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Synthesis of large chelate rings with diphosphites built on a cyclodextrin scaffold. Unexpected formation of 1,2-phenylene-capped α-cyclodextrins

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In memory of John Osborn

Abstract – Two primary face difunctionalised α-cyclodextrins (α-CDs) bearing AC and AD-positioned triarylphosphite ligands have been synthesised and their ability to form large chelate rings has been evaluated. $6^A,6^D$-Bis-*O*-{2-[(diphenoxyphosphino) oxy]phenyl}-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$-hexadeca-*O*-methyl-α-cyclodextrin (**L1**) was prepared in three steps in 59% overall yield: (*i*) treatment of $6^A,6^D$-di-*O*-(methylsulfonyl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$-hexadeca-*O*-methyl-α-cyclodextrin (**1a**) with sodium 2-(benzyloxy)phenolate, affording a mixture of the corresponding bisaryloxy substitution product **2a**; (*ii*) cleavage of the benzyl groups of **2a** with formation of bisphenol **6a**; (*iii*) reaction of **2a** with chlorodiphenylphosphite to afford **L1**. Diphosphite **L2** was obtained in a similar manner using the AC dimesylate **1b** (yield: 54%). In step (*i*) of each synthesis, the unexpected formation of a catecholato-capped CD was observed as a result of benzyl loss under the used arylation conditions. The AD-bridged product was characterised by a single crystal X-ray diffraction study. In the solid state, the CD torus adopts the usual circular shape while four glucose rings, although not distorted, are considerably tilted towards the cavity axis. Both ligands, **L1** and **L2**, when reacted with the cationic complexes $AgBF_4$ or $[Rh(norbornadiene)(THF)_2]X$ ($X = BF_4$, PF_6), produced selectively chelate complexes having up to 29-membered metallomacrocycles in high yields. Rhodium systems based on either **L1** or **L2** catalyse effectively the hyfroformylation of 1-octene (TOF up to 1200 mol mol^{-1} of Rh h^{-1}). Hydrogenation of dimethyl itaconate with a Rh(I)/**L2** complex produced dimethyl (*R*)-(+)-methylsuccinate with an EE as high as 83.6%. ***To cite this article: É. Engeldinger et al., C. R. Chimie 5 (2002) 359–372***
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metallo-cyclodextrins / bulky diphosphites / large chelate rings / rhodium / hydroformylation / hydrogenation / capped cyclodextrins

Résumé – Deux α-cyclodextrines, substituées au niveau des positions $6^A/6^D$ ou $6^A/6^C$ par deux ligands $-(C_6H_4O)P(OPh)_2$, ont été synthétisées, avec un rendement global de l'ordre de 60 % ; leurs propriétés chélatantes ont été étudiées. Au cours de la synthèse, une cyclodextrine, dans laquelle deux unités *glucose* (A et D ou A et C) sont reliées par un fragment 1,2-phénylène, a également été isolée. La structure à l'état solide a été déterminée pour l'espèce AD-pontée. La présence d'un pont court provoque le basculement de quatre cycles *glucose* vers l'axe de la cyclodextrine. En présence de complexes cationiques tels que $AgBF_4$ ou $[Rh(norbornadiène)(THF)_2]X$ ($X = BF_4$, PF_6), les deux ligands conduisent exclusivement à des complexes chélates, caractérisés par la présence de métallomacrocycles à 24 ou 29 chaînons. Associés à du rhodium, les deux diphosphites forment des catalyseurs actifs en hydrogénation et en hydroformylation d'oléfines. L'hydrogénation de l'itaconate de diméthyle en présence d'un complexe Rh(I)/**L2** fournit du (*R*)-(+)-methylsuccinate de diméthyle, avec un excès énantiomérique de 83,6 %. ***Pour citer cet article : É. Engeldinger et al., C. R. Chimie 5 (2002) 359–372*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

métallo-cyclodextrines / diphosphites / chélatants encombrés / rhodium / hydroformylation / hydrogénation / cyclodextrines pontées

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1. Introduction

Chelate complexes obtained from diphosphanes where the phosphorus centres are separated by more than twenty bonds remain relatively uncommon [1–3]. Reaction of such large bidentate ligands with transition metal complexes often produces oligomeric material rather than chelate structures [4, 5]. As already noted by Ogino, the chemical literature contains many examples of supposed chelate complexes, but for many of them the ring structure has not been firmly established [6]. This concerns in particular ligands that contain more than three or four bonds between the coordination centres. A rational way to favour chelating over bridging behaviour consists in performing the complexation reaction at high dilution, but this requires the coordination steps to proceed quickly. Alternatively, preorganisation of the complexing units brought about by increasing the ligand backbone rigidity may result in better metal chelation. We have recently studied the coordinative behaviour of a series of large bidentate ligands built on bucket-shaped units, notably cyclodextrin and calixarene backbones. All these ligands consisted of two podands tethered at the same rim of a cone-shaped cavity. We found that such long chain diphosphines *systematically* lead to chelate complexes when opposed to cationic species bearing *labile* ligands, e.g. $[Rh(COD)(solvent)_2]^+$, $[PdMe(solvent)_2(COD)]^+$, $[Ru(p\text{-cymene})(solvent)_3]^{2+}$, $[Au(solvent)_2]^+$, etc., whilst their reaction with neutral starting complexes containing poorer leaving groups (e.g. MeCN) usually affords oligomeric compounds [7, 8].

Although a number of studies have been carried out on P(III)-derivatised CDs, none deals with phosphite ligands [1, 9–17]. As part of our studies on cavity-derived bidentates, we report here on the synthesis of diphosphites **L1** and **L2** (Fig. 1), both built on an α-cyclodextrin platform, and their ability to form catalytically active large chelate complexes with transition metals. In the following, the letters '**a**' and '**b**' refer to AD- and AC-disubstituted CDs, respectively. A unique example of an α-CD capped with a short bridging fragment is also reported.

2. Results and discussion

2.1. Syntheses of ligands and complexes

The C_2-symmetrical ligand **L1** was synthesised in three steps from the known dimesylate **1a** (Fig. 2) [18]. Thus, reaction of 5 equiv of sodium 2-(benzyloxy)phenolate with **1** in DMF at 70 °C afforded a mixture of three products among which we isolated the desired compound **2a** in 65% yield. The presence of three doublets for the H-1 protons (see experimental part) as well as eight singlets for the methyl groups in the ^{1}H NMR spectrum is consistent with a molecule having C_2 symmetry, thus confirming substitution of both available mesylate groups. Partial loss of one benzyl group under these reaction conditions led to the formation of **3a** (7%). Its ^{1}H NMR spectrum reveals the absence of symmetry and indicates clearly the presence of a phenolic proton. The ^{1}H NMR spectrum of the third species **4a** (17%) is also indicative of C_2 symmetry. However, compared to **2a**, the H-1 signals of **4a** are much more spread out ($\Delta\delta = 0.30$ ppm vs 0.11 ppm for **2a**), indicating the presence of a distorted CD matrix (Fig. 3). As confirmed by a single crystal X-ray diffraction study (vide infra), the latter results from the capping of the CD platform with a short 1,2-phenylene unit, characterised by a four-proton AA'BB' system in the aromatic region of the ^{1}H NMR spectrum. Only benzyl cleavage of the monosubstituted intermediate **5a** (Fig. 4) and subsequent intramolecular substitution of the remaining mesylate group can explain the forma-

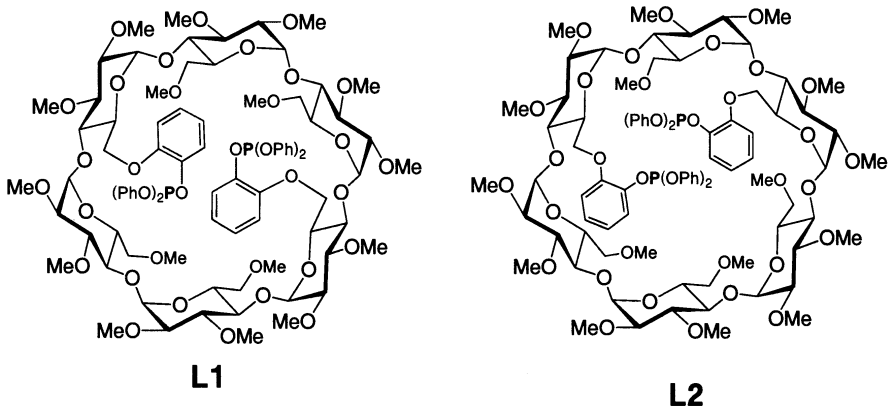


Fig. 1. Diphosphites **L1** and **L2**.

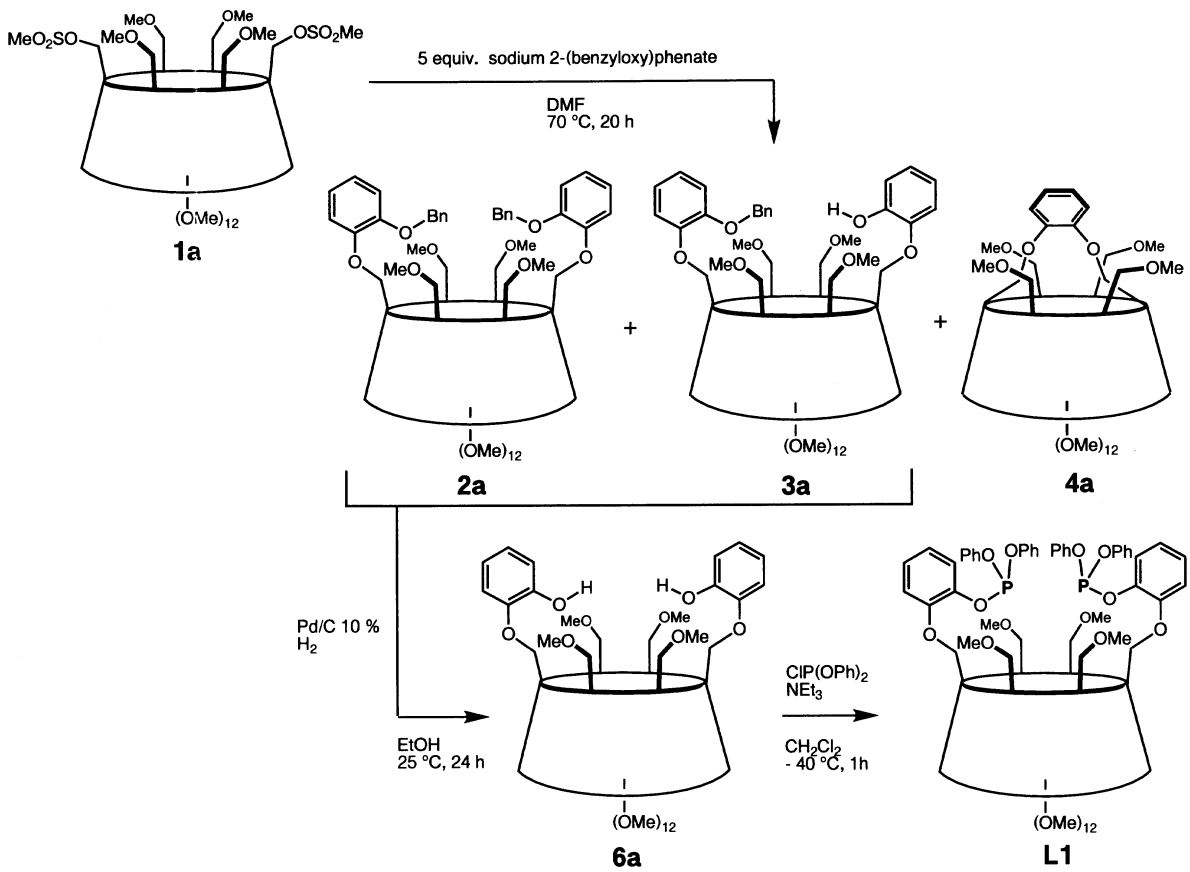


Fig. 2. Synthesis of the C_2-symmetrical ligand **L1** from the dimesylate **1a**.

tion of such a capped derivative. In the solid state (Figs. 5 and 6), the C(11) and C(21) glucose units and their symmetrical counterparts are strongly tilted with respect to the plane constituted by the six O-4 atoms (tilt angles: 35.0(3)° (C(11)) and 31.8(3)° (C(21)), vs 14.4(3)° for the C(1) ring), so as to accommodate the capping unit (the tilt angle is defined by the dihedral angle between the best plane defined by the six O-4 atoms and the plane defined by the C-1, C-4, O-4 and O-4' atoms of a particular glucose unit). Remarkably, in spite of the considerable strain imposed on the CD framework [19], all glucose units display the usual $^4C_1$ conformation [20]. The 1,2-phenylene moiety, which adopts two possible orientations (occupancy

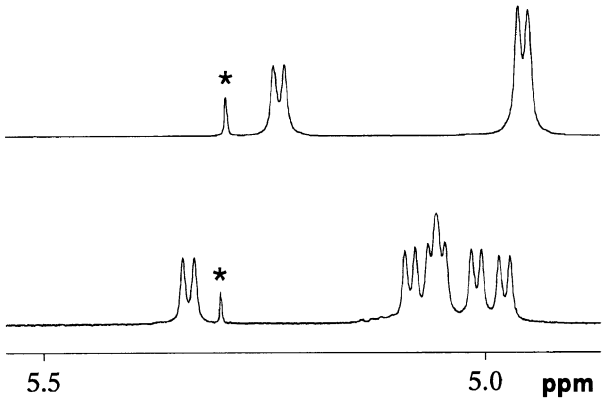


Fig. 3. Part of the ^{1}HNMR spectra ($CDCl_3$) of **4a** and **4b** showing the dispersion of the anomeric H-1 signals. The peak marked with an asterisk is due to residual CH_2Cl_2.

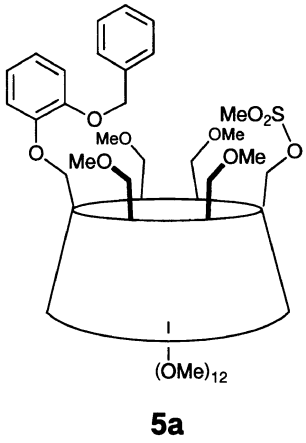


Fig. 4. Compound **5a**.

1:1), is inclined by ± 39.5° with respect to the CD axis. Note that the 2D NMR ROESY spectrum contains cross-peaks, corresponding to through-space interactions between the phenylene and all OMe-6 protons. In keeping with the fact that the molecule has averaged C_2-symmetry, this observation indicates a fan-like motion of the phenylene ring above the CD cavity in solution. The same capped species was obtained in moderate yield (ca 30%) when the dimesylate was reacted with disodium catecholate. However, in this case, some oligomeric material was formed. Treatment of **2a** and **3a** with H_2 in the presence of Pd/C afforded the diphenol **6a** quantitatively. The latter reacted smoothly with one equivalent of chlorodiphenylphosphite $ClP(OPh)_2$ in the presence of NEt_3 at –40 °C to give ligand **L1**, whose ^{31}P NMR spectrum consists of a singlet at 127.5 ppm, commensurate with the expected C_2 symmetry. In **L1**, 27 bonds separate the two phosphorus atoms.

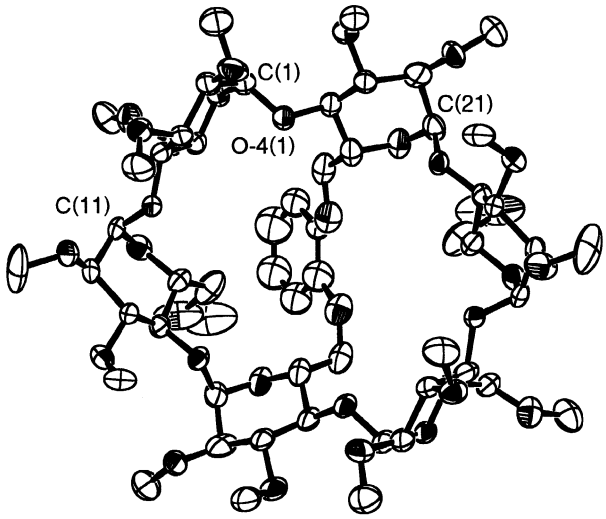


Fig. 5. View of the 1,2-phenylene-capped CD **4a** along the C_2 axis (the bridging unit lies in the backside). Only one orientation of the catecholate is shown. The included heptane molecule has been omitted for clarity.

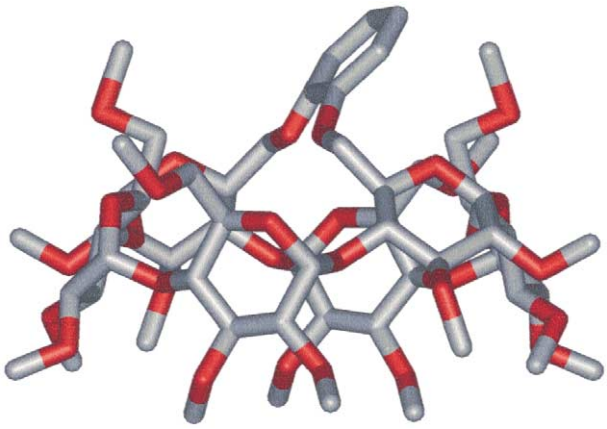


Fig. 6. Side-view of **4a** (sticks).

The bis(triaryl)phosphite regioisomer **L2** was synthesised from the known *tris*(4-*tert*-butylphenyl)methyl AC-disubstituted CD derivative **7b**. Thus, removal of the protecting groups was achieved with aqueous HBF_4 in MeCN to give diol **8b**, which was then converted to dimesylate **1b** using MsCl in pyridine in the presence of 4-(dimethylamino)pyridine (DMAP) (Fig. 7). As for **1a**, treatment of **1b** with 5 equiv of sodium 2-(benzyloxy)phenolate produced a mixture of four products, amongst which the desired disubstituted product **2b** was isolated in 57% yield. Again, bridging of two primary positions with a catechol unit was found to take place and the capped species **4b** was isolated in 18% yield. As for **4a**, the large dispersion of the H-1 signals ($\Delta\delta = 0.37$ ppm vs 0.11 ppm for **2b**) in the ^1H NMR spectrum indicates the presence of a distorted CD torus (Fig. 3). However, as revealed by 2D ROESY experiments, the phenylene protons are in close proximity to only three of the four OMe-6 protons, suggesting that the phenylene plane is tilted towards the cavity centre and does not swing in this case about the O-6^A—O-6^C axis. Again, two inseparable species whose ^1H NMR spectra are consistent (see experimental part) with products resulting from cleavage of one benzyl group from **2b** were also obtained in very low yield. Catalytic hydrogenation of **2b** afforded diphenol **6b** quantitatively, the ^1H and ^{13}C NMR spectra of which show remarkable asymmetry. The latter may result from the presence of hydrogen bonding between the two hydroxy groups and the CD matrix, which helps rigidifying the overall structure. Compound **6b** reacted smoothly with 2 equiv of $ClP(OPh)_2$ to give ligand **L2**. Surprisingly, both phosphorus atoms appear as magnetically equivalent (δ 127.5 ppm) in the ^{31}P NMR spectrum.

The bimetallic complexes **9a** and **9b** (Fig. 8) were readily obtained in high yields by reacting $[o\text{-}C_6H_4CH_2NMe_2)PdCl]_2$ with the corresponding diphosphite. Both complexes are characterised by a singlet at ca 104.5 ppm in the ^{31}P NMR spectrum. Note that for **9b** complexation does not result in the differentiation of the two formally non-equivalent phosphorus atoms. Coordination of both phosphorus-binding sites was confirmed by the presence of $^4J(PH)$ coupling constants (3.3 Hz [2 ×] in **9a** and 3.3 and 4.9 Hz in **9b**) between NMe protons and the trans-bonded phosphorus atom. The ^1H NMR spectra of both **9a** and **9b** show that the two methyl groups carried by each nitrogen atom are magnetically non-equivalent, in accord with the chirality of these molecules.

When either **L1** or **L2** was treated with 1 equiv $AgBF_4$, the exclusive formation of the chelates

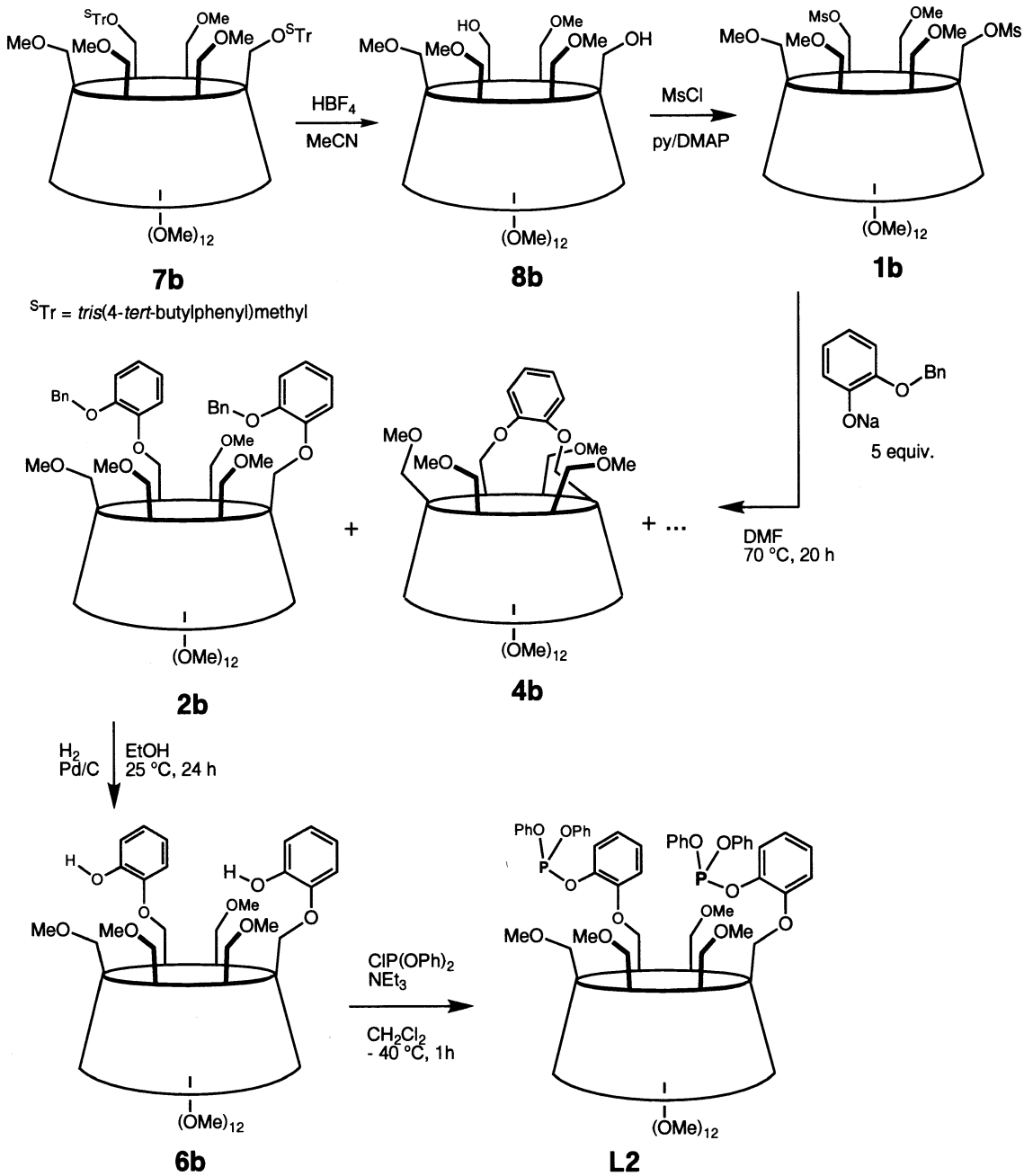


Fig. 7. Chemical route from **7b** to **L2**.

10a/10b was observed (Fig. 8). The capping of the CD cavity with an Ag^+ cation was confirmed by FAB–MS spectrometry. Both complexes produce an intense peak at 1921.3, corresponding to the molecular ion (M^+–BF_4). As expected, in the ^{31}P NMR spectrum of C_2-symmetrical **10a**, the phosphorus atoms give rise to two doublets centred at 116.7 ppm ($J(^{107}AgP) = 1083$ Hz, $J(^{109}AgP) = 1231$ Hz), whereas they resonate as two ABX systems (X = ^{107}Ag and ^{109}Ag, $\delta_A = 108.3$ and $\delta_B = 114.5$ ppm, $^2J(PP') = 256$ Hz, $J(^{107}AgP') = 977$ Hz, $J(^{109}AgP') = 1088$ Hz) in **10b**. The J(AgP) values are rather large when compared to those of *phosphine* silver complexes, but this has also been observed recently for the J(PtP) coupling constants of tris(aryl) phosphite platinum(II) complexes [21]. Unlike that of **10a**, the ^1H NMR spectrum of **10b** is somewhat broad, which suggests fluxional behaviour, possibly resulting from exchanging methoxy groups that compete for coordination to the silver cation. Similar dynamics have been observed recently in other silver-capped CDs [9]. Likewise, chelate complexes **11a**/**11b**

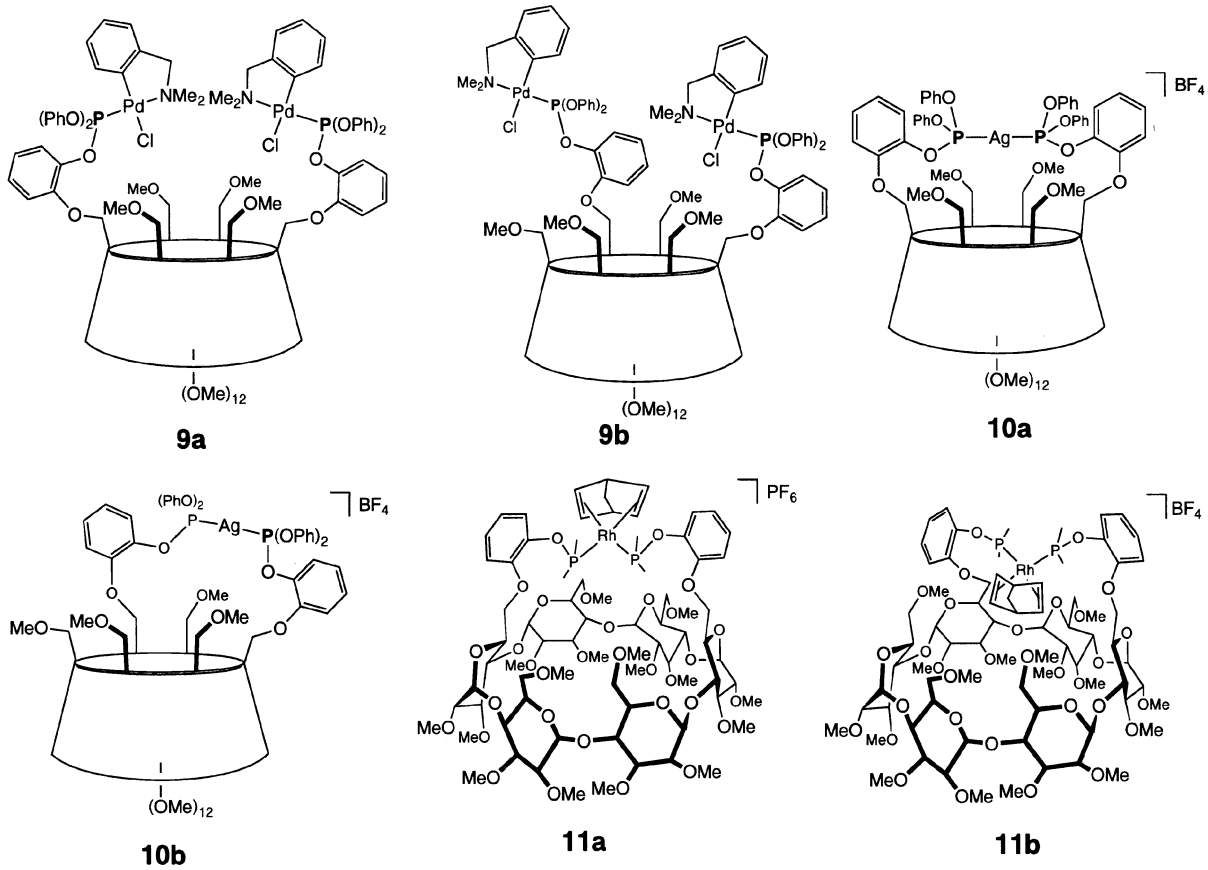


Fig. 8. Compounds **9a**, **9b**, **10a**, **10b**, **11a** and **11c**.

were obtained in high yields when the in situ formed cationic precursors $[Rh(NBD)(THF)_2]PF_6$ and $[Rh(NBD)(THF)_2]BF_4$ were reacted with one equivalent of **L1** and **L2**, respectively. Once again, the FAB-MS spectra of **11a**/**11b** (Fig. 8) left no doubt on the monomeric nature of the complexes, showing intense peaks at 2007.7 and 2008.4 for the $[M–PF_6]^+$ (**11a**) and $[M–BF_4]^+$ (**11b**) cations, respectively. Both ^{31}P NMR spectra display a single doublet centred at 110.5 ppm (J(RhP) = 264 Hz (**11a**), 259 Hz (**11b**)). It is interesting to point out that again the phosphorus atoms of **11b** give rise to an A_2X pattern (X = Rh), despite the complex lack of symmetry. This unexpected feature arises probably from the fact that the distance separating the phosphorus atoms from the chiral cavity is quite large in the absence of MeO-6 ether coordination. Furthermore, at room temperature, the ^1H NMR spectra of **11a** and **11b** are both broad, suggesting that these molecules are dynamic in solution. Recording the ^1H NMR spectrum of **11a** at 60 °C caused all signals to sharpen, but did not reduce their number. These findings suggest that the metal plane is tilted with respect to the CD axis and that the metal-containing handle is subject to conformational changes. No indication for a metal plane describing a pendulum motion about the P,P axis could be inferred from our observations. Finally, we observed that reaction of **L1** or **L2** with $[Rh(COD)_2]BF_4$, which contains poorer leaving ligands, produces a mixture of monomeric and oligomeric species. Undoubtedly, the selective formation of chelate complexes using $[Rh(NBD)(THF)_2]^+$ originates from a combination of the following features: firstly, the use of starting cationic complexes bearing highly labile ligands promotes a fast coordination of both phosphorus centres. Secondly, the rigid CD core orientates the two phosphite substituents in the same direction and therefore maintains the two phosphorus centres in close proximity.

2.2. Catalytic properties of L1 and L2

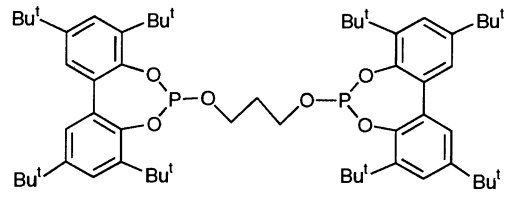
Our catalytic attempts focused on the hydroformylation of 1-octene and the hydrogenation of prochiral dimethyl itaconate, two commonly used reactions for testing P(III) ligands [22]. For the hydroformylation studies, the complexes were formed in situ according to standard literature procedures, using $[Rh(CO)_2(acac)]$ as starting complex. Thus formation of complexes other than chelate ones cannot be excluded.

2.2.1. Hydroformylation

The catalytic performances of **L1** and **L2** are summarised in Table 1. Both rates and regioselectivities are comparable to those observed with the flexible and bulky diphosphite **12** (Fig. 9; l/*b* = 2.2, TOF = 1550, isomerisation 20%) but the percentage of isomerisation does not exceed 5% in our case [23]. Consistent with van Leeuwen's observations made for other diphosphites, the flexible nature of our chelating complexes probably accounts for the observed poor linear aldehyde selectivity. Interestingly, activity is doubled on going from **L1** to **L2** (entries 3 and 4), probably reflecting a larger steric hindrance about the metal centre in the **L2**/rhodium system. This feature is likely to reduce the number of coordinated phosphorus atoms during the catalytic cycle, which in turn leads to less stable hence more reactive intermediate species. Raising the octene/rhodium ratio from 600 to 1200 produced a two-fold increase of the reaction rate. Such a substrate concentration dependency has also been observed by van Leeuwen when operating in low olefin concentration [22, 23]. No evidence was found for a supramolecular interaction between the CD cavity and the olefinic substrate under the used reaction conditions (solvent: toluene).

2.2.2. Hydrogenation

In our first experiments, the hydrogenation catalysts were formed in situ by reacting $[Rh(COD)_2]BF_4$ with either **L1** or **L2** in CH_2Cl_2 solution before adding the substrate. As described previously, under these conditions mixtures of monomeric and oligomeric compounds are formed. Both systems exhibit moderate activity (Table 2, entries 1 and 2). With EEs not exceeding 17%, the observed enantioselectivities are rather disappointing. We then repeated the tests with the preformed chelate complexes **11a** and **11b** (entries 3 and 4). To our surprise, only **11b** proved to be an active hydrogenation catalyst, whereas **11a** showed very poor activity. In addition, **11b** produces remarkable enantioselectivity (EE 83.6%, *R* isomer). Clearly, access to the metal centre is facilitated in the unsymmetrical AC-capped system, but remains below that of the less crowded oligomeric species formed when the catalysts are formed in situ. It is plausible that with complex **11b**, the chiral cavity that is rigidly positioned near the metal centre favours entrapment and orientation of the olefinic substrate, so as to induce good enantioselectivity.



12

Fig. 9. Compound **12**.

3. Conclusion

In this paper, we have shown that by grafting two phosphite ligands onto a methylated CD platform at either AC or AD positions, diphosphites with chelating properties can be obtained. Metallomacrocycles consisting of up to 29 membered-rings were produced

Table 1. Hydroformylation of 1-octene.

Entry	Ligand	L/Rh ratio	S/Rh ratio	% Conv.[a] (1 h)	Aldehyde selectivity (%)	l/*b* ratio	TOF[b]
1	L1	5	600	69	93	1.8	300
2	L1	5	1200	56	91	1.9	550
3	L2	5	600	98	95	1.9	600
4	L2	5	1200	98	93	2.0	1200

Conditions: $T = 80$ °C; 6.62×10^{-3} mmol (1.7 mg) of $[Rh(CO)_2(acac)]$ in toluene (15 ml); $P_{H_2} = P_{CO} = 10$ bar. [a] The conversion was determined after 1 h reaction time. [b] ($mol_{product}\ mol_{Rh}^{-1}\ h^{-1}$).

Table 2. Hydrogenation of dimethyl itaconate.

Entry	Catalyst	S/Rh ratio	% Conv. (24 h)[a]	EE	TOF[b]
1	$[Rh(COD)_2]BF_4$/L1[c]	500	58	10	13
2	$[Rh(COD)_2]BF_4$/L2[c]	500	47	17	10
3	11a[d]	500	1	n. d.[e]	0.2
4	11b[d]	500	17	83.6	3.5

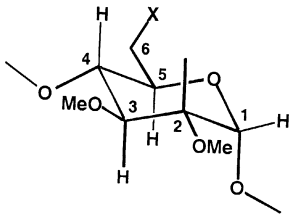
Conditions: $T = 25$ °C; CH_2Cl_2 (15 ml), $P_{H_2} = 1$ bar. [a] The conversion was determined after 24 h reaction time. [b] ($mol_{product}\ mol_{Rh}^{-1}\ h^{-1}$ after 24 h). [c] Diphosphite/Rh = 1; 2.76×10^{-2} mmol of $[Rh(COD)_2]BF_4$. [d] 2.42×10^{-2} mmol of complex. [e] Not determined.

as the sole products when the preorganised diphosphites were reacted with transition metal cations bearing labile ligands. The interesting hydrogenation properties displayed by complex **11b** illustrate the potential of unsymmetrically capped CDs as enantioselective catalysts.

4. Experimental section

4.1. General procedures

All commercial reagents were used as supplied. All manipulations involving phosphines were performed in Schlenk-type flasks under argon. 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). $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under argon over molecular sieves (4 Å). Routine ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded with FT Bruker AC200 and AC300 instruments at 25 °C, while 500-MHz spectra were recorded on an ARX 500 Bruker instrument. ^1H NMR spectral data were referenced to residual protiated solvents (7.26 for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuterated solvents (77.0 ppm for $CDCl_3$), and the ^{31}P NMR data are given relative to external H_3PO_4. All mass spectra were recorded on a ZAB HF VG Analytical spectrometer using *m*-nitrobenzyl alcohol as matrix. Cyclodextrins **1a** [18] and **7b** [24], chlorodiphenylphosphite [25, 26] and complexes $[(o\text{-}C_6H_4CH_2NMe_2)PdCl]_2$ [27], $[RhCl(NBD)]_2$ [28] and $[Rh(COD)_2]BF_4$ [13] were synthesised according to literature procedures. DMBA stands for *o*-dimethylbenzylamine. The numbering of the atoms within a glucose unit is as follows:



Hydroformylation studies were performed in a stainless steel autoclave (100 ml) containing a glass beaker and a magnetic stirring bar. The beaker was charged with toluene solutions of both the diphosphite ligand and $[Rh(CO)_2(acac)]$ (total volume 20 ml), followed by the internal standard (decane). The autoclave was flushed several times with CO/H_2 (1:1, v/v), then pressurized to 20 bar, and finally heated to 80 °C for 1 h. After depressurising and cooling down to room temperature, the substrate (1-octene) was added, and the mixture was again pressurised and heated to reaction temperature. Samples were taken at different reaction times and analysed by GC.

Hydrogenation experiments were carried out in a Schlenk tube under ambient pressure and room temperature. Experiments using $[Rh(COD)_2]BF_4$: the diphosphite ligand was dissolved in 15 ml of CH_2Cl_2. After addition of $[Rh(COD)_2]BF_4$, the solution was saturated with H_2 for 10 min, whereupon the substrate (dimethyl itaconate) was added. Samples were taken at different reaction times and analysed by GC. Enantiomeric excess was determined by ^1H NMR using an optically active shift reagent (tris [3-heptafluoropropylhydroxymethylene)-(+)-camphorato] europium (III) ((+)-Eu(hfc)$_3$)*. A $CDCl_3$ solution of the organic substrate was prepared in an NMR tube and small amounts of the shift reagent were gradually added until a clean splitting of the peaks was achieved (ca 5% of shift reagent). Experiments using **11a** or **11b**: the complex was dissolved in 15 ml of CH_2Cl_2, and the solution was saturated with H_2 for 10 min. Then dimethyl itaconate was added. The reaction was followed by GC. The enantiomeric excess was determined by GC using a chiral column.

4.2. Syntheses

*4.2.1. Synthesis of $2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F$-hexadeca-O-methyl-α-cyclodextrin (**8b**)*

Tetrafluoroboric acid (34%, 24.1 ml) was added to a solution of **7b** (12.000 g, 5.95 mmol) in MeCN (50 ml). The solution was stirred for 20 min at room temperature whereupon Et_3N (45 ml) was added. Addition of water (1000 ml) caused ^{s}TrOH to precipitate. The latter was filtered and the filtrate extracted with CH_2Cl_2 (4 × 300 ml). The organic extract was washed with saturated aqueous $NaHCO_3$ (2 × 300 ml) before being dried ($MgSO_4$), and evaporated to dryness. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 88:12,v/v) to afford **8b** as a colourless solid (6.04 g, 85%). R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.32; **Mp** 162–164 °C; ^1H NMR (200 MHz, C_6D_6): δ = 3.29 (s, 6H, OCH_3), 3.30 (s, 6H, OCH_3), 3.32 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 3.41 (s, 6H, OCH_3), 3.74 (s, 3H, OCH_3), 3.75 (s, 12H, OCH_3), 3.76 (s, 3H, OCH_3), 3.09–4.35 (36H, H-2, H-3, H-4, H-5, H-6), 5.01 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.5 Hz, 1H, H-1), 5.04–5.08 (overlapping signals, 3H, H-1), 5.11–5.12 (overlapping signals, 2H, H-1); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 57.76, 57.82 [× 2], 57.92, 58.81, 58.87 and 58.97 [× 4] (CH_3O-2, CH_3O-6), 61.50 [× 2] and 61.63 [×4] (CH_3O-3), 62.15, 62.20, 71.30, 71.39, 71.46, 71.62 (C-6), 71.10 [× 2], 71.17 [× 2], 72.33, 72.54 (C-5), 81.23 [× 6], 81.72, 81.95 [× 5], 82.11 [×5], 82.24 (C-2, C-3, C-4), 99.32, 99.52 and 99.75 [× 4] (C-1). Anal. calcd for $C_{52}H_{92}O_{30}\cdot 0.5\ CH_2Cl_2$ (1197.27 + 42.47): C 50.86, H 7.56; found: C 50.63, H 7.93.

*4.2.2. Synthesis of $6^A,6^C$-di-O-methylsulfonyl-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F$-hexadeca-O-methyl-α-cyclodextrin (**1b**)*

Methylsulfonyl chloride (1.180 g, 10.29 mmol) was added to a solution of **8b** (5.600 g, 4.68 mmol) and *N*,*N*-dimethylpyridine (0.930 g, 7.58 mmol) in anhydrous pyridine (80 ml). The reaction mixture was stirred overnight at room temperature whereupon brine (150 ml) was added. The solution was then extracted with EtOAc (4 × 200 ml), and the organic phase washed respectively with HCl 2M (2 × 200 ml), NaOH 2 M (200 ml), before being dried ($MgSO_4$) and filtered. Removal of the solvent in vacuo afforded pure **1b** as a colourless solid. R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.44; **Mp** 113–115 °C; ^{1}H NMR (200 MHz, C_6D_6): δ = 2.82 (s, 3H, OSO_2CH_3), 2.84 (s, 3H, OSO_2CH_3), 3.26 (s, 3H, OCH_3), 3.28 (s, 9H, OCH_3), 3.31 (s, 6H, OCH_3), 3.38 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.69 (s, 6H, OCH_3), 3.71 (s, 6H, OCH_3), 3.76 (s, 3H, OCH_3), 3.06–4.45 (34H, H-2, H-3, H-4, H-5, H-6), 4.76 (dd, $^3J_{H\text{-}5,H\text{-}6a}$ = 4.5 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.3 Hz, 1H, H-6), 4.92 (dd, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.3 Hz, 1H, H-6), 4.96 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.7 Hz, 1H, H-1), 5.00 (2d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.7 Hz, 2H, H-1), 5.02 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.9 Hz, 1H, H-1), 5.15 (2d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 2H, H-1); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 37.26 and 37.48 (OSO_2CH_3), 57.56, 57.63, 57.69, 58.02, 58.38, 58.81 [× 2], 59.00 [× 3] (CH_3O-2, CH_3O-6), 61.43, 61.59 [× 3], 61.69 and 61.76 (CH_3O-3), 69.53, 70.94, 71.00 [× 2], 71.20, 71.33 (C-5), 69.92 [× 3], 70.08, 71.53, 71.85 (C-6), 80.84 [× 2], 80.95 [× 2], 81.03, 81.16, 81.33, 81.49, 81.75, 81.88 [× 2], 81.98, 82.11 [× 2], 82.24 [× 2], 82.31, 83.13 (C-2, C-3, C-4), 98.60, 98.90, 99.98, 100.21 [× 2] and 100.40 (C-1). Anal. calcd for $C_{54}H_{96}O_{34}S_2 \cdot 0.5\ CHCl_3$ (1353.45 + 59.69): C 46.32, H 6.88; found: C 46.28, H 7.08.

4.2.3. Syntheses of $6^A,6^D$-bis-O-(2-benzyloxyphenyl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$-hexadeca-O-methyl-α-cyclodextrin (2a) and $6^A,6^C$-bis-O-(2-benzyloxyphenyl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F$- hexadeca-O-methyl-α-cyclodextrin (2b)

NaH (60%, 0.170 g, 4.29 mmol) was added to a solution of 2-benzyloxyphenol (0.860 g, 4.29 mmol, 0.98 ml) in DMF (25 ml). After 20 min, **1a** (1.158 g, 0.86 mmol) was added. The solution was stirred overnight whereupon water (50 ml) was added. The mixture was extracted with Et_2O (4 × 100 ml), and the ether phase was subsequently washed with an aqueous 2M NaOH solution (100 ml), dried over $MgSO_4$ and filtered. Removal of the solvent in *vacuo* gave a colourless residue (1.832 g), which was purified by column chromatography (SiO_2, hexane/ethyl acetate 20 : 80 → 0: 100, v/v) to afford three fractions:

Fraction 1. $6^A,6^D$-di-*O*-(2-benzyloxyphenyl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$-hexadeca-*O*-methyl-α-cyclodextrin **(2a)** (0.869 g, 65%). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.37; **Mp** 100–102 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.23 (s, 6H, OCH_3), 3.31 (s, 6H, OCH_3), 3.37 (s, 6H, OCH_3), 3.47 (s, 6H, OCH_3), 3.51 (s, 6H, OCH_3), 3.63 (s, 6H, OCH_3), 3.66 (s, 12H, OCH_3), 2.94–4.23 (32H, H-2, H-3, H-4, H-5, H-$6^{B,C,E,F}$), 4.31 (d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 10.1 Hz, 2H, H-$6a^{A,D}$), 4.57 (dd, ^3J= 3.2 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 10.1 Hz, 2H, H-$6b^{A,D}$), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-$1^{A,D}$), 5.08 (t, ^4J = 1.7 Hz, 4H, OCH_2Ph), 5.12 (2d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 4H, H-$1^{B,C,E,F}$), 6.84–6.99 (8H, catecholate H), 7.24–7.44 (10H, benzyl arom. H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 57.52, 57.92, 57.95, 58.93, 59.10 (CH_3O-2, CH_3O-6), 61.79, 61.85 [× 2] (CH_3O-3), 68.64 (O*C*H_2Ph), 70.90 (C-$6^{A,D}$), 71.13,71.39 [× 2] (C-5), 71.49 [× 2] (C-$6^{B,C,E,F}$), 81.29 [× 3], 82.14 [× 2], 82.27, 82.50 [× 2], 82.90 (C-2, C-3, C-4), 99.84 (C-$1^{A,D}$), 100.20, 100.27 (C-$1^{B,C,E,F}$), 114.86, 115.15, 121.41, 121.58 (catecholate CH), 126.8, 127.67, 128.50 (benzyl arom. CH), 137.58, 149.04, 149.41 (C_{ipso}). Anal. calcd for $C_{78}H_{112}O_{32}$ (1561,71): C 59.99, H 7.23; found: C 59.94, H 7.19.

Fraction 2. 6^A-*O*-(2-benzyloxyphenyl),6^D-*O*-(2-hydroxyphenyl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$-hexadeca-*O*-methyl-α-cyclodextrin **(3a)** (0.086 g, 7%). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.23; **Mp** 123–126 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.19 (s, 3H, OCH_3), 3.21 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.48 (s, 6H, OCH_3), 3.50 (s, 6H, OCH_3), 3.52 (s, 3H, OCH_3), 3.66 (s, 18H, OCH_3), 3.10–4.36 (35H, H-2, H-3, H-4, H-5, H-$6^{B,C,E,F}$, H-$6a^{A\ or\ D}$), 4.51 (dd, $^3J_{H\text{-}6b,H\text{-}5}$ = 3.2 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 10.1 Hz, 1H, H-$6b^{A\ or\ D}$), 5.00 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 1H, H-1), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 1H, H-1), 5.08 (t, ^4J = 1.7 Hz, 2H, OC*H*$_2$Ph), 5.05–5.11 (4d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 4H, H-1), 6.69 (s, 1H, OH), 6.79–7.02 (8H, catecholate H), 7.21–7.44 (5H, arom. benzyl H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 57.56, 57.86 [× 4], 58.12, 58.74, 58.81, 58.94, 59.23 (CH_3O-2, CH_3O-6), 61.56, 61.79 [× 5] (CH_3O-3), 68.20 (*O*CH_2Ph), 70.80, 70.85, 70.94 [× 3], 71.23[× 3], 71.35, 71.46, 71.50, 71.55 (C-5, C-6), 81.26 [× 4], 81.39 [× 2], 82.02 [× 5], 82.15 [× 2], 82.24 [× 2], 82.38, 82.70, 82.97 (C-2, C-3, C-4), 99.59, 99.78 [× 2], 99.90, 100.11, 100.37 (C-1), 114.60, 115.06, 115.25, 115.78, 120.04, 121.32 [× 2], 122.76 (catecholate CH), 126.76, 127.51, 128.37 (benzyl CH), 137.54, 146.56, 146.95 [× 2], 148.89 (C_{ipso}). Anal. calcd for $C_{71}H_{106}O_{32}$ (1471.59): C 57.95, H 7.26; found: C 57.71, H 7.30.

Fraction 3. $6^A,6^D$-di-*O*-(1,2-phenylene)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$-hexadeca-*O*-methyl-α-cyclodextrin **(4a)** (0.183 g, 17%). R_f (CH_2Cl_2/

MeOH, 94:6, v/v) = 0.15; **Mp** 127–130 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, assignment by ROESY and COSY; signals with unassigned multiplicity are overlapping with other signals): δ 2.90 (d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.4 Hz, 2H, H-6a^{B,E}), 3.12 (dd, 2H, $^3J_{H\text{-}2,H\text{-}1}$ = 3.6 Hz, H-2^{B,E}), 3.15 (dd, 2H, H-2^{C,F}), 3.19 (dd, 2H, H-2^{A,D}), 3.20 (s, 6H, OCH_3), 3.30 (t, 2H, H-4^{A,D}), 3.30 (s, 6H, OCH_3), 3.46 (s, 6H, OCH_3), 3.47 (s, 6H, OCH_3), 3.51 (t, 2H, H-3^{C,F}), 3.55 (s, 6H, OCH_3), 3.56 (t, 2H, H-3^{A,D}), 3.60 (dd, 2H, H-4^{B,E}), 3.60 (dd, 2H, H-5^{C,F}), 3.60 (dd, 2H, H-5^{B,E}), 3.60 (s, 6H, OCH_3), 3.62 (2H, H-6a^{C,F}), 3.67 (2H, H-3^{B,E}), 3.68 (s, 6H, OCH_3), 3.74 (2H, H-6b^{C,F}), 3.75 (s, 6H, OCH_3), 3.78 (2H, H-4^{C,F}), 3.89 (dd, 2H, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.4 Hz, $^3J_{H\text{-}6b,H\text{-}5}$ = 2.3 Hz, H-6b^{B,E}), 4.20 (2H, H-6b^{A,D}), 4.24 (d2H, H-6a^{A,D}), 4.33 (dd, 2H, $^3J_{H\text{-}5,H\text{-}6a}$ = 10.4 Hz, $^3J_{H\text{-}5,H\text{-}4}$ = 4.5 Hz, H-5^{A,D}), 4.96 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 4H, H-1^{A,D}), 4.96 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 4H, H-1^{C,F}), 5.23 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, 2H, H-1^{B,E}), 6.83–6.94 (AA'BB' system, 4H, arom. H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 57.58 [× 2], 58.93 [× 2], 59.67 (CH_3O-2, CH_3O-6), 61.00, 61.68, 61.94 (CH_3O-3), 69.39, 70.45, 71.39 (C-6), 71.03, 71.59, 72.37 (C-5), 79.56, 80.56, 80.92, 81.47 [× 2], 81.68, 82.44, 82.65 [× 2] (C-2, C-3, C-4), 97.16, 98.46, 99.59 (C-1), 112.87, 120.35 (arom. CH), 148.59 (C_{ipso}). Anal. calcd for $C_{58}H_{94}O_{30}{\cdot}C_7H_{16}$ (1271.35 + 100.20): C 56.92, H 8.08; found: C 56.78, H 7.58.

Alkylation of 2-benzyloxyphenol (0.740 g, 3.69 mmol, 0.85 ml) with dimesylate **1b** (1.000 g, 0.739 mmol) according to the previously described procedure afforded two major compounds as well as small amounts of debenzylation products, which were not separated.

Fraction 1. 6^A,6^C-di-*O*-(2-benzyloxyphenyl)-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (**2b**) (0.650 g, 57%). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.36; **Mp** 111–113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.15 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.37 (s, 9H, OCH_3), 3.47 (s, 3H, OCH_3), 3.49 (s, 6H, OCH_3), 3.51 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.64 (s, 6H, OCH_3), 3.66 (s, 9H, OCH_3), 3.08–4.54 (36H, H-2, H-3, H-4, H-5, H-6), 5.01–5.10 (10H, H-1, OCH_2Ph), 6.82–6.96 (8H, catecholate H), 7.26–7.44 (10H, arom. benzyl H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 57.40 [× 2], 57.76 [× 2], 57.82 [× 2], 58.81 [× 2], 58.94 [× 2] (CH_3O-2, CH_3O-6), 61.59 [× 2], 61.66 [× 4] (CH_3O-3), 68.41 [× 2] (OCH_2Ph), 70.67 [× 2] (C-6^{A,C}), 70.84 [× 2],71.13 [×4] (C-5), 71.20 [× 2], 71.33 [× 2] (C-6^{B,D,E,F}), 81.16 [× 4], 81.95 [× 2], 82.08 [× 4], 82.24 [× 4], 82.34 [× 2], 82.42 [× 2] (C-2, C-3, C-4), 99.75 [× 2] (C-1^{A,C}), 100.08 [× 4], (C-1^{B,D,E,F}), 114.60 [× 2], 114.96 [× 2], 121.22 [× 2], 121.35 [× 2] (catecholate CH), 126.73 [× 2], 127.48 [× 2], 128.33 [× 2] (benzyl CH), 137.41 [× 2], 148.83 [× 2], 149.25 [× 2] (C_{ipso}) (the ^{13}C NMR spectrum shows an apparent C_2 symmetry). Anal. calcd for $C_{78}H_{112}O_{32}$ (1561.71): C 59.99, H 7.23; found: C 59.79, H 7.28.

Fraction 2. 6^A,6^C-di-*O*-(1,2-phenylene)-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (**4b**) (0.183 g, 18%). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.25; **Mp** 124–126 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.03 (s, 3H, OCH_3), 3.20 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.48 (s, 6H, OCH_3), 3.49 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.60 (s, 6H, OCH_3), 3.64 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.11–4.41 (36H, H-2, H-3, H-4, H-5, H-6), 4.97 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 1H, H-1), 5.00 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H, H-1), 5.05 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.7 Hz, 2H, H-1), 5.06 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.5 Hz, 1H, H-1), 5.08 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, 1H, H-1) 5.33 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 1H, H-1), 6.81–7.00 (4H, arom. H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 57.39, 57.45, 57.62, 58.29, 58.46 [× 2], 58.58, 58.83 [× 2], 59.54 (CH_3O-2, CH_3O-6) 60.75, 61.24, 61.39 [× 2], 61.63, 61.78 (CH_3O-3), 68.01, 68.81, 71.24, 71.62, 73.09 [× 2] (C-6), 70.68 [× 3], 70.82, 70.99 [× 2] (C-5), 79.03, 79.89, 80.37, 80.82, 81.05 [× 3], 81.36 [× 3], 81.62, 81.75, 81.87, 82.03, 82.25 [× 2], 82.51, 82.75 (C-2, C-3, C-4), 94.71, 97.58, 98.82, 98.87, 99.52, 99.99 (C-1), 112.83, 118.98, 120.46, 123.03 (arom. CH), 148.00, 151.13 (C_{ipso}). Anal.calcd for $C_{58}H_{94}O_{30}$ (1271.35): C 54.80, H 7.45; found: C 55.01, H 7.55.

4.2.4. Syntheses of 6^A,6^D-bis-O-(2-hydroxyphenyl)-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D, 3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin (6a) and 6^A,6^C-bis-O-(2-hydroxyphenyl)-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin (6b)

Pd/C (10%, 0.100 g) was added to a solution of **2a** (0.869 g) in EtOH (100 ml). The mixture was stirred for 48 h under H_2 (1 atm.) before being filtered over celite. Evaporation of the filtrate in vacuo yielded pure **6a** (0.717 g, 94%). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.24; **Mp** 136–139 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.23 (s, 6H, OCH_3), 3.30 (s, 6H, OCH_3), 3.49 (s, 6H, OCH_3), 3.51 (s, 6H, OCH_3), 3.52 (s, 6H, OCH_3), 3.65 (s, 12H, OCH_3), 3.67 (s, 6H, OCH_3), 3.13–4.45 (36H, H-2, H-3, H-4, H-5, H-6), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1), 5.08 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 2H, H-1), 5.10 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 2H, H-1), 6.60 (s, 2H, OH), 6.73–7.02 (8H, arom. H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 57.92 [×2], 58.26, 58.87, 59.03 (CH_3O-2, CH_3O-6), 61.77, 61.90 [×2] (CH_3O-3), 70.93, 71.40 [×2] (C-6), 71.59 [×3] (C-5), 81.23, 81.33, 81.40, 81.92 [×2], 82.24 [×2],

82.44, 82.67 (C-2, C-3, C-4), 99.77 [×2], 100.48 (C-1), 115.53, 115.84, 120.09, 122.88 (arom. CH), 146.66, 147.05 (C_{ipso}). Anal. calcd for $C_{64}H_{100}O_{32}$ (1381.46): C 55.64, H 7.30; found: C 55.63, H 7.05.

Hydrogenolysis of **2b** (0.650 g, 0.42 mmol) was carried out according to the above procedure to afford **6b** as a colourless solid (0.540 g, 94%). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.28; **Mp** 102–104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.14 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.48 (s, 6H, OCH_3), 3.50 (s, 6H, OCH_3), 3.52 (s, 3H, OCH_3), 3.63 (s, 6H, OCH_3), 3.64 (s, 6H, OCH_3), 3.66 (s, 6H, OCH_3), 3.19–4.46 (36H, H-2, H-3, H-4, H-5, H-6), 5.01 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, 1H, H-1), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, 1H, H-1), 5.04 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H, H-1), 5.08 (3 overlapping d, 3H, H-1), 6.61 (br s, 1H, OH), 6.67 (br s, 1H, OH), 6.74–7.02 (8H, arom. H); C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 57.75 [× 3], 57.84, 58.01 [× 2], 58.75, 58.87 [× 2], 59.03 (CH_3O-2, CH_3O-6), 61.65 [× 5], 61.83 (CH_3O-3), 70.56, 70.83 [× 4], 71.30 (C-6), 71.07, 71.35 [× 4], 71.73 (C-5), 81.20 [× 4], 81.32, 81.49, 81.75, 81.89, 82.05 [× 2], 82.11 [× 3], 82.22, 82.49 [× 2], 82.66, 83.10 (C-2, C-3, C-4), 99.38, 99.72, 99.82 [× 2], 100.21 [× 2] (C-1), 115.16, 115.62 [× 2], 115.89, 119.85, 120.02, 122.57, 122.80 (arom. CH), 146.47, 146.61, 146.86 [× 2] (C_{ipso}). Anal. calcd for $C_{64}H_{100}O_{32}$ (1381.46): C 55.64, H 7.30; found: C 55.41, H 7.24.

4.2.5. Syntheses of 6^A,6^D-bis-O-{2-[(diphenoxyphosphino)oxy]phenyl}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin (L1) and 6^A,6^C-bis-O-{2-[(diphenoxyphosphino)oxy]phenyl}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin (L2)

Chlorodiphenylphosphite (0.220 g, 0.89 mmol, 0.18 ml) was added to a stirred solution of **6a** (0.500 g, 0.36 mmol) in CH_2Cl_2 (25 ml) at –40 °C. The reaction mixture was stirred for 15 min at –40 °C whereupon triethylamine (0.18 ml, 0.90 mmol, 1 equiv) was added. After 1 h, addition of pentane (200 ml) caused the triethylammonium salt to precipitate. The latter was filtered off and the filtrate was evaporated to dryness under vacuum. The residue was washed with boiling hexane (10 ml). The hot suspension was then cooled down to 0 °C and allowed to settle whereupon the hexane phase was discarded. The colourless residue was found to be pure **L1** (0.630 g, 96%). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.31; **Mp** 83–86 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.34 (s, 6H, OCH_3), 3.35 (s, 6H, OCH_3), 3.38 (s, 6H, OCH_3), 3.39 (s, 6H, OCH_3), 3.48 (s, 6H, OCH_3), 3.62 (s, 6H, OCH_3), 3.65 (s, 12H, OCH_3), 3.01–4.19 (34H, H-2, H-3, H-4, H-5, H-6a, H-6b^{B,C,E,F}), 4.90 (d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.6 Hz, 2H, H-6b^{A,D}), 4.93 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 2H, H-1), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1), 5.10 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.5 Hz, 2H, H-1), 6.84–7.40 (28H, arom. H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 57.27, 57.89 [× 2] (CH_3O-2), 58.94, 59.13 (CH_3O-6), 61.72 [× 3] (CH_3O-3), 67.95 (C-6^{A,D}), 70.84, 71.26, 71.39 (C-5), 71.62, 72.15 (C-6^{B,C,E,F}), 81.10, 81.23 [× 2], 81.65, 81.82, 81.92, 82.28, 82.47, 82.97 (C-2, C-3, C-4), 99.42 (C-1^{A,D}), 100.24, 100.47 (C-1^{B,C,E,F}), 113.98 (s, C_{para}), 120.80 (d, $^3J_{C,P}$ = 6.6 Hz, C_{ortho}), 121.37 [× 2] (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 122.45 (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 124.02 [× 2] (d, $^4J_{C,P}$ = 4.9 Hz, C_{para}), 124.63 (s, C_{meta}), 129.47 [× 2] (d, $^3J_{C,P}$ = 8.2 Hz, C_{ortho}), 141.22 (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 150.23 (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 151.48 (s, C_{ipso}), 151.81 (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 127.5 (s). Anal. calcd for $C_{88}H_{118}O_{36}P_2$ (1813.81): C 58.27, H 6.56; found: C 58.32, H 6.36; MS (FAB): *m/z* (%): 1813.6 (50) $[M+H]^+$.

Ligand **L2** was prepared in 99% yield (0.700 g) as a colourless solid according to the above procedure from chlorodiphenylphosphite (0.247 g, 0.98 mmol, 0.20 ml) and **6b** (0.540 g, 0.39 mmol). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.38; **Mp** 61–63 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.29 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 3.34 (s, 6H, OCH_3) 3.36 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.64 (s, 6H, OCH_3), 2.98–4.18 (34H, H-2, H-3, H-4, H-5, H-6a, H-6b^{B,D,E,F}), 4.75 (dd, $^2J_{H\text{-}6a,H\text{-}6b}$ = 10.5 Hz, 2H, H-6b$^{A\text{ or }C}$), 4.80 (dd, $^2J_{H\text{-}6a,H\text{-}6b}$ = 10.7 Hz, 2H, H-6b$^{C\text{ or }A}$), 4.85 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, 1H, H-1), 4.91 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H, H-1), 5.01 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H, H-1), 5.05 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, 1H, H-1), 5.07 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.8 Hz, 1H, H-1), 5.08 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H, H-1), 6.84–7.35 (28H, arom. H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ = 57.27 [× 2], 57.82 [× 4] (CH_3O-2), 58.81, 58.91, 59.00 [× 2] (CH_3O-6), 61.66 [× 6] (CH_3O-3), 67.85 [× 2] (C-6^{A,C}), 70.51 [× 2], 70.67 [× 2], 71.30 [× 2] (C-5), 71.50 [× 2], 71.92 [× 2] (C-6^{B,D,E,F}), 81.16 [× 8], 81.62 [× 2], 81.85 [× 2], 82.18 [× 2], 82.34, 82.57 [× 2], 82.83 (C-2, C-3, C-4), 99.42 (C-1^{A,C}), 100.11 [× 2], 100.27 [× 2] (C-1^{B,C,E,F}), 113.81 [× 2] (s, C_{para}), 120.74 [×2] (d, $^3J_{C,P}$ = 8.2 Hz, C_{ortho}), 121.26 [× 4] (d, $^4J_{C,P}$ = 6.6 Hz, C_{meta}), 122.38 [× 2] (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 123.98 [× 4] (d, $^4J_{C,P}$ = 3.3 Hz, C_{para}), 124.56 [× 2] (s, C_{meta}), 129.42 [× 4] (d, $^3J_{C,P}$ = 9.9 Hz, C_{ortho}), 141.19 [× 2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 150.13 [× 2] (s, C_{ipso}), 151.44 [× 2] (s, C_{ipso}), 151.74

[× 2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 127.5 [× 2] (s). Anal. calcd for $C_{88}H_{118}O_{36}P_2$ (1813.81): C 58.27, H 6.56; found: C 58.32, H 6.36.

*4.2.6. Syntheses of P,P'-(6^A,6^D-di-O-{2-[(diphenoxyphosphino)oxy]phenyl}-2^A,2^B, 2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin)-bis[chloro(o-dimethylaminobenzyl)palladium(II)] (**9a**) and P,P'-(6^A,6^C-di-O-{2-[(diphenoxyphosphino)oxy]phenyl}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin)-bis[chloro(o-dimethylaminobenzylpalladium(II)] (**9b**)*

$[(o\text{-}C_6H_4CH_2NMe_2)PdCl]_2$ (0.030 g, 0.055 mmol) was added to a solution of **L1** (0.100 g, 0.055 mmol) in CH_2Cl_2 (5 ml). After 20 min, the product was precipitated by addition of pentane (250 ml) and then collected on Celite. The precipitate was dissolved in CH_2Cl_2 (15 ml), and upon filtration, the organic solution was evaporated to dryness in vacuo to afford pure **9a** as a yellow powder (0.073 g, 56%). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.40; **Mp** 123–125 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.61 (d, 6 H, $^4J_{H,P}$ = 3.9 Hz, NCH_3), 2.63 (d, 6H, $^4J_{H,P}$ = 4.2 Hz, NCH_3), 3.30 (s, 6H, OCH_3), 3.33 (s, 12H, OCH_3), 3.35 (s, 6H, OCH_3), 3.47 (s, 6H, OCH_3), 3.60 (s, 6H, OCH_3), 3.63 (s, 12H, OCH_3), 2.84–4.15 (38H, H-2, H-3, H-4, H-5, H-6a, H-6b^{B,C,E,F}, CH_2Ph), 4.86 (d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 9.3 Hz, 2H, H-6b^{A,D}), 5.01 (2d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 4H, H-1^{B,C,E,F}), 5.13 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1^{A,D}), 6.83–7.72 (36H, arom. H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 50.00 (d, $^3J_{C,P}$ = 3.3 Hz, NCH_3), 50.15 (d, $^3J_{C,P}$ = 3.3 Hz, NCH_3), 57.40, 57.86 [× 2] (CH_3O-2), 58.91, 59.17 (CH_3O-6), 61.53, 61.66, 61.72 (CH_3O-3), 67.69 (C-6^{A,D}), 70.90, 71.17, 71.39 (C-5), 71.59, 72.21 (C-6^{B,C,E,F}), 72.68 (CH_2Ph), 81.23 [× 3], 81.65, 81.75, 81.79, 82.21, 82.28, 82.93 (C-2, C-3, C-4), 99.39 (C-1^{A,D}), 100.14, 100.44 (C-1^{B,C,E,F}), 114.04 (s, C_{para}), 120.67 (s, DMBA), 121.21 (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 121.95 (d, $^4J_{C,P}$ = 6.6 Hz, DMBA), 122.41 (s C_{ortho}), 124.57 (s, C_{meta}), 124.80 (s, C_{para}), 125.23 (s, C_{meta}), 125.92 (d, $^4J_{C,P}$ = 6.6 Hz, DMBA), 129.29 (d, $^3J_{C,P}$ = 3.3 Hz, C_{ortho}), 136.92 (d, $^3J_{C,P}$ = 11.5 Hz, DMBA), 140.81 (d, $^2J_{C,P}$ = 4.9 Hz, C_{ipso}), 147.62 (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 149.83 [× 2] (d, $^2J_{C,P}$ = 4.9 Hz, C_{ipso}), 151.06 (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 151.22 (s, C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 104.5 (s). Anal. calcd for $C_{106}H_{142}Cl_2N_2O_{36}P_2Pd_2$ (2365.96): C 53.81, H 6.05; found: C 54.07, H 6.07.

Complex **9b** was prepared in 75% yield (0.100 g) according to the above procedure from **L2** (0.103 g, 0.057 mmol) and $[(o\text{-}C_6H_4CH_2NMe_2)PdCl]_2$ (0.031 g, 0.057 mmol). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.30; **Mp** 97–99 °C; ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.60 (d, 6 H, $^4J_{H,P}$ = 3.9 Hz, NCH_3), 2.62 (d, 6H, $^4J_{H,P}$ = 3.7 Hz, NCH_3), 3.21 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3), 3.31 (s, 6H, OCH_3), 3.32 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 3.62 (s, 6H, OCH_3), 3.64 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 2.94–4.17 (38H, H-2, H-3, H-4, H-5, H-6a, H-6b^{B,D,E,F}, CH_2Ph), 4.73 (dd, $^2J_{H\text{-}6a,H\text{-}6b}$ = 10.6 Hz, ^3J H-6a,H-5 = 3.0 Hz, 1H, H-6b$^{A\ or\ C}$), 4.79 (dd, $^2J_{H\text{-}6a,H\text{-}6b}$ = 10.6 Hz, $^3J_{H\text{-}6a,H\text{-}5}$ = 2.8 Hz, 1H, H-6b$^{C\ or\ A}$), 4.94 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, 1H, H-1), 4.99 (2d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.6 Hz, 1H, H-1), 5.00 (2d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 1H, H-1), 5.05 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, 1H, H-1), 5.11 (2d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 2H, H-1), 6.85–6.91 (8H, arom. H), 6.98–7.10 (8H, arom. H), 7.20–7.33 (18H, arom. H), 7.63–7.72 (2H, arom. H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 49.98 (d, $^3J_{C,P}$ = 3.3 Hz, NCH_3), 50.14 (d, $^3J_{C,P}$ = 4.9 Hz, NCH_3), 57.40 [× 2], 57.79 [× 4] (CH_3O-2), 58.81, 58.94, 59.00, 59.07 (CH_3O-6), 61.50 [× 2], 61.65, 61.69 [× 2], 61.76 (CH_3O-3), 67.59 (C-6^{A,C}), 70.61, 70.71, 71.26 (C-5), 71.39, 71.98 (C-6^{B,D,E,F}), 72.64, 72.74 (CH_2Ph), 81.20 [× 2], 81.69 [× 2], 81.85, 82.18, 82.28, 82.51, 82.93 (C-2, C-3, C-4), 99.45 (C-1^{A,C}), 100.08, 100.31 (C-1^{B,D,E,F}), 113.88 [× 2] (s, C_{para}), 120.63 [× 2] (s, DMBA), 121.17 [× 4] (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 122.03 [× 2] (d, $^4J_{C,P}$ = 8.2 Hz, DMBA), 122.37 [× 2] (s C_{ortho}), 124.50 [× 2] (s, C_{meta}), 124.80 [× 4] (d, $^5J_{C,P}$ = 3.3 Hz, C_{para}), 125.19 [× 2] (s, C_{meta}), 125.86 [× 2] (d, $^4J_{C,P}$ = 8.2 Hz, DMBA), 129.22 [× 4] (d, $^3J_{C,P}$ = 3.3 Hz, C_{ortho}), 136.88 [× 2] (d, $^3J_{C,P}$ = 11.5 Hz, DMBA), 140.77 [× 2] (d, $^2J_{C,P}$ = 4.9 Hz, C_{ipso}), 147.55 [× 2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 149.72 [× 4] (d, $^2J_{C,P}$ = 4.9 Hz, C_{ipso}), 151.02 [× 2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 151.18 [× 2] (s, C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 104.6 [×2] (s). Anal. calcd for $C_{106}H_{142}Cl_2N_2O_{36}P_2Pd_2$ (2365.96): C 53.81, H 6.05; found: C 53.78, H 6.16.

*4.2.7. Syntheses of P,P'-(6^A,6^D-bis-O-{2-[(diphenoxyphosphino)oxy]phenyl}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin) silver (I) tetrafluoroborate (**10a**) and P,P'-(6^A,6^C-bis-O-{2-[(diphenoxyphosphino)oxy]phenyl}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin)silver(I) tetrafluoroborate (**10b**)*

A solution of $AgBF_4$ (0.011 g, 0.055 mmol) in THF (20 ml) was added to a solution of **L1** (0.100 g, 0.055 mmol) in CH_2Cl_2 (200 ml) under vigorous stirring. After 20 min, the reaction mixture was concentrated to 5 ml and pentane (250 ml) was added to

precipitate the product, which was collected on celite. The precipitate was dissolved in CH_2Cl_2 (15 ml), and upon filtration, the organic solution was evaporated to dryness in vacuo to afford pure **10a** as a colourless powder (0.060 g, 55%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.16 (s, 6H, OCH_3), 3.37 (s, 6H, OCH_3), 3.41 (s, 6H, OCH_3), 3.42 (s, 6H, OCH_3), 3.44 (s, 6H, OCH_3), 3.59 (s, 6H, OCH_3), 3.61 (s, 12H, OCH_3), 2.86–4.67 (36H, H-2, H-3, H-4, H-5, H-6), 4.92 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 2H, H-1), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 2H, H-1), 5.07 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1), 6.90–7.46 (28H, arom. H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 57.59, 57.79, 57.99 (CH_3O-2), 60.28 [× 2] (CH_3O-6), 61.53, 61.63, 61.65 (CH_3O-3), 68.71 (C-6^{A,D}), 69.69, 70.67, 71.26 (C-5), 71.59, 71.85 (C-6^{B,C,E,F}), 80.77, 81.29 [× 3], 82.02 [× 5] (C-2, C-3, C-4), 99.95 [× 2] (C-1^{B,C,E,F}), 101.09 (C-1^{A,D}), 115.58 (s, C_{para}), 121.06 (d, $^3J_{C,P}$ = 6.6 Hz, C_{ortho}), 121.26 [× 2] (d, $^4J_{C,P}$ = 6.6 Hz, C_{meta}), 122.60 (d, $^4J_{C,P}$ = 3.3 Hz, C_{meta}), 126.17 [× 2] (s, C_{para}), 127.32 (s, C_{meta}), 130.40 [× 2] (d, $^4J_{C,P}$ = 6.6 Hz, C_{ortho}), 138.40 (s, C_{ipso}), 149.74 [× 2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 150.04 (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 116.7 [2d, $^{107}J_{Ag,P}$ = 1083 Hz, $^{109}J_{Ag,P}$ = 1231 Hz]. Anal. calcd for $C_{88}H_{118}AgBF_4O_{36}P_2 \cdot 1.5\ CHCl_3$ (2008.48 + 179.07): C 49.14, H 5.51; found: C 49.05, H 5.38; MS (FAB): *m/z* (%): 1937.3 (20) [*M*–*B*F_4+O]$^+$, 1921.3 (100) [*M*–*B*F_4]$^+$.

Complex **10b** was prepared in 81% yield (0.090 g) according to the above procedure from L2 (0.11 g, 0.056 mmol) and $AgBF_4$ (0.011 g, 0.056 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.40 (s, 6H, OCH_3), 3.43 (s, 6H, OCH_3), 3.47 (s, 6H, OCH_3), 3.56 (s, 6H, OCH_3), 3.60 (s, 6H, OCH_3), 3.62 (s, 6H, OCH_3), 3.63 (s, 6H, OCH_3), 3.64 (s, 6H, OCH_3), 2.86–4.25 (36H, H-2, H-3, H-4, H-5, H-6), 4.96 (br d, 1H, H-1), 4.99 (2d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1), 5.04 (br d, 1H, H-1), 5.11 (br d, 1H, H-1), 5.20 (br d, 1H, H-1), 6.60–7.60 (28H, arom. H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 57.43 [× 2], 57.53 [× 2], 57.76 [× 2] (CH_3O-2), 58.91 [× 2], 59.04 [× 2] (CH_3O-6), 61.66 [× 2], 61.72 [× 2], 61.79 [× 2] (CH_3O-3), 70.21 [× 2], 70.90 [× 4], 71.17 [× 2], 71.50 [× 2] (C-5, C-6), 80.97 [× 2], 81.23 [× 6], 82.02 [× 2], 82.10 [× 2], 82.28 [× 6] (C-2, C-3, C-4), 100.11 [×6] (C-1), 115.35–129.94 (arom. CH), 140.00–150.26 (C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 108.3 and 114.5 (ABX, $^{107}J_{Ag,P}$ = 1095 Hz, $^{109}J_{Ag,P}$ = 1203 Hz and $^{107}J_{Ag,P'}$ = 977 Hz, $^{109}J_{Ag,P'}$ = 1088 Hz, $^2J_{P,P'}$ = 256 Hz, P and P'). Anal. calcd for $C_{88}H_{118}AgBF_4O_{36}P_2 \cdot 0.75\ (CH_3)_2CO$ (2008.48 + 43.56): C 52.83, H 6.02; found: C 53.10, H 6.09; MS (FAB): *m/z* (%): 1937.3 (20) [*M*–*B*F_4+O]$^+$, 1921.3 (100) [*M*–*B*F_4]$^+$.

4.2.8. Syntheses of cis-P,P'-(6^A,6^D-bis-O-{2-[(diphenoxyphosphino)oxy]pheny}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-O-methyl-α-cyclodextrin)-[(norbornadiene)rhodium(I)] hexafluorophosphate (11a) and cis-P,P'-(6^A,6^C-bis-O-{2-[(diphenoxyphosphino)oxy]pheny}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E, 6^F-hexadeca-O-methyl-α-cyclodextrin)-[(norbornadiene)rhodium(I)] tetrafluoroborate (11b)

Powdered $TlPF_6$ (0.022 g, 0.063 mmol) was added to a solution of $[RhCl(NBD)]_2$ (0.013 g, 0.028 mmol) in THF/CH_2Cl_2 (50:50, v/v, 50 ml). After stirring the suspension vigorously for 15 min, the precipitate was collected on celite and the filtrate was directly added to a solution of **L1** (0.106 g, 0.058 mmol) in CH_2Cl_2 (200 ml) under vigorous stirring. The reaction mixture was then stirred at room temperature for 20 min before being concentrated to 5 ml. Addition of pentane (250 ml) caused the product to precipitate. The solid was then filtered over celite before being dissolved in CH_2Cl_2 (15 ml). Upon filtration, the organic solution was evaporated to dryness in vacuo to afford pure **11a** as an orange powder (0.110 g, 90%). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.10; **Mp** 118 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$, 54 °C): δ = 3.21 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3), 3.25 (s, 3H, O-CH_3), 3.26 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.37 (s, 6H, OCH_3), 3.40 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 3.64 (s, 6H, OCH_3), 3.66 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 2.95–5.04 (50 H, H-1, H-2, H-3, H-4, H-5, H-6, HC=CH and CH of NBD), 6.75–7.50 (28H, arom. H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = (all signals are broad) 47.24 (CH_2 of NBD), 57.66 (CH_3O-2), 58.71, 59.10 (CH_3O-6), 61.72 (CH_3O-3), 69.82 (CH of NBD), 71.13 (C-5, C-6), 81.29 (HC=CH of NBD), 82.27 (C-2, C-3, C-4), 100.18 (C-1), 115.32, 119.29, 120.53, 126.10, 127.25, 129.68, 130.30 (arom. CH), 138.63, 150.53 (C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = –145 (hept. PF_6), 110.5 (d, $J_{Rh,P}$ = 264 Hz). Anal. calcd for $C_{95}H_{126}F_6O_{36}P_3Rh \cdot CHCl_3$ (2153.86 + 119.38): C 50.72, H 5.63; found: C 50.72, H 5.73; MS (FAB): *m/z* (%): 2023.6 (37) [*M*–*P*F_6+O], 2007.7 (49) [*M*–*P*F_6]$^+$, 1915.5 (58) [*M*–*P*F_6-NBD]$^+$.

Complex **11b** was prepared in 83% yield (0.120 g) according to the above procedure from **L2** (0.125 g, 0.069 mmol) and the in situ prepared $[Rh(THF)_2(NBD)]BF_4$ obtained from treatment of $[RhCl(NBD)]_2$ (0.016 g, 0.035 mmol) with $AgBF_4$ (0.013 g, 0.067 mmol). R_f (CH_2Cl_2/MeOH, 94:6, v/v) = 0.30; **Mp** 155° dec. All ^{1}H signals are broad. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): all signals are broad, δ = 57.46 (CH_3O-2), 58.81 (CH_3O-6), 61.63 (CH_3O-3), 70.71 (C-5, C-6), 81.36, 82.31 (C-2, C-3, C-4), 100.18 (C-1), 115.35, 120.47, 126.07, 129.28, 129.55, 130.27 (arom. CH), 138.50, 150.43 (C_{ipso});

$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 110.5$ (d, $J_{Rh,P} = 259$ Hz). Anal. calcd for $C_{95}H_{126}BF_4O_{36}Rh$ (2096.64): C 54.42, H 6.06; found: C 54.21, H 6.10; MS (FAB): *m/z* (%): 2024.4 (10) $[M–BF_4+O]^+$, 2008.4 (18) $[M–BF_4]^+$, 1915.3 (40) $[M–BF_4\text{-NBD}]^+$.

4.3. X-ray crystallography

Crystals of compound **4a** suitable for diffraction study were obtained by slow diffusion of heptane into an EtOAc solution of the compound.

Crystal data. $C_{58}H_{94}O_{30}\cdot C_7H_{16}$, $M = 1371.52$, hexagonal, space group $P6_222$, colourless crystals, $a = 31.2588(2)$, $c = 15.0373(1)$ Å, $V = 12724.6(1)$ Å^{-3}, $Z = 6$, $D_x = 1.072$ mg m^{-3}, $\mu = 0.84$ cm^{-1}, $F(000) = 4428$. Data were collected on a Nonius KappaCCD (graphite-monochromated Mo Kα radiation 0.710 73 Å) at 100 K. 119 971 reflections collected, 4864 with $I > 2\,\sigma(I)$. The structure was solved with SHELLXD [29], which revealed the non-hydrogen atoms of the structure. After anisotropic refinement of the cyclodextrin moiety, the bridging aromatic ring appeared as having two well-defined orientations each of 50% occupancy. The presence of a disordered *n*-heptane chain in the cavity was also detected. The whole structure was refined with SHELLXL by the full-matrix least-squares techniques (use of F^2; x, y, z, β_{ij} for the cyclodextrin O and C atoms, x, y, z, B_{iso} for the other non-H atoms and x, y, z in riding mode for H atoms; 391 variables, 4864 observations with $I > 2.0\,\sigma(I)$, $w = 1/[\sigma^2(F_o^2) + (0.2\,P)^2]$ where $P = [F_o^2 + 2\,F_c^2]/3$). Final results $R = 0.122$, $wR = 0.331$ and $S_w = 1.32$.

. Supplementary material

The supplementary material has been sent to the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary material No. 178633 and can be obtained by contacting the CCDC (quoting the article details and the corresponding SUP number).

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