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# Phosphane-Phosphite Chelators Built on a α-Cyclodextrin Scaffold: Application in Rh-Catalysed Asymmetric Hydrogenation and Hydroformylation

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Four hybrid phosphane-phosphite ligands were synthesised by regioselective A,B-functionalisation of a methylated  $\alpha$ cyclodextrin ( $\alpha$ -CD) scaffold. In all these ligands the phosphite part comprises a 2,2'-bisaryloxyphosphanyloxy group. The ligands, which display inherent chirality, readily form 12-membered chelate rings with d<sup>8</sup>-metal ions. In the most flexible chelates (those with an unsubstituted 2,2'-bisphenoxy group), the metal plane describes a fan-like motion about the P···P' axis with concomitant fast atropisomerisation of the biaryl unit. When the latter is blocked, as in the 2,2'- binaphthyloxyphosphites, the fan-like motion no longer takes place. Rhodium complexes of the CDs were assessed in asymmetric hydrogenation of  $\alpha$ -dehydroamino acid esters and hydroformylation of styrene. Poor enantiodiscrimination was observed for the highly mobile chelate complexes, whereas the more rigid ones all resulted in significant *ee* values. The best performing hydrogenation catalyst is the one in which both chiral components – CD and (*S*)-binaphthyl – behave in a synergistic way.

# Introduction

Despite the presence of numerous stereogenic centres embedded in their rigid skeleton, to date only few cyclodextrin (CD) derived ligands have been used in asymmetric catalysis. In the corresponding metal catalysts the reaction usually takes place outside the cavity, far from the centres of chirality in which efficient asymmetric induction could occur. Nevertheless, when the catalytic centre of these complexes is maintained in a rigid manner with respect to the CD backbone, significant ee values can be obtained. Such a feature has been observed, for example, in metallocyclodextrins capable of forming transient inclusion complexes in water with prochiral substrates to be transformed.<sup>[1]</sup> Chirality transfer from the glucose units to the metal first sphere of coordination is also often very effective when rigid chelate complexes are obtained from CDs bearing two close pendant arms.<sup>[2]</sup> A potential strategy for enhancing chiral induction consists in making the CD shape inherently chiral by anchoring a set of distinct groups on its conical backbone so as to produce a CD with a substitution pattern non superimposable with its mirror image.<sup>[3]</sup> However, whether the effects of inherent chirality will synergistically add to those induced by the asymmetric centres of the backbone is difficult to predict. It is worth mentioning here that di-

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phosphanes based on other inherently chiral macrocycles have already been reported.<sup>[3b]</sup>

In this paper we describe the first inherently chiral CDs bearing two distinct  $P^{III}$  substituents, namely a phosphane unit and a phosphite one. These hybrid ligands, which are ideal for chelate formation, have been assessed in the rho-dium-catalysed hydrogenation of  $\alpha$ -dehydroamino acid esters and hydroformylation of styrene. Chiral phosphanyl-phosphites constitute a class of ligands that have found many applications in asymmetric catalytic transformations,<sup>[4]</sup> notably hydrogenation<sup>[5]</sup> and hydroformylation<sup>[6]</sup> of prochiral olefins.

# **Results and Discussion**

## Synthesis of Phosphane-Phosphite Ligands

The synthesis of the ligands started with the deprotection of phosphane borane adduct  $1 \cdot BH_3^{[7]}$  with boiling diethylamine to give 1 quantitatively (Scheme 1). Surprisingly, phosphorochloridites 2–5 did not react with the CD primary hydroxy groups in the presence of a tertiary amine such as Et<sub>3</sub>N, which are the general reaction conditions used for the formation of phosphites from secondary and tertiary alcohols. Only the CD alkoxide obtained by reacting 1 with NaH in hot toluene, was sufficiently nucleophilic to give the corresponding phosphane-phosphite ligands 6–9 with isolated yields ranging from 37 to 62%.

The chemical shifts for the two phosphorus donor atoms are typical of phosphite (146.6  $\leq \delta \leq$  150.7 ppm) and diarylalkylphosphane (-21.4  $\leq \delta \leq$  -20.3 ppm) functionalities. All NMR spectra displayed sharp signals at room tem-

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Scheme 1. Synthesis of phosphane-phosphite ligands 6-9.

perature except for biphenyl derivative 7, the <sup>31</sup>P NMR spectrum of which, recorded at 60 °C, showed a broad singlet for the phosphite phosphorus atom, whereas the phosphane signal was sharp. This is likely because of fluxional behaviour involving the *t*Bu-substituted biphenyl unit, which is sufficiently congested to interact sterically with the CD platform so that slow interconversion of biphenyl occurs on the NMR time scale as previously noticed for similar bulky diphosphites.<sup>[8]</sup> This is obviously not the case with less sterically-demanding ligand **6** in which the same process is much faster, neither so for binaphthyl derivatives **8** and **9** in which free rotation about the aryl-aryl bond is prevented. None of the ligands displayed <sup>31</sup>P–<sup>31</sup>P throughspace coupling, unlike other sugar-based phosphane-phosphite ligands.<sup>[9]</sup>

#### **Chelating Properties**

Despite the 10-bond separation between the two donor atoms, we were delighted to find out that all CD ligands form readily chelate complexes, as could easily be deduced from a combination of ESI-MS and NMR spectroscopy. Thus, neutral  $Pt^{II}$  complex **10** (Figure 1) was obtained quantitatively by reacting a stoichiometric amount of the phosphane-phosphite ligand **6** with  $[PtCl_2(PhCN)_2]$  in

CH<sub>2</sub>Cl<sub>2</sub> (mass spectrum showing a peak corresponding to the  $[M + Na]^+$  cation). It is noteworthy that chelate formation did not require high dilution conditions. Cationic complexes could also be obtained, again with no oligomeric material being formed, by simply mixing the ligand with a metal precursor. For example, Rh complexes 11-14 were obtained by reacting  $[Rh(1,5-cyclooctadiene)_2]BF_4$  with the appropriate heterobidentate ligand (6-9). The NMR spectra of platinum complex 10, and rhodium complexes 12 and 13, are broad at room temperature. Upon raising the temperature to 60 °C, all NMR spectra became sharp. The <sup>31</sup>P-<sup>31</sup>P coupling constants for all five complexes are typical of *cis* stereochemistry (23 Hz  $\leq {}^{2}J_{P,P'} \leq 42$  Hz).<sup>[5a]</sup> As expected for  $C_1$ -symmetric compounds, four distinct signals were detected for the vinylic protons of the coordinated cyclooctadiene in all Rh<sup>I</sup> complexes (see Experimental Section).

As revealed by a variable-temperature (VT) NMR spectroscopic study, complex **10** displayed fluxional behaviour in solution. The <sup>31</sup>P NMR spectrum, recorded in CDCl<sub>3</sub> at -60 °C,<sup>[10]</sup> revealed the presence of four species, two of them having broad signals at this temperature, and the other two, present in a 60:40 ratio, displayed sharp ones (see the Supporting Information). Each of the latter are characterized by an ABX pattern [<sup>2</sup>J(AB) = 23 Hz, <sup>1</sup>J(P<sup>A</sup>Pt) = 3343 Hz



Figure 1. Chelate complexes obtained from heterobidentate ligands 6-9.



Figure 2. Two energy-minimized conformers of 10 (SPARTAN) that are consistent with the ROESY spectrum, which revealed crosspeaks between *ortho* aromatic protons of both phenyl rings of the PPh<sub>2</sub> unit and the same H-4<sup>A</sup> proton (distances given).

and  ${}^{1}J(P^{B}Pt) = 5878 \text{ Hz}$  (major species) and  ${}^{2}J(AB) =$ 23 Hz,  ${}^{1}J(P^{A}Pt) = 3364$  Hz and  ${}^{1}J(P^{B}Pt) = 5965$  Hz (minor species)] indicative of cis complexes. Upon raising the temperature, the signals first broadened, then coalesced near -30 °C, and finally merged at 60 °C into a single ABX spectrum  $[^{2}J(AB) = 23 \text{ Hz}, ^{1}J(P^{A}Pt) = 3408 \text{ and } ^{1}J(P^{B}Pt) =$ 6136 Hz]. The best way to rationalise the observed data is to consider two different motions. One of them involves interconversion of the sterically unhindered biphenyl unit, whereas the second one is related to a fan-like movement of the P<sub>2</sub>PtCl<sub>2</sub> plane about the P<sup>A</sup>...P<sup>B</sup> axle. Confirmation of the flexibility of the rather large chelate ring came from a ROESY experiment at 60 °C, which showed that 10 gave rise to cross-peaks originating from through-space correlations between the outer-cavity H-4<sup>A</sup> proton and ortho aromatic protons of both phenyl rings of the PPh2 unit. SPAR-TAN calculations produced two energy-minimized conformers, one of them having its P<sub>2</sub>PtCl<sub>2</sub> unit oriented towards the centre of the cavity, the other being clearly located outside (Figure 2). In keeping with the observed NMR spectroscopic data, the phenyl ring that comes close to the CD is different in each conformer. The calculations also revealed that in the "in" and "out" conformers the bisaryl moieties have opposite configurations.

VT <sup>31</sup>P NMR spectroscopic studies were also performed for rhodium complexes **13** and **14**. In these binaphthyl-con-

taining complexes atropoisomerisation is blocked, so that the only possible motion is the fanning motion of the chelate ring. Both <sup>31</sup>P NMR spectra recorded in CDCl<sub>3</sub><sup>[10]</sup> remained sharp upon cooling the samples to -60 °C suggesting that a single conformer was present in both cases. Careful analysis of the 2D ROESY spectrum of **14** revealed that here the H-4<sup>A</sup> atom correlates with the *ortho* protons of only one P-phenyl ring unlike that of **10** in which two crosspeaks were observed. This confirms that only one conformer of **14** is present in solution, but its identification ("in" or "out" form) was not achieved.<sup>[11]</sup> Clearly, the nature of the biaryl unit has a deep impact on the mobility of the chelate ring.

#### **Catalytic Studies**

Five different  $\alpha$ -dehydroamino esters **15–19** were used to assess the performance of complexes **11–14** in asymmetric catalysis (Scheme 2). As shown in Table 1, all phosphanephosphite Rh complexes promoted olefin hydrogenation with reasonable reaction rates at 5 bar of H<sub>2</sub> at room temperature. Not surprisingly the presence of bulky *tert*-butyl groups in 7 slowed down the reaction to a certain extent (Table 1, Entries 6–10). However, as noticed previously by van Leeuwen<sup>[12]</sup> and Ruiz,<sup>[9]</sup> these groups are extremely beneficial for efficient asymmetric induction. Ligand 7 is no exception and led to significantly higher ee values than those obtained with much more flexible 6 (4.5 fold increase on average depending on the substrate used). The fact that modification of this particular unit produced dramatic changes in the enantioselectivity indicates that the phosphite unit is predominantly responsible for enantiodiscrimination. Without the presence of stereogenic biaryl units, the formation of the (R) enantiomer was always favoured regardless of the substrate used. It is clear that the chirality of the cyclodextrin platform is somehow transferred to the chelate ring, but the question whether enantiodiscrimination is caused by the inherent chirality of the CD platform and/or by a particular conformation of the metallocycle remains open. Interestingly, a permethylated 6<sup>A</sup>,6<sup>B</sup>-diphosphanyl-β-CD reported by Wong et al.<sup>[2b]</sup> produced enantioselectivities similar to those obtained with catalyst 12 in the asymmetric hydrogenation of 15 (Table 1, Entry 6).

A clear match/mismatch relationship was observed upon introducing a stereogenic binaphthyl unit into the phosphite-coordinating unit. Whereas (S)-binaphthyl-based catalyst **14** led to a significant increase in the amount of (R)enantiomer being produced, reaching 92% for bulky naphthyl-containing substrate **19** (Table 1, Entry 20), the presence of (R)-binaphthyl counterpart **13** reversed the sense of enantiodiscrimination [formation of the (S)-product], and led to significantly lower *ee* values (Table 1, Entries 11–15,). Clearly, the introduction of a (S)-binaphthyl



Scheme 2. Rhodium-catalysed asymmetric hydrogenation of  $\alpha$ -de-hydroamino esters.

Table 1. Enantioselective hydrogenation of  $\alpha$ -dehydroamino esters with phosphane-phosphite complexes 11–14.<sup>[a]</sup>

Entry	Complex	R	Conv. [%]	ee [%] [c]	Config.
1	11	Ph	100	8	S
2		$4-F-C_6H_4$	100	14	R
3		$4-Cl-C_6H_4$	100	8	R
4		3,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	100	12	R
5		2-naphthyl	100	10	R
6	12	Ph	73	60	R
7		$4-F-C_6H_4$	95	48	R
8		$4-Cl-C_6H_4$	62	56	R
9		3,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	97	34	R
10		2-naphthyl	16	52	R
11	13	Ph	100	24	S
12		$4-F-C_6H_4$	100	46	S
13		$4-Cl-C_6H_4$	100	34	S
14		3,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	100	24	S
15		2-naphthyl	100	70	S
16	14	Ph	100	58	R
17		$4-F-C_6H_4$	100	58	R
18		$4-Cl-C_6H_4$	100	62	R
19		3,4-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	100	52	R
20		2-naphthyl	100	92	R

[a] General conditions:  $P(H_2) = 5$  bar, T = 25 °C, 24 h; [substrate/ complex = 100:1]. [b] Conversions were determined by means of <sup>1</sup>H NMR spectroscopic analysis. [c] Enantioselectivities were determined by chiral GC analysis with a CHROMPAK chiral fused silica 25 m × 0.25 mm. Coating Chirasil-L-Val column.

moiety enhances the enantiodiscrimination brought about by the CD skeleton. We further observed a significant *ee* increase upon lowering the  $H_2$  pressure to 1 bar (Table 2, Entry 3).

Ligand 7 was also assessed in the asymmetric hydroformylation of styrene (Table 3). The linear and branched aldehydes were formed in a standard l:b ratio of 0.3. Relative to other phosphane-phosphite ligands, the activity of the catalyst is above average and the observed enantioselectivities, despite being moderate [up to 50% *ee* in favour of the (*R*)-product], are similar to those obtained with the best performing sugar-based phosphane-phosphites.<sup>[6,13]</sup>

Table 2. Optimization of the catalytic hydrogenation of 17 with best-performing complex 14.

Entry	<i>T</i> [°C]	$P(\mathrm{H}_2)$	Time [h]	Charge [mol-%]	Conversion [%] <sup>[a]</sup>	ee [%] <sup>[b]</sup>	Configuration
1	25	5	24	1	100	62	R
2	0	5	4	1	63	60	R
3	25	1	24	1	100	75	R
4	25	5	24	0.25	75	71	R

[a] Conversions were determined by means of <sup>1</sup>H NMR spectroscopic analysis. [b] Enantioselectivities were determined by chiral GC analysis with a CHROMPAK chiral fused silica  $25m \times 0.25$  mm. Coating Chirasil-L-Val column.

Table 3. Rhodium-catalyzed hydroformylation of styrene.[a]

Entry	Complex	Conversion [%] <sup>[b]</sup> (time [h])	TOF <sup>[c]</sup>	Aldehydes <sup>[b]</sup> 1 [%] b [%]	1/b <sup>[d]</sup>	ee (%) <sup>[b]</sup>
1	12	59.8 (4)	374	24.2 75.8	0.3	50
2	12	>99 (7)	104	23.8 76.2	0.3	50

[a] Styrene (5 mmol), styrene/complex = 2500,  $P(CO/H_2) = 20$  bar, T = 80 °C, toluene/*n*-decane (15 mL/0.5 mL), incubation overnight at 80 °C under  $P(CO/H_2) = 20$  bar. [b] Determined by GC analysis with decane as internal standard. [c] Mol(converted styrene) mol(Rh)  $^{-1}h^{-1}$ . [d] l:b aldehyde ratio.

## Conclusion

Access to the first  $C_1$ -symmetric heterobidentate ligands built on a cavity-shaped molecule was made possible by proximally functionalising a methylated  $\alpha$ -CD with two different coordinating groups. Despite the large separation between the two donor atoms, all the phosphane-phosphite ligands proved to be sufficiently preorganized to form quantitatively both neutral Pt<sup>II</sup> and cationic Rh<sup>I</sup> chelate complexes. As shown by extensive NMR spectroscopic studies, chelate comlex 10 undergoes two motions in solution, one being associated with atropoisomerisation of the biphenyl unit, the other being a fan-like movement of the metallocyclic unit about the PA--PB axle, which displaces the metal centre from above the cavity to its exterior. Such motions are impeded in binaphthyl complexes 13 and 14. Poor enantiodiscrimination was observed by using 11 in the asymmetric hydrogenation of  $\alpha$ -dehydroamino acid esters. On the contrary, more rigid complexes 12–14 all resulted in significant ee values, with the best performing system (14) being the one in which both chiral components - CD and (S)-binaphthyl – behave in a synergistic way. Even higher *ee* values are expected with analogues having bulkier biaryl units, which are likely to enhance the inherently chiral properties of the  $C_1$ -symmetric CD platform.

#### **Experimental Section**

General Methods: All commercial reagents were used as supplied. All manipulations were performed in Schlenk-type flasks under N<sub>2</sub> with degassed solvent. Solvents were dried by conventional methods and distilled immediately prior to use. Column chromatography was performed on silica gel 60 (particle size 40-63 µm, 230-240 mesh), dried, in advance, overnight at 150 °C. CDCl<sub>3</sub> was passed down a 5-cm-thick alumina column and stored under N<sub>2</sub> over molecular sieves (3 Å). Routine <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded with Bruker FT instruments (AVANCE 400, 500, 600 spectrometers). <sup>1</sup>H NMR spectral data were referenced to residual protiated solvents ( $\delta = 7.26$  ppm for CDCl<sub>3</sub>, 5.32 ppm for  $CD_2Cl_2$ ) and <sup>13</sup>C chemical shifts are reported relative to deuterated solvents ( $\delta = 77.16$  ppm for CDCl<sub>3</sub>). Mass spectra were recorded with a Bruker MicroTOF spectrometer (ESI) by using CH<sub>2</sub>Cl<sub>2</sub>, MeCN or MeOH as solvent. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie UMR 7177, Strasbourg. Melting points were determined with a Büchi 535 capillary melting point apparatus. Optical rotations were measured on a Perkin-Elmer 341 digital polarimeter with a path length of 1 dm. The catalytic solutions were analysed by using a Varian 3900 gas chromatograph equipped with a wall-coated open tubular fusedsilica column (25 m  $\times$  0.25 mm) or with a Chirasil-DEX CB column (25 m $\times$  0.25 mm). Phosphane-borane 1·BH<sub>3</sub><sup>[7]</sup> (1,1'-biphenyl-2,2'-diyl)chlorophosphite (2),<sup>[14]</sup> (4,4',6,6'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)chlorophosphite (3),<sup>[14]</sup> [(R)-1,1'-binaphthyl-2,2'-diyl]chlorophosphite (4), [(S)-1,1'-binaphthyl-2,2'-diyl]chlorophosphite (5)<sup>[15]</sup> and [PtCl<sub>2</sub>(PhCN)<sub>2</sub>]<sup>[16]</sup> were synthesised according to literature procedures. In this publication, the glucose units are arranged clockwise when looking at the primary face. The numbering of the atoms within a glucose unit is as follows:



6<sup>A</sup>-Deoxy-6<sup>A</sup>-diphenylphosphanyl-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>,2<sup>E</sup>,2<sup>F</sup>,3<sup>A</sup>,3<sup>B</sup>,3<sup>C</sup>,  $3^{D}$ ,  $3^{E}$ ,  $3^{F}$ ,  $6^{C}$ ,  $6^{D}$ ,  $6^{E}$ ,  $6^{F}$ -hexadeca-O-methyl- $\alpha$ -cyclodextrin (1): A solution of 1·BH<sub>3</sub> (1.258 g, 0.91 mmol) in degassed Et<sub>2</sub>NH (20 mL) was heated to reflux for 12 h. After cooling to room temperature, the reaction mixture was evaporated to dryness. The residue was then taken up in toluene and the resulting suspension filtered through a pad of Celite. Removal of the solvent in vacuo afforded analytically pure 1 (1.241 g, 99%) as a colourless solid.  $R_{\rm f}$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/ MeOH, 90:10, v/v) = 0.64, m.p. dec. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = [assignment by combined COSY and heteronuclear single quantum coherence (HSQC)] =  $1.49 \text{ (m, 1 H, OH^B)}$ , 2.60 (ddd,  ${}^{2}J_{6a-H,6b-H} = 15.6, {}^{2}J_{6b-H,P} = 2.6, {}^{3}J_{6a-H,5-H} = 5.9 \text{ Hz}, 1 \text{ H}, 6a^{\text{A}}\text{-H}),$ 2.70 (td,  ${}^{2}J_{6a-H,6b-H} = 15.6$ ,  ${}^{2}J_{6b-H,P} = {}^{3}J_{6b-H,5-H} = 3.9$  Hz, 1 H, 6b<sup>A</sup>-H), 3.06 (dd,  ${}^{3}J_{2-H,3-H} = 9.2$ ,  ${}^{3}J_{2-H,1-H} = 3.0$  Hz, 1 H, 2-H), 3.08 (s, 3 H, OMe), 3.12-3.20 (5 H, 2-H), 3.21 (m, 1 H, 6-H), 3.39 (s, 3 H, OMe), 3.40 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 9 H, OMe), 3.49 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 9 H, OMe), 3.64 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.37–3.92 (26 H, 3-H, 4-H, 5-H, 6-H), 4.18 (m, 1 H, 5<sup>A</sup>-H), 4.91 (d,  ${}^{3}J_{1-H 2-H} = 3.2$  Hz, 1 H, 1-H), 5.00–5.03 (2 H, 1-H), 5.04-5.07 (3 H, 1-H), 7.14-7.19 (2 H, p-H), 7.22-7.33 (4 H, m-H), 7.39–7.48 (4 H, o-H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = (assignment by HSQC) = 31.83 (d,  ${}^{1}J_{C,P}$  = 18.3 Hz, C-6<sup>A</sup>), 57.77, 57.91, 57.93, 58.16, 58.89, 59.12 [× 5] (OMe), 61.41 (C-6<sup>B</sup>), 61.66, 61.76, 61.86, 61.91 [× 3] (OMe), 70.79, 70.92, 71.05 (C-5), 71.09, 71.19 (C-6), 71.35, 71.45 (C-5), 71.52 [× 2] (C-6), 72.14 (C-5), 81.11, 81.21, 81.24, 81.28, 81.33 [ $\times$  2], 81.78, 81.97, 82.06, 82.14, 82.17 [× 2], 82.31 [× 2], 82.36, 82.48 [× 2] (C-2, C-3, C-4), 87.14 (d,  ${}^{3}J_{C,P}$  = 11.6 Hz, C-4<sup>A</sup>), 99.32, 99.85, 99.93, 100.07, 100.22, 100.48 (C-1), 128.15–128.70 [× 6], 132.79–133.20 [× 4] (C-arom), 137.94 (d,  ${}^{1}J_{C,P}$  = 14.1 Hz, C-*ipso*<sup>A</sup>), 140.34 (d,  ${}^{1}J_{C,P}$  = 12.3 Hz, C*ipso*<sup>A'</sup>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -22.8$ (s) ppm.  $C_{64}H_{101}O_{29}P\cdot 2H_2O$  (1365.44 + 36.03): calcd. for C 54.85, H 7.55; found C 55.15, H 7.53. MS (ESI-TOF): m/z (%) = 1387.61  $(100) [M + Na]^+$ .

6<sup>A</sup>,6<sup>B</sup>-Dideoxy-6<sup>A</sup>-diphenylphosphanyl-6<sup>B</sup>-(2,2'-bisphenoxyphosphanyloxy)-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>,2<sup>E</sup>, 2<sup>F</sup>,3<sup>A</sup>,3<sup>B</sup>,3<sup>C</sup>,3<sup>D</sup>,3<sup>E</sup>,3<sup>F</sup>,6<sup>C</sup>,6<sup>D</sup>,6<sup>E</sup>,6<sup>F</sup>-hexadeca-O-methyl-a-cyclodextrin (6): Powdered sodium hydride (60% dispersion in oil; 0.019 g, 0.47 mmol) was added to a solution of anhydrous 1 (0.255 g, 0.19 mmol) in toluene (7.0 mL). The suspension was stirred at 100 °C for 16 h before being cooled to 0 °C. A solution of (1,1'-biphenyl-2,2'-diyl)chlorophosphite (2; 0.187 g, 0.75 mmol) in toluene (7.5 mL) was then added at 0 °C and the resulting reaction mixture stirred at 0 °C for 1 h. The temperature was subsequently raised to 100 °C and the slurry stirred at this temperature for an additional 16 h. After cooling, the reaction mixture was evaporated to dryness in vacuo. The residue was subjected to column chromatography [short pad of Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, followed by CH<sub>2</sub>Cl<sub>2</sub>/THF (50:50, v/v)]. If necessary, the resulting colourless solid was further purified by column chromatography (SiO<sub>2</sub>;  $CH_2Cl_2/THF$ , 90:10 to 85:15, v/v) to afford analytically pure 6 (0.145 g, 49%).  $R_{\rm f}$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 90:10, v/v) = 0.72, m.p. dec.  $[a]_D^{20} = +105 (CH_2Cl_2, c = 4.0)$ . <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = (assignment by combined COSY and HMQC) = 2.55  $(dt, {}^{2}J_{6a-H,6b-H} = 14.7, {}^{2}J_{6b-H,P} = {}^{3}J_{6b-H,5-H} = 3.2 \text{ Hz}, 1 \text{ H}, 6b^{\text{A}}\text{-H}),$ 

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2.60 (ddd,  ${}^{2}J_{6a-H,6b-H} = 14.7$ ,  ${}^{2}J_{6a-H,P} = 2.9$ ,  ${}^{3}J_{6a-H,5-H} = 8.3$  Hz, 1 H, 6a<sup>A</sup>-H), 3.01 (s, 3 H, OMe), 3.07 (dd,  ${}^{3}J_{2-H,3-H} = 9.9$ ,  ${}^{3}J_{2-H,1-H}$ = 3.4 Hz, 1 H, 2-H), 3.09 (dd,  ${}^{3}J_{2-H,3-H}$  = 10.6,  ${}^{3}J_{2-H,1-H}$  = 3.3 Hz, 1 H, 2-H), 3.14–3.20 (3 H, 2-H), 3.22 (dd,  ${}^{3}J_{2-H,3-H} = 9.4$ ,  ${}^{3}J_{2-H,1-H}$ = 2.9 Hz, 1 H, 2-H), 3.32 (dd,  ${}^{2}J_{6-Ha,6b-H}$  = 11.9,  ${}^{3}J_{6b-H,5-H}$  = 2.2 Hz, 1 H, 6b-H), 3.37 (s, 6 H, OMe), 3.38 (s, 3 H, OMe), 3.44 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.48 (s, 9 H, OMe), 3.51 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 6 H, OMe), 3.64 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.33-3.96 (25 H, 3-H, 4-H, 5-H, 6-H), 4.14 (ddd,  ${}^{2}J_{6a-H,6b-H} = 11.8$ ,  ${}^{2}J_{6a-H,P} = 2.5$ ,  ${}^{3}J_{6a-H,5-H} = 9.4 \text{ Hz}, 1 \text{ H}, 6a^{\text{B}}-\text{H}), 4.22 \text{ (ddd, } {}^{3}J_{5-H,6-Hb} = 3.2,$  ${}^{3}J_{5-H,6a-H} = 8.3$ ,  ${}^{3}J_{5-H,4-H} = 17.7$  Hz, 1 H, 5<sup>A</sup>-H), 4.89 (d,  ${}^{3}J_{1-H,2-H}$ = 3.3 Hz, 1 H, 1-H), 4.93 (d,  ${}^{3}J_{1-H,2-H}$  = 2.9 Hz, 1 H, 1-H), 4.95 (d,  ${}^{3}J_{1-H,2-H} = 3.2$  Hz, 1 H, 1-H), 5.05 (d,  ${}^{3}J_{1-H,2-H} = 3.2$  Hz, 1 H, 1-H), 5.06 (d,  ${}^{3}J_{1-H,H,2}$  = 3.6 Hz, 1 H, 1-H), 5.08 (d,  ${}^{3}J_{1-H,2-H}$  = 3.4 Hz, 1 H, 1-H), 7.09 (d, J = 7.8 Hz, 1 H, H-arom), 7.12 (d, J = 7.9 Hz, 1 H, H-arom), 7.17-7.50 (16 H, H-arom) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = (assignment by HMQC) = 31.57 (d,  ${}^{1}J_{C,P} = 14.0 \text{ Hz}, \text{ C-6}^{\text{A}}$ ), 57.74, 57.78, 57.81, 57.97, 58.11, 58.18, 58.72, 59.05, 59.11 [× 2], 61.69, 61.78 [× 2], 61.87, 61.90 [× 2] (OMe), 63.37 (d,  ${}^{2}J_{C,P}$  = 9.5 Hz, C-6<sup>B</sup>), 70.89 (C-5<sup>A</sup>), 71.04 (C-6), 71.09 [× 2] (C-5), 71.19, 71.24 (C-6), 71.33, 71.45 [× 2] (C-5), 71.54 (C-6), 80.89, 81.20, 81.31 [× 2], 81.40, 81.59, 81.68, 81.96, 82.02 [× 2], 82.06 [× 2], 82.15, 82.41, 82.45, 82.55 [× 2] (C-2, C-3, C-4), 87.66 (C-4<sup>A</sup>), 99.20, 99.55, 100.04, 100.06, 100.09, 100.47 (C-1), 124.96, 125.08 (C-arom), 128.02 (d,  ${}^{1}J_{C,P} = 10.1$  Hz, C-ip $so^{\rm A}$ ), 128.28, 128.36, 128.42, 128.51, 128.57, 128.70, 128.77, 128.87, 129.01 [× 2], 129.86, 129.92, 130.59, 132.59 (C-arom), 131.50 (d,  ${}^{1}J_{C,P} = 12.5 \text{ Hz}, \text{ C-ipso'}^{\text{A}}$ ), 132.76, 133.04, 133.24, 133.52, 136.14, 138.97 (C-arom) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -21.4$  (s, P<sup>A</sup>), 146.6 (s, P<sup>B</sup>) ppm. C<sub>76</sub>H<sub>108</sub>O<sub>31</sub>P<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (1579.60 + 84.93): calcd. for C 55.56, H 6.66; found C 55.86, H 6.61. MS (ESI-TOF): m/z (%) = 1601.60 (100) [M + Na]<sup>+</sup>.

6<sup>A</sup>,6<sup>B</sup>-Dideoxy-6<sup>A</sup>-diphenylphosphanyl-6<sup>B</sup>-(4,4',6,6'-tetra-tert-butyl-2,2'-bisphenoxyphosphanyloxy)-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>,2<sup>E</sup>,2<sup>F</sup>,3<sup>A</sup>,3<sup>B</sup>,3<sup>C</sup>,3<sup>D</sup>,3<sup>E</sup>,3<sup>F</sup>,  $6^{\rm C}, 6^{\rm D}, 6^{\rm E}, 6^{\rm F}$ -hexadeca-O-methyl- $\alpha$ -cyclodextrin (7): This compound was prepared according to the procedure used for the synthesis of 6, by reacting 1 (0.200 g, 0.15 mmol) with (4,4',6,6'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)chlorophosphite (3; 0.278 g, 0.58 mmol). The crude mixture was subjected to column chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97:3, v/v) to afford 7 (0.164 g, 62%) as a colourless solid.  $R_{\rm f}$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 90:10, v/v) = 0.72, m.p. dec.  $[a]_{\rm D}^{20}$  $= +140 (CH_2Cl_2, c = 5.0); {}^{1}H NMR (500.1 MHz, CDCl_3, 25 {}^{\circ}C):$  $\delta$  = (assignment by COSY) = 1.34 (s, 9 H, tBu), 1.35 (s, 9 H, tBu), 144 (s, 9 H, *t*Bu), 1.46 (s, 9 H, *t*Bu), 2.37 (ddd,  ${}^{2}J_{6a-H,6b-H} = 14.9$ ,  ${}^{2}J_{6a-H,P} = 2.9, {}^{3}J_{6a-H,5-H} = 10.7 \text{ Hz}, 1 \text{ H}, 6a^{\text{A}}-\text{H}), 2.67 \text{ (dt,}$  ${}^{2}J_{6a-H,6b-H} = 14.9, {}^{2}J_{6b-H,P} = {}^{3}J_{6b-H,5-H} = 2.8 \text{ Hz}, 1 \text{ H}, 6b^{\text{A}}\text{-H}), 3.05$ (s, 3 H, OMe), 3.08 (dd,  ${}^{3}J_{2-H,3-H} = 10.1$ ,  ${}^{3}J_{2-H,1-H} = 2.9$  Hz, 1 H, 2-H), 3.09 (dd,  ${}^{3}J_{2-H,3-H} = 10.1$ ,  ${}^{3}J_{2-H,1-H} = 3.1$  Hz, 1 H, 2-H), 3.15 (dd,  ${}^{3}J_{2-H,3-H} = 10.1$ ,  ${}^{3}J_{2-H,1-H} = 3.2$  Hz, 1 H, 2-H), 3.20 (dd,  ${}^{3}J_{2-H,3-H} = 3.2$  $_{\rm H,3-H}$  = 9.7,  ${}^{3}J_{2-\rm H,1-\rm H}$  = 3.3 Hz, 1 H, 2-H), 3.21 (dd,  ${}^{3}J_{2-\rm H,3-\rm H}$  = 9.2,  ${}^{3}J_{2-H,1-H} = 3.7$  Hz, 1 H, 2-H), 3.22 (dd,  ${}^{3}J_{2-H,3-H} = 10.1$ ,  ${}^{3}J_{2-H,1-H} =$ 3.2 Hz, 1 H, 2-H), 3.36 (s, 3 H, OMe), 3.37 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.58 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.64 (s, 6 H, OMe), 3.65 (s, 3 H, OMe), 3.33-3.96 (27 H, 3-H, 4-H, 5-H, 6-H), 4.24 (m, 1 H, 5<sup>A</sup>-H), 4.85 (d,  ${}^{3}J_{H-1,2-H} = 3.7$  Hz, 1 H, 1-H), 4.95 (d,  ${}^{3}J_{1-H,2-H}$  = 3.1 Hz, 1 H, 1-H), 5.02 (d,  ${}^{3}J_{1-H,2-H}$  = 3.2 Hz, 1 H, 1-H), 5.07 (d,  ${}^{3}J_{1-H,2-H}$  = 3.2 Hz, 1 H, 1-H), 5.08 (d,  ${}^{3}J_{1-H,2-H}$  = 3.3 Hz, 1 H, 1-H), 5.12 (d,  ${}^{3}J_{1-H,2-H} = 2.9$  Hz, 1 H, 1-H), 7.14 (d,  ${}^{4}J = 2.4$  Hz, 1 H, H-*arom*<sup>B</sup>), 7.15 (d,  ${}^{4}J = 2.3$  Hz, 1 H, H-*arom*<sup>B</sup>), 7.19–7.33 (8 H, H-arom<sup>A</sup>), 7.40 (d,  ${}^{4}J = 2.4$  Hz, 1 H, H-arom<sup>B</sup>),

7.41 (d,  ${}^{4}J$  = 2.3 Hz, 1 H, H-*arom*<sup>B</sup>), 7.43–7.47 (2 H, H*arom*<sup>A</sup>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 31.09, 31.12, 31.35, 31.53 [× 9] (CH<sub>3</sub>-tBu), 32.54 (d,  ${}^{1}J_{C,P}$  = 13.8 Hz, C-6<sup>A</sup>), 34.58, 34.53, 35.29, 35.33 (C-*t*Bu), 57.57, 57.59, 57.68, 57.95, 58.20 [× 2], 58.64, 58.80, 59.08 [× 2], 61.55, 61.66, 61.73, 61.87, 61.89, 61.92 (OMe), 62.77 (d,  ${}^{2}J_{C,P} = 23.3 \text{ Hz}, \text{ C-6}^{\text{B}}$ ), 70.85 (C-6), 70.99, 71.07, 71.10 (C-5), 71.16 (C-6), 71.18 (C-5), 71.23 (C-6), 71.45, 71.53 (C-5), 71.59 (C-6), 80.82, 81.16, 81.28 [× 2], 81.32, 81.42, 81.54, 81.59, 81.73, 81.93, 81.96 [× 2], 82.08, 82.41, 82.56, 82.69, 82.74 (C-2, C-3, C-4), 89.15 (d,  ${}^{3}J_{C,P} = 11.6$  Hz, C-4<sup>A</sup>), 98.96, 99.48, 99.97, 100.01, 100.58, 100.89 (C-1), 123.77, 124.08, 126.24, 126.51, 128.18, 128.24, 128.29, 128.58, 128.64, 128.85, 132.41, 132.56, 132.97, 133.13, 133.35 (C-arom), 139.22 (d,  ${}^{1}J_{C,P}$  = 11.6 Hz, C-*ipso*<sup>A</sup>), 139.77, 140.07 (C-*arom*), 141.24 (d,  ${}^{1}J_{C,P}$ = 11.6 Hz, C-ipso<sup>A'</sup>), 145.44, 145.74, 145.80, 145.85, 146.32 (C*arom*) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>, 60 °C):  $\delta = -20.6$ (s,  $P^A$ ), 149.2 (br. s,  $P^B$ ) ppm.  $C_{92}H_{140}O_{31}P_2 \cdot 2H_2O$  (1802.89 + 36.02): calcd. for C 60.05, H 7.89; found C 59.75, H 7.94. MS (ESI-TOF): m/z (%) = 1826.88 (100) [M + Na]<sup>+</sup>.

6<sup>A</sup>,6<sup>B</sup>-Dideoxy-6<sup>A</sup>-diphenylphosphanyl-6<sup>B</sup>-(*R*)-(1,1'-binaphthyl-2,2'bisoxyphosphanyloxy)-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>,2<sup>E</sup>,2<sup>F</sup>,3<sup>A</sup>,3<sup>B</sup>,3<sup>C</sup>,3<sup>D</sup>,3<sup>E</sup>,3<sup>F</sup>,6<sup>C</sup>,6<sup>D</sup>, 6<sup>E</sup>,6<sup>F</sup>-hexadeca-O-methyl-α-cyclodextrin (8): This compound was prepared in 49% (0.128 g) according to the procedure used for the synthesis of 6, by reacting 1 (0.216 g, 0.16 mmol) with [(R)-1,1'binaphthyl-2,2'-diyl]chlorophosphite (4; 0.222 g, 0.63 mmol).  $R_{\rm f}$  $(SiO_2, CH_2Cl_2/MeOH, 90:10, v/v) = 0.72, m.p. dec. [a]_D^{20} = +20$  $(CH_2Cl_2, c = 5.0)$ ; <sup>1</sup>H NMR (400.1 MHz, CDCl\_3, 25 °C):  $\delta$  = (assignment by combined COSY and HSQC) = 2.51 (dt,  ${}^{2}J_{6a-H.6b-H}$  = 14.9,  ${}^{2}J_{6b-H,P} = {}^{3}J_{6b-H,5-H} = 3.4$  Hz, 1 H, 6b<sup>A</sup>-H), 2.61 (ddd,  ${}^{2}J_{6a-H,6b-H} = 14.9, \, {}^{2}J_{6a-H,P} = 3.1, \, {}^{3}J_{6a-H,5-H} = 8.4 \text{ Hz}, \, 1 \text{ H}, \, 6a^{\text{A}}\text{-H}),$ 3.00 (s, 3 H, OMe), 3.06 (dd,  ${}^{3}J_{2-H,3-H} = 9.0$ ,  ${}^{3}J_{2-H,1-H} = 2.9$  Hz, 1 H, 2-H), 3.07 (dd,  ${}^{3}J_{2-H,3-H} = 9.7$ ,  ${}^{3}J_{2-H,1-H} = 3.3$  Hz, 1 H, 2-H), 3.15 (dd,  ${}^{3}J_{2-H,3-H} = 9.9$ ,  ${}^{3}J_{2-H,1-H} = 3.3$  Hz, 1 H, 2-H), 3.18 (s, 3 H, OMe), 3.16–3.22 (2 H, 2-H), 3.24 (dd,  ${}^{3}J_{2-H,3-H} = 9.8$ ,  ${}^{3}J_{2-H,1-H} =$ 3.2 Hz, 1 H, 2-H), 3.29 (dd,  ${}^{2}J_{6b-H,6a-H} = 10.9$ ,  ${}^{3}J_{6b-H,5-H} = 1.5$  Hz, 1 H, 6b-H), 3.37 (s, 3 H, OMe), 3.42 (m, 1 H, 6b<sup>B</sup>-H), 3.45 (s, 6 H, OMe), 3.47 (s, 3 H, OMe), 3.49 (s, 6 H, OMe), 3.50 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.44-3.99 (24 H, 3-H, 4-H, 5-H, 6-H), 4.17 (t,  ${}^{2}J_{6a-H,6b-H} = {}^{3}J_{6a-H,5-H} = 10.5 \text{ Hz}, 1 \text{ H}, 6a^{B}-\text{H}), 4.22 \text{ (ddd,}$  ${}^{3}J_{5-H,6b-H} = 3.4, {}^{3}J_{5-H,6a-H} = 8.4, {}^{3}J_{5-H,4-H} = 17.7 \text{ Hz}, 1 \text{ H}, 5^{\text{A}}-\text{H}),$ 4.77 (d,  ${}^{3}J_{1-H,2-H} = 3.3$  Hz, 1 H, 1-H), 4.93 (d,  ${}^{3}J_{1-H,2-H} = 3.2$  Hz, 1 H, 1-H), 4.99 (d,  ${}^{3}J_{1-H,2-H}$  = 2.9 Hz, 1 H, 1-H), 5.05 (d,  ${}^{3}J_{1-H,2-H}$ = 3.1 Hz, 1 H, 1-H), 5.07 (d,  ${}^{3}J_{1-H,2-H}$  = 3.1 Hz, 1 H, 1-H), 5.11 (d,  ${}^{3}J_{1-H,2-H} = 3.3 \text{ Hz}, 1 \text{ H}, 1-\text{H}), 7.14-7.49 (17 \text{ H}, \text{H}-arom), 7.77-7.99$ (5 H, H-arom) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, 25 °C): δ = (assignment by HSQC) = 32.15 (d,  ${}^{1}J_{C,P}$  = 14.3 Hz, C-6<sup>A</sup>), 57.48, 57.78, 57.82, 57.95, 58.13, 58.26, 58.67, 59.12 [× 2], 59.18, 61.69, 61.70, 61.73, 61.86, 61.89, 61.92 (OMe), 63.34 (d,  ${}^{2}J_{C,P}$  = 16.6 Hz, C-6<sup>B</sup>), 71.06 [ $\times$  2], 71.11 (C-5), 71.17, 71.22 (C-6), 71.32 (C-5), 71.40 (C-6), 71.45 [× 2] (C-5), 71.53 (C-6), 80.79, 81.18, 81.33 [× 4], 81.40, 81.60, 81.74, 81.99 [× 2], 82.17, 82.23, 82.43, 82.45, 82.61, 82.62 (C-2, C-3, C-4), 88.00 (d,  ${}^{3}J_{C,P} = 11.2 \text{ Hz}, \text{ C-4}^{\text{A}}$ ), 99.09, 99.20, 100.03, 100.11, 100.35, 100.48 (C-1), 121.86, 122.52, 124.03, 124.28, 124.80, 125.06, 125.33, 126.04, 126.26, 127.00, 127.11, 127.47, 128.16, 128.34, 128.39, 128.43, 128.60, 128.67, 128.86, 129.06, 129.44, 130.23, 131.02, 131.40, 131.50, 132.36, 132.54, 133.07, 133.28, 139.69, 140.65, 141.44 (C-arom) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -20.3$  (s, P<sup>A</sup>), 148.9 (s, P<sup>B</sup>) ppm.  $C_{84}H_{112}O_{31}P_2 \cdot H_2O$  (1679.72 + 18.01): calcd. for C 59.43, H 6.77; found C 59.72, H 6.99. MS (ESI-TOF): m/z (%) =  $1701.66 (100) [M + Na]^+$ .



6<sup>A</sup>,6<sup>B</sup>-Dideoxy-6<sup>A</sup>-diphenylphosphanyl-6<sup>B</sup>-(S)-(1,1'-binaphthyl-2,2'bisoxyphosphanyloxy)-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>,2<sup>E</sup>,2<sup>F</sup>,3<sup>A</sup>,3<sup>B</sup>,3<sup>C</sup>,3<sup>D</sup>,3<sup>E</sup>,3<sup>F</sup>,6<sup>C</sup>,6<sup>D</sup>,  $6^{E}$ ,  $6^{F}$ -hexadeca-O-methyl- $\alpha$ -cyclodextrin (9): This compound was prepared in 37% (0.110 g) according to the procedure used for the synthesis of 6, by reacting 1 (0.245 g, 0.18 mmol) with [(S)-1,1'binaphthyl-2,2'-diyl]chlorophosphite (5; 0.252 g, 0.72 mmol).  $R_{\rm f}$  $(SiO_2, CH_2Cl_2/MeOH, 90:10, v/v) = 0.72, m.p. dec. [a]_D^{20} = +224$  $(CH_2Cl_2, c = 5.0)$ ; <sup>1</sup>H NMR (400.1 MHz, CDCl\_3, 25 °C):  $\delta = (as$ signment by combined COSY and HSQC) = 2.64 (dt,  ${}^{2}J_{6a-H.6b-H}$  = 14.6,  ${}^{2}J_{6b-H,P} = {}^{3}J_{6b-H,5-H} = 3.2$  Hz, 1 H, 6b<sup>A</sup>-H), 2.71 (ddd,  ${}^{2}J_{6a-H,6b-H} = 14.8, \, {}^{2}J_{6a-H,P} = 2.6, \, {}^{3}J_{6a-H,5-H} = 7.4 \text{ Hz}, \, 1 \text{ H}, \, 6a^{\text{A}}\text{-H}),$ 3.02 (dd,  ${}^{3}J_{2-H,3-H} = 9.0$ ,  ${}^{3}J_{2-H,1-H} = 3.1$  Hz, 1 H, 2-H), 3.04 (s, 3 H, OMe), 3.12–3.19 (4 H, 2-H), 3.22 (dd,  ${}^{3}J_{2-H,3-H} = 10.1$ ,  ${}^{3}J_{2-H,1-}$ <sub>H</sub> = 3.1 Hz, 1 H, 2-H), 3.34 (s, 3 H, OMe), 3.35 (s, 3 H, OMe), 3.37 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 3.48 (s, 9 H, OMe), 3.49 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.63 (s, 9 H, OMe), 3.64 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.31-3.93 (26 H, 3-H, 4-H, 5-H, 6-H), 4.14 (t,  ${}^{2}J_{6a-H,6b-H} = {}^{3}J_{6a-H,5-H} = 10.8$  Hz, 1 H, 6a<sup>B</sup>-H), 4.23 (ddd,  ${}^{3}J_{5-H,6b-H} = 3.2$ ,  ${}^{3}J_{5-H,6a-H} = 7.4$ ,  ${}^{3}J_{5-H,4-H}$ = 17.0 Hz, 1 H, 5<sup>A</sup>-H), 4.82 (d,  ${}^{3}J_{1-H,2-H}$  = 3.3 Hz, 1 H, 1-H), 4.94 (d,  ${}^{3}J_{1-H,2-H} = 3.1$  Hz, 2 H, 1-H), 5.04–5.07 (3 H, 1-H), 7.18–7.54 (18 H, H-arom), 7.82 (d, J = 8.7 Hz, 1 H, H-arom), 7.85 (d, J = 8.2 Hz, 1 H, H-arom), 7.90-7.97 (2 H, H-arom) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = (assignment by HSQC) = 32.15 (d,  ${}^{1}J_{C,P}$  = 14.2 Hz, C-6<sup>A</sup>), 57.65, 57.77, 57.85, 58.00, 58.08, 58.14, 58.76, 59.11 [× 3], 61.66, 61.80 [× 2], 61.83, 61.89 [× 2] (OMe), 63.46 (d,  ${}^{2}J_{C,P}$  = 15.2 Hz, C-6<sup>B</sup>), 71.10 [× 2] (C-5), 71.18, 71.24 (C-6), 71.33, 71.39, 71.41, 71.46 (C-5), 71.56 [× 2] (C-6), 80.91, 81.21, 81.24, 81.27, 81.38, 81.45, 81.75, 81.93, 82.06, 82.15 [×2], 82.20, 82.29, 82.33, 82.47, 82.50, 82.56 (C-2, C-3, C-4), 87.89  $(d, {}^{3}J_{C,P} = 10.5 \text{ Hz}, \text{ C-4}^{\text{A}}), 99.35, 99.58, 100.0, 100.02, 100.04,$ 100.43 (C-1), 120.57 (d,  ${}^{2}J_{C,P} = 6.5 \text{ Hz}$ , C-*ipso*<sup>B</sup>), 121.84, 122.12, 122.92 (C-*arom*), 124.36 (d,  ${}^{2}J_{C,P}$  = 5.2 Hz, C-*ipso*<sup>B</sup>'), 124.86, 125.02, 126.13, 126.22, 127.03, 127.05, 128.15, 128.27, 128.34, 128.41 [× 2], 128.47, 128.50, 128.56, 128.73, 129.36, 130.22, 131.02, 131.49, 132.74, 132.89 [× 2], 132.96, 133.11 (C-arom), 139.41 (d,  ${}^{1}J_{C,P} = 11.8 \text{ Hz}, \text{ C-ipso}^{A}$ ), 140.82 (d,  ${}^{1}J_{C,P} = 12.0 \text{ Hz}, \text{ C-ipso}^{A'}$ ), 147.47 (C-arom) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -20.9$  (s, P<sup>A</sup>), 150.7 (s, P<sup>B</sup>) ppm. C<sub>84</sub>H<sub>112</sub>O<sub>31</sub>P<sub>2</sub>·CHCl<sub>3</sub> (1679.72) + 119.38): calcd. for C 56.75, H 6.33; found C 56.75, H 6.65. MS (ESI-TOF): m/z (%) = 1701.66 (100) [M + Na]<sup>+</sup>.

cis-P,P'-Dichloro-[6<sup>A</sup>,6<sup>B</sup>-dideoxy-6<sup>A</sup>-diphenylphosphanyl-6<sup>B</sup>-(2,2'-bisphenoxyphosphanyloxy)-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>,2<sup>E</sup>,2<sup>F</sup>,3<sup>A</sup>,3<sup>B</sup>,3<sup>C</sup>,3<sup>D</sup>,3<sup>E</sup>,3<sup>F</sup>,6<sup>C</sup>,6<sup>D</sup>,  $6^{E}$ ,  $6^{F}$ -hexadeca-O-methyl- $\alpha$ -cyclodextrin|platinum (II) (10): A solution of [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] (0.009 g, 0.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added dropwise to a solution of 6 (0.030 g, 0.02 mmol) in  $CH_2Cl_2$ (2 mL) under vigorous stirring. After 5 min, the reaction mixture was evaporated to dryness in vacuo to afford analytically pure 10 (0.035 g, 99%) as a pale yellow solid. R<sub>f</sub> (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 90:10, v/v = 0.74, m.p. dec. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = (assignment by combined COSY and HSQC) = 1.70 (m, 1 H, 6<sup>B</sup>-H), 3.01 (s, 3 H, OMe), 3.09 (s, 3 H, OMe), 3.10-3.21 (6 H, 2-H, 6<sup>A</sup>-H), 3.27 (dd,  ${}^{3}J_{2-H,3-H} = 9.2$ ,  ${}^{3}J_{2-H,1-H} = 3.1$  Hz, 1 H, 2-H), 3.36 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.50 (s, 6 H, OMe), 3.51 (s, 3 H OMe), 3.52 (s, 6 H, OMe), 3.61 (s, 3 H, OMe), 3.63 (s, 9 H, OMe), 3.64 (s, 3 H OMe), 3.45-3.71 (15 H, 3-H, 4-H, 6-H), 3.71-3.85 (5 H, 6-H), 3.86-4.08 (5 H, 4-H, 5-H), 4.30 (m, 1 H, 5<sup>A</sup>-H), 4.45 (br. m, 1 H, 5<sup>B</sup>-H), 4.78 (d,  ${}^{3}J_{1-H,2-H} = 3.2$  Hz, 1 H, 1-H), 4.84 (br. m, 1 H, 6-H<sup>A</sup>), 4.86 (m, 1 H, 1-H), 5.05 (m, 2 H, 1-H), 5.12 (d,  ${}^{3}J_{1-H,2-H} = 3.4$  Hz, 1 H, 1-H), 5.25 (br. m, 1 H, 1-H), 7.20-7.46 (10 H, H-arom), 7.56-7.62 (4 H, H-arom), 7.84–7.93 (4 H, H-arom) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>, 50 °C):  $\delta$  = (assignment by HSQC) = 24.90

(dd,  ${}^{1}J_{C,PA} = 10.5$ ,  ${}^{3}J_{C,PB} = 8.0$  Hz, C-6<sup>A</sup>), 57.66 [× 2], 57.82 [× 2], 58.02, 58.29 [× 2], 58.85, 59.09, 59.22, 59.67, 61.30, 61.56 [× 2], 61.86 [× 2] (OMe), 70.01 (virtual t,  ${}^{2}J_{C,PB} = {}^{4}J_{C,PA} = 16.0$  Hz,  $C-6^{B}$ ), 70.54, 71.12 (C-6), 71.24, 71.52 [× 2, C-5), 71.59 (C-6), 71.72 [× 3] (C-5), 72.01 (C-6), 80.42 [× 2], 80.67 [× 2], 81.16 [× 2], 81.28, 81.37, 81.82, 81.87, 82.08 [× 3], 82.15, 82.30, 82.44, 82.56 (C-2, C-3, C-4), 83.76 (d,  ${}^{3}J_{C,P} = 9.8$  Hz, C-4<sup>A</sup>), 98.30, 99.45, 99.77, 100.31, 100.38, 100.62 (C-1), 126.26, 126.43 [× 2], 127.63, 127.76, 127.86, 127.94, 128.03, 128.55, 128.85, 129.21, 129.52, 129.65,  $129.74 \times 2$ ,  $130.26 \times 2$ , 130.86, 130.92, 132.34,  $134.06 \times 2$ (C-arom), 148.13 (dd,  ${}^{1}J_{C,PA} = 9.1$ ,  ${}^{3}J_{C,PB} = 3.0$  Hz, C-*ipso*<sup>A</sup>), 148.50 (dd,  ${}^{1}J_{C,PA} = 10.1$ ,  ${}^{3}J_{C,PB} = 3.1$  Hz, C-*ipso*<sup>A'</sup>) ppm.  ${}^{31}P{}^{1}H{}$ NMR (161.9 MHz, CDCl<sub>3</sub>, 60 °C):  $\delta = 6.7$  (d with Pt satellites,  ${}^{2}J_{PA,PB} = 22.7$ ,  ${}^{1}J_{PA,Pt} = 3407.9$  Hz, P<sup>A</sup>), 82.1 (d with Pt satellites,  ${}^{2}J_{PB,PA} = 22.7, \; {}^{1}J_{PB,Pt} = 6136.4 \text{ Hz}, \; P^{B}) \text{ ppm. } C_{76}H_{108}Cl_{2}O_{31}P_{2}Pt$ (1845.45): calcd. for C 49.46, H 5.90; found C 49.23, H 6.08. MS (ESI-TOF): m/z (%) = 1826.60 (100) [M - Cl + H<sub>2</sub>O]<sup>+</sup>, 1867.63 (48)  $[M + Na]^+$ .

cis-P,P'-(Cycloocta-1,5-diene)-[6<sup>A</sup>,6<sup>B</sup>-dideoxy-6<sup>A</sup>-diphenylphosphanyl-6<sup>B</sup>-(2,2'-bisphenoxyphosphanyloxy)-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>,2<sup>E</sup>,2<sup>F</sup>,3<sup>A</sup>,3<sup>B</sup>,3<sup>C</sup>, 3<sup>D</sup>,3<sup>E</sup>,3<sup>F</sup>,6<sup>C</sup>,6<sup>D</sup>,6<sup>E</sup>,6<sup>F</sup>-hexadeca-*O*-methyl-α-cyclodextrin]rhodium (I) (11): A solution of [Rh(COD)<sub>2</sub>]BF<sub>4</sub> (0.031 g, 0.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added dropwise to a solution of 6 (0.120 g, 0.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) under vigorous stirring. After 5 min, the volume of the reaction mixture was reduced to 1 mL and pentane (20 mL) was added to precipitate 11, which was collected by filtration to afford a bright yellow powder (0.141 g, 99%). R<sub>f</sub> (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/ MeOH, 90:10, v/v) = 0.30, m.p. dec. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = (assignment by COSY) = 1.55–1.66 (br. m, 1 H, allylic protons of COD), 1.73-1.82 (br. m, 1 H, allylic protons of COD), 1.98-2.33 (6 H, allylic protons of COD), 2.35 (s, 3 H, OMe), 2.97 (s, 3 H, OMe), 3.25 (s, 3 H, OMe), 3.35 (s, 3 H, OMe), 3.41 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.55 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.58 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.62 (s, 6 H, OMe), 2.65-4.31 (37 H, 1-H, 2-H, 3-H, 4-H, 5-H, 6-H), 4.33 (m, 1 H, vinylic protons of COD), 4.40 (m, 1 H, 1-H), 4.93 (m, 1 H, vinylic protons of COD), 5.00 (d,  ${}^{3}J_{1-H,2-H} = 3.1$  Hz, 1 H, 1-H), 5.08 (d,  ${}^{3}J_{1-H,2-H} = 2.9$  Hz, 1 H, 1-H), 5.09 (d,  ${}^{3}J_{1-H,2-H} =$ 3.2 Hz, 1 H, 1-H), 5.10 (d,  ${}^{3}J_{1-H,2-H} = 3.0$  Hz, 1 H, 1-H), 5.35 (m, 1 H, vinylic protons of COD), 5.92 (m, 1 H, vinylic protons of COD), 7.01-7.59 (12 H, H-arom), 7.64-7.97 (4 H, H-arom), 8.30 (m, 2 H, H-arom) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 21.7 (dd, <sup>1</sup> $J_{PA,Rh}$  = 142.0, <sup>2</sup> $J_{PA,PB}$  = 40.9 Hz, P<sup>A</sup>), 121.2  $(dd, {}^{1}J_{PB,Rh} = 269.2, {}^{2}J_{PB,PA} = 40.9 \text{ Hz}, P^{B}) \text{ ppm}.$  $C_{84}H_{120}BF_4O_{31}P_2Rh \cdot CH_2Cl_2$  (1877.49 + 84.93): calcd. for C 52.02, H 6.27; found C 52.00, H 6.50. MS (ESI-TOF): m/z (%) = 1681.54  $(100) [M - COD - BF_4]^+$ .

*cis-P,P'*-(Cycloocta-1,5-diene)-[6<sup>A</sup>,6<sup>B</sup>-dideoxy-6<sup>A</sup>-diphenylphosphanyl-6<sup>B</sup>-(4,4',6,6'-tetra-*tert*-butyl-2,2'-bisphenoxyphosphanyloxy)-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>,2<sup>E</sup>,2<sup>F</sup>,3<sup>A</sup>,3<sup>B</sup>,3<sup>C</sup>,3<sup>D</sup>,3<sup>E</sup>,3<sup>F</sup>,6<sup>C</sup>,6<sup>D</sup>,6<sup>E</sup>,6<sup>F</sup>-hexadeca-*O*-methyl*a*-cyclodextrin|rhodium (I) (12): This compound was prepared in 99% yield (0.155 g) according to the procedure used for 11, by reacting 7 (0.134 g, 0.07 mmol) with [Rh(COD)<sub>2</sub>]BF<sub>4</sub> (0.030 g, 0.07 mmol). *R*<sub>f</sub> (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 90:10, v/v) = 0.30, m.p. dec. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 60 °C): δ = (assignment by COSY) = 1.33 (s, 9 H, *t*Bu), 1.40 (s, 9 H, *t*Bu), 1.59 (s, 9 H, *t*Bu), 1.88 (s, 9 H, *t*Bu), 1.98–2.08 (br. m, 1 H, allylic protons of COD), 2.18– 2.31 (br. m, 1 H, allylic protons of COD), 2.32–2.56 (6 H, allylic protons of COD), 2.41 (t, <sup>3</sup>*J*<sub>4-H,3-H</sub> = <sup>3</sup>*J*<sub>4-H,5-H</sub> = 8.4 Hz, 1 H, 4-H), 2.80–2.87 (2 H, 2-H, 6-H), 2.97–3.03 (2 H, 2-H), 3.10 (s, 3 H, OMe), 3.29 (s, 3 H, OMe), 3.32 (s, 3 H, OMe), 3.40 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.54 (s, 3 H, OMe), 3.56 (s, 6 H, OMe), 3.57 (s, 3 H, OMe), 3.58 (s, 3 H, OMe), 3.61 (s, 6 H, OMe), 3.05–3.97 (29 H, 2-H, 3-H, 4-H, 5-H, 6-H), 3.99–4.08 (3 H, 1-H, 5-H, vinylic protons of COD), 4.13 (m, 1 H, vinylic protons of COD), 4.28 (m, 1 H, 5-H), 4.35 (m, 1 H, 1-H), 4.76 (d,  ${}^{3}J_{1-H,2-H} = 2.8$  Hz, 1 H, 1-H), 4.83 (m, 1 H, vinylic protons of COD), 5.05–5.10 (3 H, 1-H), 5.83 (m, 1 H, vinylic protons of COD), 7.12–7.19 (3 H, 1-H), 5.83 (m, 1 H, vinylic protons of COD), 7.12–7.19 (3 H, H-*arom*), 7.35–7.45 (4 H, H-*arom*), 7.52 (s, 1 H, H-*arom*), 8.30–8.38 (2 H, H-*arom*) pm.  ${}^{31}P{}^{1}H{}$  NMR (161.9 MHz, CDCl<sub>3</sub>, 60 °C):  $\delta$  = 19.6 (dd,  ${}^{1}J_{PA,Rh}$  = 142.9,  ${}^{2}J_{PA,PB}$  = 37.4 Hz, P<sup>A</sup>), 121.1 (dd,  ${}^{1}J_{PB,Rh}$  = 266.7,  ${}^{2}J_{PB,PA}$  = 37.4 Hz, P<sup>B</sup>) ppm. C<sub>100</sub>H<sub>152</sub>BF<sub>4</sub>O<sub>31</sub>P<sub>2</sub>Rh·2CH<sub>2</sub>Cl<sub>2</sub> (2101.92 + 169.87): calcd. for C 53.93, H 6.92; found C 54.02, H 7.18. MS (ESI-TOF): *m/z* (%) = 1905.80 (100) [M – COD – BF<sub>4</sub>]<sup>+</sup>, 2014.90 (6) [M – BF<sub>4</sub>]<sup>+</sup>.

cis-P,P'-(Cycloocta-1,5-diene)-[6<sup>A</sup>,6<sup>B</sup>-dideoxy-6<sup>A</sup>-diphenylphosphanyl-6<sup>B</sup>-(R)-(1,1'-binaphthyl-2,2'-bisoxyphosphanyloxy)-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>, 2<sup>E</sup>,2<sup>F</sup>,3<sup>A</sup>,3<sup>B</sup>,3<sup>C</sup>,3<sup>D</sup>,3<sup>E</sup>,3<sup>F</sup>,6<sup>C</sup>,6<sup>D</sup>,6<sup>E</sup>,6<sup>F</sup>-hexadeca-O-methyl-α-cyclodextrin]rhodium (I) (13): This compound was prepared in 99% yield (0.126 g) according to the procedure used for the synthesis of 11, by reacting 8 (0.108 g, 0.06 mmol) with [Rh(COD)<sub>2</sub>]BF<sub>4</sub> (0.026 g, 0.06 mmol).  $R_{\rm f}$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 90:10, v/v) = 0.30, m.p. dec. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 60 °C):  $\delta$  = (assignment by COSY and HSQC = 1.68–1.84 (br. m, 1 H, allylic protons of COD), 1.94– 2.05 (br. m, 1 H, allylic protons of COD), 2.07-2.17 (4 H, allylic protons of COD), 2.40 (t,  ${}^{3}J_{4-H,3-H} = {}^{3}J_{4-H,5-H} = 9.6$  Hz, 1 H, 4<sup>B</sup>-H), 2.34–2.46 (2 H, allylic protons of COD), 2.84 (dd,  ${}^{3}J_{2-H,3-H} =$ 9.9,  ${}^{3}J_{2-H,1-H} = 3.5$  Hz, 1 H, 2-H), 2.90 (dd,  ${}^{2}J_{6a-H,6b-H} = 11.7$ ,  ${}^{3}J_{6b-H,5-H} = 2.5 \text{ Hz}, 1 \text{ H}, 6b^{\text{A}}-\text{H}), 3.01 \text{ (s, 3 H, OMe)}, 3.01-3.03 \text{ (m,}$ 1 H, 6a<sup>A</sup>-H), 3.05 (dd,  ${}^{3}J_{2-H,3-H} = 9.7$ ,  ${}^{3}J_{2-H,1-H} = 3.3$  Hz, 1 H, 2-H), 3.26 (s, 3 H, OMe), 3.29 (s, 3 H, OMe), 3.38 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.56 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.14-3.87 (25 H, 2-H, 3-H, 4-H, 5-H, 6-H), 3.91-3.96 (m, 1 H, 5-H), 3.99-4.10 (4 H, 5-H, 6-H), 4.15 (d,  ${}^{3}J_{1-H,2-H} = 3.3$  Hz, 1 H, 1-H), 4.19 (m, 1 H, vinylic protons of COD), 4.33 (m, 1 H, 5-H), 4.41 (d,  ${}^{3}J_{1-H,2-H}$  = 2.6 Hz, 1 H, 1-H), 4.45 (m, 1 H, vinylic protons of COD), 5.04 (d,  ${}^{3}J_{1-H,2-H} = 3.2 \text{ Hz}, 1 \text{ H}, 1-\text{H}), 5.07 \text{ (d, } {}^{3}J_{1-H,2-H} = 3.1 \text{ Hz}, 1 \text{ H}, 1-\text{H}),$ 5.08 (d,  ${}^{3}J_{1-H,2-H}$  = 3.1 Hz, 1 H, 1-H), 5.10 (d,  ${}^{3}J_{1-H,2-H}$  = 3.5 Hz, 1 H, 1-H), 5.25 (m, 1 H, vinylic protons of COD), 5.58 (m, 1 H, vinylic protons of COD), 7.14–7.60 (14 H, H-arom), 7.80 (t, J = 7.3 Hz, 1 H, H-arom), 7.88-8.07 (4 H, H-arom), 8.33-8.41 (3 H, H-arom) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = (assignment by HSQC) = 28.58-28.80 (4 C, allylic C of COD), 31.0  $(d, {}^{1}J_{C,P} = 20.6 \text{ Hz}, \text{ C-6}^{\text{A}}), 56.44, 56.56, 56.59, 56.69, 56.83, 56.90,$ 57.18, 57.33, 57.96, 58.06, 58.12, 60.60, 60.78, 60.80, 60.90, 60.92, (OMe), 65.62 (d,  ${}^{3}J_{C,P}$  = 6.3 Hz, C-5<sup>B</sup>), 66.81 (C-6), 69.05, 69.16 (C-5), 69.54 (d,  ${}^{2}J_{C,P}$  = 14.1 Hz, C-6<sup>B</sup>), 69.65 (C-5), 69.97, 70.15 (C-6), 70.29 (d,  ${}^{2}J_{C,P}$  = 19.2 Hz, C-5<sup>A</sup>), 71.24 (C-5),71.41 (C-6), 77.69, 77.82, 80.84, 81.21, 81.32, 81.38, 81.47, 81.58, 81.79 [× 2], 82.40, 82.54, 82.60, 82.63, 82.91, 82.96, 83.07 (C-2, C-3, C-4), 87.03 (d,  ${}^{3}J_{CP}$  = 13.5 Hz, C-4<sup>A</sup>), 94.84 (vinylic C of COD), 97.21, 97.48, 99.09, 99.39, 99.71, 100.27 (C-1), 100.45, 106.02, 111.49, (vinylic C of COD), 116.74, 119.37, 119.74, 123.05, 123.29, 124.29, 124.73, 124.83, 125.72, 125.80, 126.11, 126.29, 126.44, 127.22, 127.40, 127.44, 128.03, 128.38, 128.49, 128.82, 128.93, 129.02, 129.70, 129.79, 129.95, 130.37, 130.63, 130.78, 132.42, 132.67, 145.21 (d,  ${}^{1}J_{C,P} = 9.1 \text{ Hz}, \text{ C-}ipso^{\text{A}}$ ), 146.36 (d,  ${}^{1}J_{C,P} = 11.9 \text{ Hz}, \text{ C-}ipso^{\text{A}'}$ ) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>, 60 °C):  $\delta$  = 21.9 (dd, <sup>1</sup>J<sub>PA,Rh</sub> = 142.0,  ${}^{2}J_{PA,PB}$  = 42.0 Hz, P<sup>A</sup>), 122.1 (dd,  ${}^{1}J_{PB,Rh}$  = 270.0,  ${}^{2}J_{PB,PA}$ = 42.0 Hz,  $P^{B}$ ) ppm.  $C_{92}H_{124}BF_{4}O_{31}P_{2}Rh$  (1977.62): calcd. for C

55.87, H 6.32; found C 55.68, H 6.57. MS (ESI-TOF): m/z (%) = 1781.55 (100) [M - COD - BF<sub>4</sub>]<sup>+</sup>.

cis-P,P'-(Cycloocta-1,5-diene)-[6<sup>A</sup>,6<sup>B</sup>-dideoxy-6<sup>A</sup>-diphenylphosphanyl-6<sup>B</sup>-(S)-(1,1'-binaphthyl-2,2'-bisoxyphosphanyloxy)-2<sup>A</sup>,2<sup>B</sup>,2<sup>C</sup>,2<sup>D</sup>,  $2^{\mathrm{E}},\!2^{\mathrm{F}},\!3^{\mathrm{A}},\!3^{\mathrm{B}},\!3^{\mathrm{C}},\!3^{\mathrm{D}},\!3^{\mathrm{E}},\!3^{\mathrm{F}},\!6^{\mathrm{C}},\!6^{\mathrm{D}},\!6^{\mathrm{E}},\!6^{\mathrm{F}}\text{-hexadeca-}\textit{O}\text{-methyl-}\alpha\text{-cyclodex-}$ trin|rhodium (I) (14): This compound was prepared in 99% yield (0.110 g) according to the procedure used for the synthesis of 11, by reacting 9 (0.095 g, 0.06 mmol) with [Rh(COD)<sub>2</sub>]BF<sub>4</sub> (0.023 g, 0.06 mmol).  $R_{\rm f}$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 90:10, v/v) = 0.30, m.p. dec. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = (assignment by combined COSY and HSQC) = 1.71 (br. m, 1 H, allylic protons of COD), 1.91 (br. m, 1 H, allylic protons of COD), 2.00-2.29 (6 H, allylic protons of COD), 2.38 (dd,  ${}^{3}J_{2-H,3-H} = 9.6$ ,  ${}^{3}J_{2-H,1-H} =$ 3.1 Hz, 1 H, 2-H<sup>A</sup>), 2.81 (br. d,  ${}^{2}J_{6a-H,6b-H} = 9.6$  Hz, 1 H, 6-H), 2.84 (t,  ${}^{3}J_{4-H,3-H} = {}^{3}J_{4-H,5-H} = 8.7$  Hz, 1 H, 4<sup>B</sup>-H), 2.88 (s, 3 H, OMe), 2.91 (dd,  ${}^{2}J_{6a-H,6b-H} = 11.7$ ,  ${}^{3}J_{6b-H,5-H} = 2.3$  Hz, 1 H, 6b-H), 3.00 (dd,  ${}^{2}J_{6a-H,6b-H} = 11.7$ ,  ${}^{3}J_{6b-H,5-H} = 2.9$  Hz, 1 H, 6b-H), 3.02 (s, 3 H, OMe), 3.04-3.10 (3 H, 2-H), 3.11 (dd,  ${}^{3}J_{2-H,3-H} = 10.2$ ,  ${}^{3}J_{2-\text{H},1-\text{H}} = 3.9 \text{ Hz}, 1 \text{ H}, 2^{\text{B}}-\text{H}), 3.15-3.22 (3 \text{ H}, 2-\text{H}, 3-\text{H}, 6-\text{H}),$ 3.23 (dd,  ${}^{2}J_{6a-H,6b-H} = 9.7$ ,  ${}^{3}J_{6b-H,5-H} = 2.0$  Hz, 1 H, 6b-H), 3.28 (s, 3 H, OMe), 3.33 (s, 3 H, OMe), 3.40 (s, 3 H, OMe), 3.44 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.55 (s, 3 H, OMe), 3.58 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.27-3.68 (17 H, 1-H, 3-H, 4-H, 5-H, 6-H), 3.72-3.77 (2 H, 5-H, vinylic protons of COD), 3.79 (d,  ${}^{2}J_{6a-H,6b-H} = 10.2$  Hz, 1 H, 6-H), 3.86 (m, 1 H, 5-H), 3.88–3.95 (2 H, 6-H, 6<sup>B</sup>-H), 4.30 (m, 1 H, 6<sup>A</sup>-H), 4.40 (m, 1 H, 5<sup>A</sup>-H), 4.50 (d,  ${}^{3}J_{1-H}{}_{2-H} = 2.5$  Hz, 1 H, 1-H), 4.56 (m, 1 H, vinylic protons of COD), 4.67 (m, 1 H, vinylic protons of COD), 4.90 (d,  ${}^{3}J_{1-H,2-H}$  = 3.2 Hz, 1 H, 1-H), 4.92 (d,  ${}^{3}J_{1-H,2-H} = 3.3$  Hz, 1 H, 1-H), 5.02 (d,  ${}^{3}J_{1-H,2-H} = 3.2$  Hz, 1 H, 1-H), 5.04 (d,  ${}^{3}J_{1-H,2-H} = 3.1$  Hz, 1 H, 1-H), 5.40 (m, 1 H, vinylic protons of COD), 7.23-7.54 (10 H, H-arom), 7.62-7.67 (3 H, Harom), 7.72–7.78 (2 H, H-arom), 7.83 (d, J = 9.5 Hz, 1 H, H-arom), 7.89 (d, J = 9.8 Hz, 1 H, H-arom), 7.99 (d, J = 9.6 Hz, 1 H, H*arom*), 8.02 (d, J = 10.1 Hz, 1 H, H-*arom*), 8.05–8.10 (2 H, H*arom*), 8.31 (d, J = 10.2 Hz, 1 H, H-*arom*) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = (assignment by HSQC) = 28.85  $(d, {}^{1}J_{C,P} = 18.9 \text{ Hz}, \text{ C-6}^{A}), 29.64-29.94 (4 \text{ C}, allylic C of COD),$ 57.53, 58.10, 58.15 [× 2], 58.23, 58.29, 58.84, 59.11, 59.16, 59.88, 61.04, 61.18, 61.36, 61.44, 61.69, 61.92 (OMe), 68.47 (d,  ${}^{3}J_{C,P}$  = 4.9 Hz, C-5<sup>B</sup>), 69.14 (d,  ${}^{2}J_{C,P}$  = 14.0 Hz, C-6<sup>B</sup>), 70.00, 70.59 (C-6), 71.26 (d,  ${}^{2}J_{C,P}$  = 23.3 Hz, C-5<sup>A</sup>), 71.34, 71.38 (C-5), 71.43 [× 2, C-6), 71.76, 72.32 (C-5), 79.96, 80.21, 80.83, 80.91, 81.03, 81.10, 81.27, 81.52, 81.70, 81.88, 82.02, 82.28, 82.42, 82.47 [× 2], 82.72, 83.64 (C-2, C-3, C-4), 88.19 (d,  ${}^{3}J_{C,P} = 7.1$  Hz, C-4<sup>A</sup>), 94.40 (vinylic C of COD), 98.53, 98.71, 99.44, 99.85, 100.37 [× 2] (C-1), 100.16, 108.48, 112.75 (vinylic C of COD), 120.27, 121.47, 122.52, 122.43, 126.08, 126.21, 126.79, 127.04, 127.07, 127.80, 128.19, 128.27, 128.28, 128.41, 128.89, 128.96, 129.04, 129.62, 129.97, 130.84, 130.98, 131.20, 131.92, 132.17, 132.45, 132.80, 133.51, 133.60, 133.65, 133.74, 146.64 (d,  ${}^{1}J_{C,P}$  = 6.6 Hz, C-*ipso*<sup>A</sup>), 148.75 (d,  ${}^{1}J_{C,P}$ = 13.8 Hz, C-*ipso*<sup>A'</sup>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 20.7$  (dd,  ${}^{1}J_{PA,Rh} = 139.7$ ,  ${}^{2}J_{PA,PB} = 41.3$  Hz, P<sup>A</sup>), 122.6 (dd,  ${}^{1}J_{PB,Rh} = 2708$ ,  ${}^{2}J_{PB,PA} = 41.3$  Hz, P<sup>B</sup>) ppm.  $C_{92}H_{124}BF_4O_{31}P_2Rh\cdot 2CH_2Cl_2$  (1977.62 + 169.87): calcd. for C 52.57, H 6.01; found C 52.59, H 6.30. MS (ESI-TOF): m/z (%) =  $1781.62 (100) [M - COD - BF_4]^+$ .

**General Procedure for Hydrogenation Experiments:** Hydrogenation experiments were carried out in a glass-lined, 100 mL stainless steel autoclave containing a magnetic stirring bar. In a typical run, the autoclave was charged with preformed rhodium complexes **11–14** (0.01 mmol) and substrate **15–19** (1.0 mmol), then closed and



flushed with nitrogen. CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added and the autoclave flushed with H<sub>2</sub>. The solution was stirred under H<sub>2</sub> (5 atm) at 25 °C. After completion of the reaction, the solution was subjected to filtration through a short silica gel column. Conversion was determined by <sup>1</sup>H NMR spectroscopy. *ee* values were determined by GC with CHROMPAK chiral fused silica 25 m × 0.25 mm Coating Chirasil-L-Val column.

General Procedure for Hydroformylation Experiments: Hydroformylation experiments were carried out in a glass-lined, 100 mL stainless steel autoclave containing a magnetic stirring bar. In a typical run, the autoclave was charged under nitrogen with a solution of preformed rhodium complex **12** (0.002 mmol) in toluene (1 mL) and toluene (14 mL). Once closed, the autoclave was flushed twice with syngas (CO/H<sub>2</sub>, 1:1 v/v), pressurised with 20 bar of a CO/H<sub>2</sub> mixture and heated at 80 °C. After 16 h, the autoclave was depressurised before styrene (0.57 mL, 0.521 g, 5.0 mmol) and decane (0.50 mL) were added to the reaction mixture. The autoclave was then heated (80 °C) and pressurised (20 bar). The progress of the reaction was checked by monitoring the pressure decrease. During the experiments, several samples were taken and analysed by gas chromatography.

**Supporting Information** (see footnote on the first page of this article): <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra are presented.

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- A. Schlatter, M. K. Kundu, W. D. Woggon, Angew. Chem. 2004, 116, 6899–6902; Angew. Chem. Int. Ed. 2004, 43, 6731– 6734.
- [2] a) E. Engeldinger, D. Armspach, D. Matt, L. Toupet, M. Wesolek, C. R. Chim. 2002, 5, 359–372; b) Y. T. Wong, C. Yang, K. C. Ying, G. C. Jia, Organometallics 2002, 21, 1782–1787; c) A. Schlatter, W. D. Woggon, Adv. Synth. Catal. 2008, 350, 995–1000.
- [3] a) V. Böhmer, D. Kraft, M. Tabatabai, J. Inclusion Phenom. Mol. Recognit. Chem. 1994, 19, 17–39; b) C. Dieleman, S.

Steyer, C. Jeunesse, D. Matt, J. Chem. Soc., Dalton Trans. 2001, 2508–2517; c) S. Guieu, E. Zaborova, Y. Blériot, G. Poli, A. Jutand, D. Madec, G. Prestat, M. Sollogoub, Angew. Chem. 2010, 122, 2364–2368; Angew. Chem. Int. Ed. 2010, 49, 2314–2318; d) S. Y. Li, Y. W. Xu, J. M. Liu, C. Y. Su, Int. J. Mol. Sci. 2011, 12, 429–455.

- [4] a) M. Diéguez, O. Pàmies, A. Ruiz, Y. Díaz, S. Castillón, C. Claver, *Coord. Chem. Rev.* 2004, 248, 2165–2192; b) M. Diéguez, O. P. Pàmies, C. Claver, *Chem. Rev.* 2004, 104, 3189–3215; c) H. Fernández-Pérez, P. Etayo, A. Panossian, A. Vidal-Ferran, *Chem. Rev.* 2011, 111, 2119–2176.
- [5] a) O. Pàmies, M. Diéguez, G. Net, A. Ruiz, C. Claver, *Chem. Commun.* 2000, 2383–2384; b) O. Pàmies, G. P. F. van Strijdonck, M. Diéguez, S. Deerenberg, G. Net, A. Ruiz, C. Claver, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Org. Chem.* 2001, 66, 8867–8871; c) A. Suárez, A. Pizzano, *Tetrahedron: Asymmetry* 2001, *12*, 2501–2504.
- [6] A. Kless, J. Holz, D. Heller, R. Kadyrov, R. Selke, C. Fischer, A. Börner, *Tetrahedron: Asymmetry* 1996, 7, 33–36.
- [7] M. Jouffroy, R. Gramage-Doria, D. Armspach, D. Matt, L. Toupet, Chem. Commun. 2012, 48, 6028–6030.
- [8] S. D. Pastor, S. P. Shum, R. K. Rodebaugh, A. D. Debellis, F. H. Clarke, *Helv. Chim. Acta* **1993**, *76*, 900–914.
- [9] O. Pàmies, M. Diéguez, G. Net, A. Ruiz, C. Claver, J. Org. Chem. 2001, 66, 8364–8369.
- [10] CD<sub>2</sub>Cl<sub>2</sub> was not used for the VT NMR spectroscopic studies because of poor solubility of the complexes in this solvent at low temperature.
- [11] ROESY spectra performed on both complexes 13 and 14 did not provide any useful information about the location of the metal unit with respect to the CD cavity.
- [12] G. J. H. Buisman, M. E. Martin, E. J. Vos, A. Klootwijk, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Tetrahedron: Asymmetry* **1995**, *6*, 719–738.
- [13] a) K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, J. Am. Chem. Soc. 1997, 119, 4413– 4423; b) K. Nozaki, H. Takaya, T. Hiyama, Top. Catal. 1997, 4, 175–185.
- [14] G. J. H. Buisman, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Tetrahedron: Asymmetry* 1993, 4, 1625–1634.
- [15] N. Cramer, S. Laschat, A. Baro, Organometallics 2006, 25, 2284–2291.
- [16] F. R. Hartley, *The Chemistry of Platinum and Palladium*, Wiley, New York, **1973**.

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