1 H), 7.00 (d, *J* = 7.5 Hz, 1 H), 7.08–7.38 (m, 7 H), 7.50–7.55 (m, 1 H, H4′), 7.60–7.65 (m, 2 H, H3′), 7.70–7.73 (m, 4 H, H2″, H2′), 7.96 (d, $^3J_{H,P}$ = 29.7 Hz, 1 H, H9[a]), 8.03–8.08 (m, 1 H, H3), 8.07 (d, $^3J_{H,P}$ = 32.4 Hz, 1 H, H12[a]), 9.62 (s, 1 H, OH) ([a] interchangeable assignments).

^{31}P NMR (121.468 MHz, $CDCl_3$): δ = 18.3 (s).

Reduction: To a soln of *rac*-ox-**1e** (128 mg, 0.296 mmol, 1.0 equiv) in toluene (8 mL) in a pressure vessel was added trichlorosilane (140 μL, 188 mg, 1.385 mmol, 4.7 equiv) at 0 °C. The mixture was stirred for 10 min at r.t. and then it was heated to 110 °C overnight. The mixture was cooled to r.t., cautiously poured into aq 2 M NaOH (15 mL), and the H_2O phase was extracted with toluene (2 × 10 mL). The combined organic phases were washed with H_2O (3 × 8 mL), dried ($MgSO_4$) and evaporated to dryness in vacuo. The residue was purified by flash chromatography (silica gel, cyclohexane–EtOAc, 5:1) to give *rac*-**1e** in analytically pure form as a colorless solid; yield: 106 mg (86%); mp 205–210 °C.

Resolution via preparative HPLC (Chiralpak AD-H, *n*-heptane–EtOH, 50:50):

(–)-**1e**: $[\alpha]_D^{20}$ –13.9 (*c* 0.77, $CHCl_3$).

(+)-**1e**: $[\alpha]_D^{20}$ +13.4 (*c* 0.76, $CHCl_3$).

^{1}H NMR (300.064 MHz, $CDCl_3$): δ = 5.11 (s, 1 H, OH), 6.55–6.58 (m, 1 H, H6), 6.83 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, H3‴), 6.88–6.93 (m, 1 H, H5‴), 7.00–7.03 (m, 2 H, H4, H5), 7.10–7.16 (m, 1 H, H4‴), 7.23–7.35 (m, 4 H, H3″, H4″, H6‴), 7.46–7.51 (m, 1 H, H4′), 7.57–7.62 (m, 2 H, H3′), 7.67–7.70 (m, 2 H, H2″), 7.75–7.78 (m, 2 H, H2′), 7.78–7.84 (m, 1 H, H3), 8.06 (d, $^3J_{H,P}$ = 6.2 Hz, 1 H, H9[a]), 8.07 (d, $^3J_{H,P}$ = 6.0 Hz, 1 H, H12[a]) ([a] interchangeable assignments).

^{13}C NMR (75.451 MHz, $CDCl_3$): δ = 63.8 (d, $^3J_{C,P}$ = 2.6 Hz, C8), 115.9 (C3‴), 120.9 (C5‴), 124.2 (d, $^3J_{C,P}$ = 13.2 Hz, C4), 124.4 (d, $^3J_{C,P}$ = 1.2 Hz, C6), 125.9 (d, $^3J_{C,P}$ = 12.7 Hz, 2 C, C2″), 126.6 (d, $^2J_{C,P}$ = 23.0 Hz, C1‴), 127.3 (d, $^4J_{C,P}$ = 1.7 Hz, C5), 127.6 (C4′), 127.7 (d, $^5J_{C,P}$ = 1.7 Hz, C4″), 128.6 (d, $^4J_{C,P}$ = 1.2 Hz, 2 C, C3″), 128.8 (2 C, C2′), 128.9 (d, $^3J_{C,P}$ = 10.7 Hz, C6‴), 128.9 (C4‴), 129.1 (2 C, C3′), 131.8 (d, $^2J_{C,P}$ = 38.6 Hz, C3), 138.5 (d, $^2J_{C,P}$ = 24.5 Hz, C1″), 140.9 (C1′), 141.1 (d, $^1J_{C,P}$ = 12.4 Hz, C2), 147.1 (d, $^2J_{C,P}$ = 4.6 Hz, C9), 150.2 (d, $^1J_{C,P}$ = 18.4 Hz, C11), 150.6 (d, $^2J_{C,P}$ = 4.0 Hz, C12), 152.2 (d, $^3J_{C,P}$ = 2.6 Hz, C2‴), 152.8 (d, $^1J_{C,P}$ = 17.6 Hz, C10), 154.9 (d, $^2J_{C,P}$ = 3.3 Hz, C7).

^{31}P NMR (121.468 MHz, $CDCl_3$): δ = –63.0 (s).

HRMS: *m*/*z* calcd for $C_{29}H_{21}OP$: 416.1330; found: 416.1320.

Bidentate Ligands 5 and 6; General Procedure

To a soln of (*S*)-(1,1′-binaphthyl-2,2′-dioxy)chlorophosphine (**4**, 1.3–1.5 equiv) in toluene was added slowly a soln of enantiomerically pure phosphabarrelene (+)- or (–)-**1d** or (+)- or (–)-**1e** in toluene at –40 °C. Subsequently Et_3N (1.3–1.5 equiv) was added and the soln was warmed to r.t. over 5 h and stirred overnight. The organic phase was washed with H_2O (3 × 15 mL), the aqueous phases were reextracted with toluene (3 × 10 mL), and the combined organic phases were dried ($MgSO_4$). After evaporation of the solvent in vacuo, the residue was dissolved in CH_2Cl_2 (10 mL) and filtered through a small pad of neutral alumina (2 × 3 cm, activity grade IV). The alumina was flushed with additional CH_2Cl_2 (60 mL) and the combined filtrates were evaporated to dryness in vacuo to give the bidentate phosphabarrelenes in analytically pure form.

3-{8,11-Diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaen-10-yl}phenyl (*S*)-1,1′-Binaphthyl-2,2′-diyl Phosphite [(+)-5a] from (+)-1d

Starting from **4** (88.7 mg, 0.253 mmol) in toluene (4.0 mL) and (+)-**1d** (81.0 mg, 0.195 mmol) in toluene (8.0 mL) and using Et_3N (27.0 mg, 0.264 mmol), **5a** was obtained as a colorless solid; yield: 124 mg (87%); mp 132–138 °C.

$[\alpha]_D^{20}$ +77.9 (*c* 1.09, $CHCl_3$).

^{1}H NMR (499.870 MHz, $CDCl_3$): δ = 6.60 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, H6), 7.01–7.07 (m, 2 H, H4, H5), 7.13–7.15 (m, 1 H, H4‴), 7.26–7.35 (m, 7 H), 7.37–7.49 (m, 4 H), 7.51–7.57 (m, 3 H, H4′, H2‴, H6‴), 7.60 (d, *J* = 8.8 Hz, 1 H), 7.64 (pt, $^3J_{H,H}$ = 7.6 Hz, 2 H, H3′), 7.74 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, H2″), 7.83 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, H2′), 7.86–7.88 (m, 1 H, H3), 7.90–7.93 (m, 2 H), 7.95 (d, *J* = 8.2 Hz, 1 H), 8.01 (d, *J* = 8.8 Hz, 1 H), 8.11 (d, $^3J_{H,P}$ = 5.8 Hz, 1 H, H9[a]), 8.12 (d, $^3J_{H,P}$ = 5.7 Hz, 1 H, H12[a]) ([a] interchangeable assignments).

^{13}C NMR (125.692 MHz, $CDCl_3$): δ = 63.8 (d, $^3J_{C,P}$ = 2.1 Hz, C8), 117.9 (dd, $^3J_{C,P}$ = 13.3 Hz, $^3J_{C,P}$ = 7.0 Hz, C2‴), 119.3 (d, $^3J_{C,P}$ = 8.8 Hz, C4‴), 121.68, 121.71, 122.0 (d, $^3J_{C,P}$ = 13.6 Hz, C6‴), 122.9 (d, *J* = 2.4 Hz, 2 C, quart. C), 124.1 (d, $^3J_{C,P}$ = 13.3 Hz, C4), 124.3 (C6), 125.0, 125.2, 125.9 (d, $^3J_{C,P}$ = 13.0 Hz, 2 C, C2″), 126.2, 126.4, 126.9, 127.0, 127.2 (d, $^4J_{C,P}$ = 1.5 Hz, C5), 127.6 (C4′), 127.7 (d, $^5J_{C,P}$ = 1.2 Hz, C4″), 128.3, 128.4, 128.6 (d, $^4J_{C,P}$ = 0.9 Hz, 2 C, C3″), 128.9 (2 C, C2′), 129.1 (2 C, C3′), 129.8, 129.9, 130.5, 131.3 (quart. C), 131.6 (quart. C), 131.8 (d, $^2J_{C,P}$ = 39.1 Hz, C3), 132.6 (d, *J* = 1.2 Hz, quart. C), 132.8 (d, *J* = 1.2 Hz, quart. C), 138.5 (d, $^2J_{C,P}$ = 24.8 Hz, C1″), 140.6 (d, $^2J_{C,P}$ = 25.1 Hz, C1‴), 140.8 (d, $^1J_{C,P}$ = 11.2 Hz, C2), 141.0 (C1′), 146.9 (d, *J* = 2.4 Hz, quart. C), 147.2 (d, $^2J_{C,P}$ = 4.5 Hz, C9[a]), 147.5 (d, *J* = 4.5 Hz, quart. C), 148.4 (d, $^2J_{C,P}$ = 4.8 Hz, C12[a]), 151.8 (d, $^1J_{C,P}$ = 16.1 Hz, C10[b]), 151.9 (dd, $^2J_{C,P}$ = 7.9 Hz, $^4J_{C,P}$ = 1.2 Hz, C3‴), 152.4 (d, $^1J_{C,P}$ = 16.0 Hz, C11[b]), 155.0 (d, $^2J_{C,P}$ = 3.3 Hz, C7) ([a] and [b] interchangeable assignments).

^{31}P NMR (121.474 MHz, $CDCl_3$): δ = 144.8 (s, P13), –68.9 (s, P1).

HRMS: *m*/*z* calcd for $C_{49}H_{32}O_3P_2$: 730.1827; found: 730.1812.

3-{8,11-Diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaen-10-yl}phenyl (*S*)-1,1′-Binaphthyl-2,2′-diyl Phosphite [(+)-5b] from (–)-1d

Starting from **4** (38.3 mg, 0.109 mmol) in toluene (3.0 mL) and (–)-**1d** (35.0 mg, 0.084 mmol) in toluene (5.0 mL) using Et_3N (11.6 mg (0.114 mmol), **5b** was obtained as a colorless solid; yield: 59 mg (96%); mp 132–138 °C.

$[\alpha]_D^{20}$ +73.2 (*c* 1.05, $CHCl_3$).

^{1}H NMR (499.870 MHz, $CDCl_3$): δ = 6.58 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, H6), 7.00–7.06 (m, 2 H, H4, H5), 7.11–7.13 (m, 1 H, H4‴), 7.25–7.37 (m, 7 H), 7.40–7.47 (m, 4 H), 7.50–7.53 (m, 3 H, H4′, H2‴, H6‴), 7.58 (d, *J* = 8.8 Hz, 1 H), 7.63 (pt, $^3J_{H,H}$ = 7.7 Hz, 2 H, H3′), 7.70 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, H2″), 7.81 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, H2′), 7.83–7.84 (m, 1 H, H3), 7.87 (d, *J* = 8.6 Hz, 2 H), 7.94 (d, *J* = 8.3

Hz, 1 H), 8.00 (d, J = 8.8 Hz, 1 H), 8.08 (d, $^3J_{H,P}$ = 6.2 Hz, 1 H, H9[a]), 8.11 (d, $^3J_{H,P}$ = 5.8 Hz, 1 H, H12[a]) ([a] interchangeable assignments).

^{13}C NMR (125.692 MHz, $CDCl_3$): δ = 63.9 (d, $^3J_{C,P}$ = 1.81 Hz, C8), 117.9 (dd, $^3J_{C,P}$ = 13.2 Hz, $^3J_{C,P}$ = 7.5 Hz, C2‴), 119.3 (dd, $^3J_{C,P13}$ = 8.8 Hz, $^5J_{C,P}$ = 0.9 Hz, C4‴), 121.7 (br s, 2 C), 122.0 (d, $^3J_{C,P}$ = 13.3 Hz, C6‴), 122.8 (d, J = 2.4, 2 C, quart. C), 124.2 (d, $^3J_{C,P}$ = 13.3 Hz, C4), 124.4 (d, $^3J_{C,P}$ = 0.9 Hz, C6), 125.0, 125.2, 125.9 (d, $^3J_{C,P}$ = 13.0 Hz, 2 C, C2″), 126.2, 126.4, 126.9, 127.0, 127.3 (d, $^4J_{C,P}$ = 1.5 Hz, C5), 127.6 (C4′), 127.7 (d, $^5J_{C,P}$ = 1.5 Hz, C4″), 128.3, 128.4, 128.6 (d, $^4J_{C,P}$ = 0.9 Hz, 2 C, C3″), 128.9 (2 C, C2′), 129.1 (2 C, C3′), 129.8, 129.9, 130.5, 131.3 (quart. C), 131.7 (quart. C), 131.8 (d, $^2J_{C,P}$ = 39.1 Hz, C3), 132.6 (d, J = 1.2 Hz, quart. C), 132.8 (d, J = 1.5 Hz, quart. C), 138.5 (d, $^2J_{C,P}$ = 24.5 Hz, C1″), 140.7 (d, $^2J_{C,P}$ = 25.1 Hz, C1‴), 140.8 (d, $^1J_{C,P}$ = 11.2 Hz, C2), 141.0 (C1′), 147.0 (d, J = 2.4 Hz), 147.2 (d, $^2J_{C,P}$ = 4.5 Hz, C9[a]), 147.5 (d, J = 4.5 Hz), 148.4 (d, $^2J_{C,P}$ = 4.9 Hz, C12[a]), 151.8 (d, $^1J_{C,P}$ = 16.4 Hz, C10[b]), 151.9 (dd, $^2J_{C,P}$ = 7.9 Hz, $^4J_{C,P}$ = 1.2 Hz, C3‴), 152.5 (d, $^1J_{C,P}$ = 16.1 Hz, C11[b]), 155.1 (d, $^2J_{C,P}$ = 3.6 Hz, C7) ([a] and [b] interchangeable assignments).

^{31}P NMR (121.474 MHz, $CDCl_3$): δ = 144.6 (s, P13), –69.0 (s, P1).

HRMS: m/z calcd for $C_{49}H_{32}O_3P_2$: 730.1827; found: 730.1819.

2-{8,11-Diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaen-10-yl}phenyl (*S*)-1,1′-Binaphthyl-2,2′-diyl Phosphite [(+)-6a] from (+)-1e

Starting from **4** (95.3 mg, 0.272 mmol) in toluene (4.0 mL) and (+)-**1e** (87.0 mg, 0.209 mmol) in toluene (8.0 mL) using Et_3N (29.1 mg, 0.286 mmol), **6a** was obtained as a colorless solid; yield: 142 mg (93%); mp 140 °C.

$[\alpha]_D^{20}$ +158.0 (c 1.10, $CHCl_3$).

^{1}H NMR (499.870 MHz, $CDCl_3$): δ = 6.51 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, H6), 6.92–6.97 (m, 2 H, H4, H5), 7.11–7.14 (m, 2 H), 7.16–7.20 (m, 2 H), 7.24–7.26 (m, 4 H), 7.30–7.36 (m, 4 H), 7.38–7.45 (m, 3 H), 7.48–7.50 (m, 3 H), 7.55 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H2″), 7.68–7.69 (m, 2 H), 7.71 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, H2′), 7.79 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 7.88 (d, $^2J_{H,P}$ = 5.8 Hz, 1 H, H9[a]), 7.90–7.92 (m, 2 H), 8.18 (d, $^2J_{H,P}$ = 5.9 Hz, 1 H, H12[a]) ([a] interchangeable assignments).

^{13}C NMR (125.602 MHz, $CDCl_3$): δ = 63.8 (d, $^3J_{C,P}$ = 1.5 Hz, C8), 120.4 (d, J = 12.7 Hz), 121.7, 121.73 (d, J = 0.9 Hz), 122.7 (d, J = 2.4 Hz, 2 C, quart. C), 123.9 (d, $^3J_{C,P}$ = 13.0 Hz, C4), 124.2, 124.3, 124.8, 125.1, 126.0 (d, $^3J_{C,P}$ = 13.0 Hz, 2 C, C2″), 126.1, 126.2, 126.9, 126.94, 127.1, 127.4 (2 C), 128.3 (2 C, C3″), 128.34, 128.4, 128.9 (2 C, C2′ or C3′), 129.0 (2 C, C2′ or C3′), 129.9, 130.0, 130.1, 130.2, 131.1 (quart. C), 131.6 (quart. C), 131.9 (d, $^2J_{C,P}$ = 38.5 Hz, C3), 132.5 (quart. C), 132.8 (quart. C), 138.7 (d, $^2J_{C,P}$ = 24.5 Hz, C1″), 141.1 (C1′), 141.3 (d, $^1J_{C,P}$ = 12.7 Hz, C2), 146.9 (d, J = 2.1 Hz, quart. C), 147.2 (d, $^2J_{C,P}$ = 4.2 Hz, C12[a]), 147.8 (d, J = 4.8 Hz, quart. C), 148.6 (dd, J = 2.4 Hz, J = 1.5 Hz, quart. C), 149.2 (d, $^1J_{C,P}$ = 17.6 Hz, C10[b]), 151.1 (d, $^2J_{C,P}$ = 3.9 Hz, C9[a]), 152.8 (d, $^1J_{C,P}$ = 17.9 Hz, C11[b]), 155.0 (d, $^2J_{C,P}$ = 3.3 Hz, C7) ([a] and [b] interchangeable assignments; signal for C1‴ not detectable).

^{31}P NMR (121.474 MHz, $CDCl_3$): δ = 144.3 (d, $^5J_{P,P}$ = 7.8 Hz, P13), –63.2 (d, $^5J_{P,P}$ = 7.8 Hz, P1).

HRMS: m/z calcd for $C_{49}H_{32}O_3P_2$: 730.1827; found: 730.1816.

2-{8,11-Diphenyl-1-phosphatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaen-10-yl}phenyl (*S*)-1,1′-Binaphthyl-2,2′-diyl Phosphite [(+)-6b] from (–)-1e

Starting from **4** (35.0 mg, 0.100 mmol) in toluene (1.5 mL) and (–)-**1e** (28.0 mg, 0.067 mmol) in toluene (2.5 mL) using Et_3N (10.4 mg, 0.103 mmol), **6b** was obtained as a colorless solid; yield: 48 mg (98%); mp 189–193 °C.

$[\alpha]_D^{20}$ +132.0 (c 1.00, $CHCl_3$).

^{1}H NMR (499.870 MHz, C_6D_6): δ = 6.67–6.69 (m, 2 H, H4, H6), 6.73–6.76 (m, 1 H, H5), 6.85–6.93 (m, 4 H), 7.01 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H), 7.07–7.12 (m, 4 H), 7.15–7.21 (m, 5 H), 7.30 (d, J = 7.1 Hz, 1 H), 7.34 (d, J = 8.8 Hz, 1 H), 7.42 (d, J = 8.5 Hz, 2 H), 7.51–7.59 (m, 6 H), 7.68 (d, $^2J_{H,H}$ = 7.7 Hz, 2 H, H2″), 7.84–7.88 (m, 1 H, H3), 7.91 (d, $^2J_{H,P}$ = 5.9 Hz, 1 H, H9[a]), 8.27 (d, $^2J_{H,P}$ = 6.0 Hz, 1 H, H12[a]) ([a] interchangeable assignments).

^{13}C NMR (125.692 MHz, C_6D_6): δ = 64.5 (d, $^3J_{C,P}$ = 2.4 Hz, C8), 121.3 (d, J = 10.6 Hz), 122.0, 122.1 (d, J = 1.2 Hz), 123.3 (d, J = 2.4 Hz, 2 C, quart. C), 124.4 (d, $^3J_{C,P}$ = 13.0 Hz, C4), 124.8 (2 C), 125.0, 125.3, 126.4, 126.5 (d, $^3J_{C,P}$ = 13.0 Hz, 2 C, C2″), 126.6, 127.2, 127.3, 127.4, 127.5, 127.7, 128.6 (2 C, C3″), 128.7, 128.72, 129.1 (2 C, C2′), 129.4 (2 C, C3′), 130.2, 130.5, 130.6, 130.7, 131.6 (quart. C), 132.1 (quart. C), 132.2 (d, $^2J_{C,P}$ = 38.8 Hz, C3), 134.0 (d, J = 1.2 Hz, quart. C), 133.3 (d, J = 1.5 Hz, quart. C), 139.3 (d, $^2J_{C,P}$ = 24.8 Hz, C1″), 141.6 (C1′), 141.9 (d, $^1J_{C,P}$ = 13.0 Hz, C2), 147.5 (d, J = 2.1 Hz, quart. C), 147.9 (d, $^2J_{C,P}$ = 4.2 Hz, C9[a]), 148.5 (d, J = 4.2 Hz, quart. C), 149.0 (dd, J = 5.9 Hz, J = 3.2 Hz, quart. C), 149.1 (d, $^1J_{C,P}$ = 17.6 Hz, C10[b]), 152.8 (d, $^2J_{C,P}$ = 3.9 Hz, C12[a]), 153.2 (d, $^1J_{C,P}$ = 17.6 Hz, C11[b]), 155.6 (d, $^2J_{C,P}$ = 3.3 Hz, C7) ([a] and [b] interchangeable assignments; signal for C1‴ not detectable).

^{31}P NMR (121.474 MHz, C_6D_6): δ = 145.3 (d, $^5J_{P,P}$ = 6.1 Hz, P13), –63.6 (d, $^5J_{P,P}$ = 6.1 Hz, P1).

HRMS: m/z calcd for $C_{49}H_{32}O_3P_2$: 730.1827; found: 730.1820.

Hydrogenation Experiments; General Procedure

Monodentate ligands: $[Rh(cod)_2]BF_4$ (2.0 mg, 4.9 μmol, 1.0 mol%) and the particular monodentate phosphabarrelene ligand (13.8 μmol, 2.7 mol%) were dissolved in CH_2Cl_2 (6 mL) and stirred at r.t. for 20 min.

Bidentate ligands: $[Rh(cod)_2]BF_4$ (2.0 mg, 4.9 μmol, 1.0 mol%) and the particular bidentate phosphabarrelene ligand (6.8 μmol, 1.3 mol%) were dissolved in CH_2Cl_2 (6 mL) and stirred at r.t. for 90 min.

Subsequently the appropriate substrate **7–9** (0.51 mmol, 1.0 equiv) was added in one portion. The reaction vessel was evacuated and refilled with H_2 gas five times. The mixture was vigorously stirred under a H_2 atmosphere (hydrogen balloon) at r.t. Conversion was determined by ^{1}H NMR after the noted time (Table 2). Enantiomeric excess was determined by chiral GC or HPLC analysis.

Dimethyl Itaconate (Dimethyl 2-Methylenebutanedioate, 7)

GC: G-TA, trifluoroacetyl-γ-cyclodextrin column, 30 m × 0.5 mm, 75 °C, t_R [(*S*)-enantiomer] = 32.2 min, t_R [(*R*)-enantiomer] = 35.2 min.

Methyl 2-Acetamidoacrylate (8)

GC: Hydrodex-β-TBDAc column, 25 m × 0.25 mm, 120 °C, t_R [(*R*)-enantiomer] = 14.0 min, t_R [(*S*)-enantiomer] = 20.3 min.

Methyl α-Acetamidocinnamate (9)

HPLC: Chiralpak-AD column, 25 cm × 4.6 mm, *n*-heptane–*i*-PrOH, 90:10), 254 nm, t_R [(*R*)-enantiomer] = 15.0 min, t_R [(*S*)-enantiomer] = 19.5 min.

Acknowledgment

The authors thank the DFG (GRK 1038), the Fonds der Chemischen Industrie, the Alfried-Krupp Award for young university teachers (to B.B.) as well as BASF AG for financial support. We also thank S. Berger for technical and Dr. R. Krieger and G. Fehrenbach for analytical assistance.

References

(1) Breit, B.; Fuchs, E. *Chem. Commun.* **2004**, 694.
(2) (a) Dunne, B. J.; Morris, R. B.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 653. (b) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206.
(3) Ochida, S.; Hara, K.; Ito, H.; Sawamura, M. *Org. Lett.* **2003**, *5*, 2671.
(4) Dimroth, K.; Reichardt, C.; Vogel, K. *Org. Synth. Coll. Vol. V*; John Wiley & Sons: London, **2004**, 1135.
(5) Breit, B.; Winde, R.; Mackewitz, T.; Paciello, R.; Harms, K. *Chem. Eur. J.* **2001**, *14*, 3106.
(6) Märkl, G.; Lieb, F.; Martin, C. *Tetrahedron Lett.* **1971**, *12*, 1249.
(7) Scherer, J.; Huttner, G.; Büchner, M.; Bakos, J. *J. Organomet. Chem.* **1996**, *520*, 45.
(8) ^{31}P NMR data of [Rh(cod)(**6a**)]BF_4 (121.468 MHz, $CDCl_3$): $P_{phosphite}$: δ = 125.2 (dd, $^1J_{P,Rh}$ = 254.8 Hz, $^2J_{P,P}$ = 52.4 Hz; $P_{barrelene}$: δ = –14.2 (dd, $^1J_{P,Rh}$ = 154.8 Hz, $^2J_{P,P}$ = 52.4 Hz).
(9) (a) Reetz, M. T.; Sell, T.; Meiswinkel, A.; Mehler, G. *Angew. Chem. Int. Ed.* **2003**, *42*, 790; *Angew. Chem.* 2003, **115**, 814. (b) Reetz, M. T. *Chim. Oggi* **2003**, *21*, 5. (c) Reetz, M. T.; Mehler, G. *Tetrahedron Lett.* **2003**, *44*, 4593. (d) Reetz, M. T.; Li, X. *Tetrahedron* **2004**, *60*, 9709.
(10) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.