Cyclodextrin Phosphanes as First and Second Coordination Sphere Cavitands

Eric Engeldinger,[a] Dominique Armspach,*[a] Dominique Matt,*[a] and Peter G. Jones[b]

Abstract: The binding properties of two α-cyclodextrins, each containing two C(5)-linked "CH_2PPh_2" units, **L1** (A,D-substituted) and **L2** (A,C-substituted), have been investigated. Both ligands readily form transition-metal chelate complexes in which the metal centres are immobilised at the cavity entrance. Although diphosphane **L1** displays a marked tendency to behave only as a *trans*-spanning ligand, the ligand possesses a certain degree of flexibility, for example, allowing the stabilisation of a trigonal silver(I) complex in which the bite angle drops to 143°. Another feature of **L1** concerns its ability to function as an hemilabile ligand. Together with four methoxy groups anchored onto the primary face, the two P^{III} centres of **L1** form a circularly arranged P_2O_4 12-electron donor set able to complex an Ag^+ ion in a dynamic way, each of the four oxygen atoms coordinating successively to the silver ion. Furthermore, the particular structures of **L1** and **L2**, characterised by the presence of P^{III} units lying close to the cavity entrance, lead upon complexation to complexes whereby the first coordination sphere is partly entrapped in the cyclodextrin. Thus, when treated with metal chlorides, both ligands systematically produce complexes in which the M–Cl unit is maintained inside the cyclodextrin through weak Cl···H-5 interactions. The chelate complex [Ag(**L1**)]BF_4 reacts with acetonitrile in excess to afford a mixture of two equilibrating complexes, [Ag(acetonitrile)(**L1**)]BF_4 and [Ag(acetonitrile)$_2$(**L1**)]BF_4, whose coordinated nitriles lie inside the cyclodextrin cavity. The inner-cavity ligands can be substituted by a benzonitrile molecule. The present study provides the first identification of an [Ag(acetonitrile)$_2$(phosphane)$_2$]$^+$ ion. The unexpected stabilisation of this species probably rests on a *cavity effect*, the cyclodextrin walls favouring recombination of the complex after facile dissociation of the nitrile ligands.

Keywords: cavitands · cyclodextrins · inclusion compounds · metallocavitands · phosphanes ·

Introduction

α-Cyclodextrins (CDs) are cavity-shaped receptors able to accommodate a variety of organic substrates.[1] In addition, like other conical molecules, they constitute valuable platforms on which functional groups can be assembled in a controlled manner.[2] The combination of these two features has allowed the preparation of a number of functionalised CDs, which have found a wide range of practical applications such as the recognition and separation of chiral compounds,[3–5] the stabilisation of photoisomerisable molecules,[6] the solubilisation of drugs (and their slow release in the human body)[7–10] and the construction of enzyme mimics.[11–16] Overall, CD derivatives have largely contributed to the spectacular development of host–guest chemistry in the last 20 years.[17, 18]

A relatively new field in cavitand chemistry focuses on the design and synthesis of CDs bearing appended transition-metal centres.[19–32] Reetz et al., for example, described a fascinating rhodium catalyst based on a β-CD-derivative, which displays shape selectivity in hydrogenation and hydroformylation reactions, thus opening the way to supramolecular catalysis of industrial relevance.[33] Therefore, anchoring reactive coordination centres onto CDs is a desirable goal. However, little has been reported on CDs in which the metal centre is rigidly held at the receptor entrance, neither have systems with free coordination sites that point towards the cavity interior been described. It may be reasonably anticipated that in such metallocyclodextrins the cavity, acting as a second coordination sphere, will strongly favour noncovalent interactions between a coordinated substrate and the inner cavity walls.

As part of our studies on phosphane- and amine-modified cavitands,[24, 25, 30, 34] we now report on the synthesis and coordinative properties of the two α-CD-derived ligands **L1** and **L2**. Both CDs have been prepared by anchoring phosphane ligands on non-adjacent glucose units, the phosphorus binding sites being closely linked to the CD skeleton.

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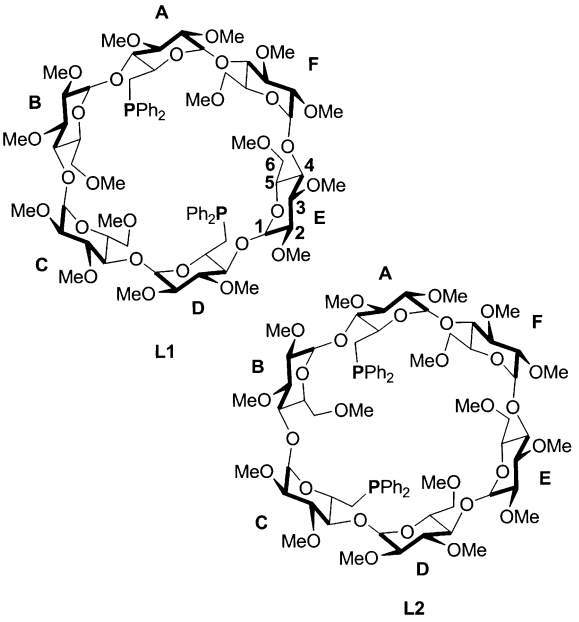
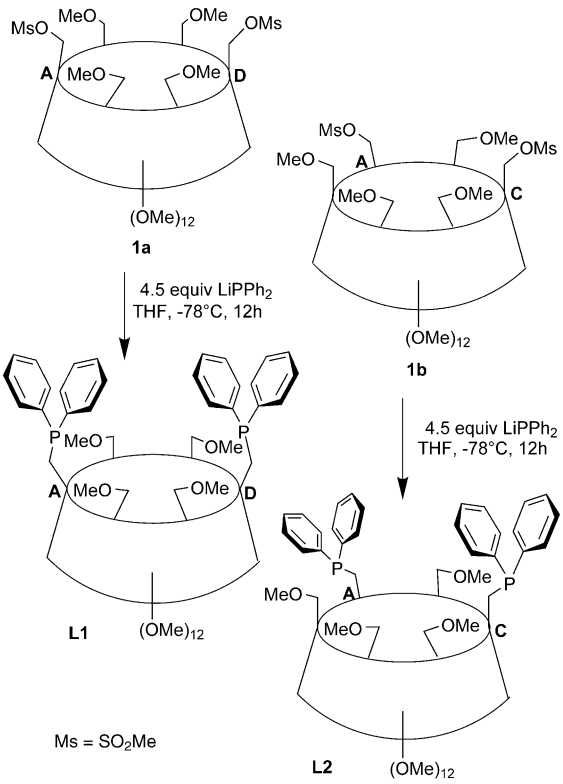


These features make them suitable for the formation of chelate complexes in which the metal centre is positioned at the cavity mouth. Having somewhat large P···P separations, they both behave as chelators with large bite angles. In particular, our results shed light on the way the cavity is able to entrap up to two metal-ligated substrates, such as nitrile or chloride ligands, in chelate complexes derived from **L1** and **L2**. This study also shows how the presence of the cavity, which to some extent is wrapped around the first coordination sphere of a silver ion, favours the formation of an unprecedented ionic $[AgP_2(acetonitrile)_2]^+$ species (P = phosphane). Note that other cavitands, based on calix[4]-[34–36] and calix[6]arenes,[37–44] as well as resorcinarenes[45] were recently used as second sphere ligands. The following results complement two preliminary communications on this topic.[46, 47]

Results and Discussion

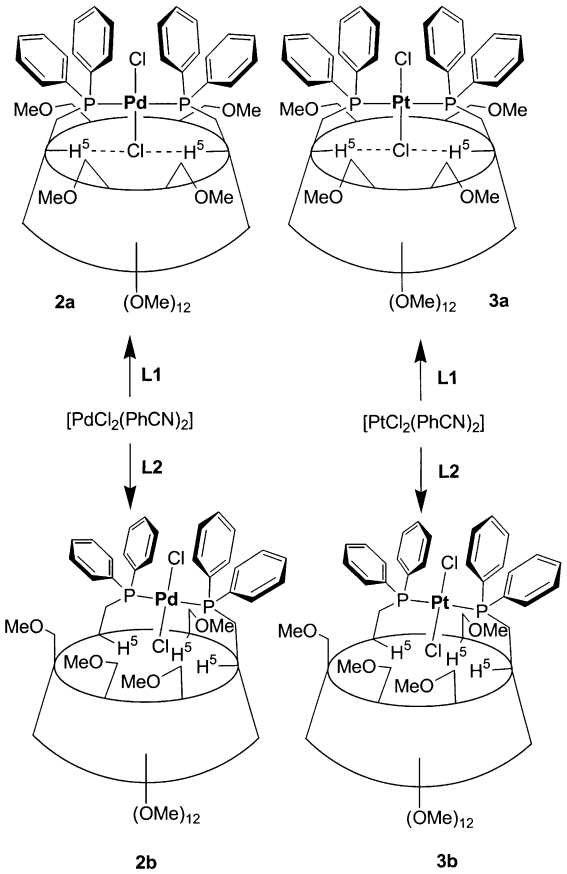
Assessing the *trans*-binding properties of diphosphanes L1 and L2: The two cyclodextrin phosphanes **L1** and **L2** were obtained in high yield by reaction of PPh_2Li with the precursors **1a**[26] and **1b**, respectively (Scheme 1). Both phosphanes are fairly soluble in hexane. The ^{31}P NMR spectrum of **L1** shows a singlet at -17.9 ppm, in keeping with a C_2-symmetrical compound, while the phosphorus signals of **L2**, which has no symmetry element, appear at -22.7 and -22.3 ppm. The C_2 symmetry of **L1** is further confirmed by the presence of three distinct doublets (vs six for **L2**) for the H-1 protons and of eight methoxy singlets (vs 16 for **L2**) in the ^1H NMR spectrum. It is worth mentioning that the close proximity of the chiral CD core to the PPh_2 units produces a strong differentiation between the two Ph rings carried by each phosphorus atom of **L1**, as revealed by ^{13}C NMR spectroscopy. Such a discrimination was not observed in other C_2-symmetrical CD diphosphanes whereby the phosphinyl units lie further away from the cavity.[22]



Scheme 1. Synthesis of the cyclodextrin phosphanes **L1** and **L2**.

Molecular models show that both diphosphanes are ideally suited for forming *trans*-chelate complexes. Thus, reaction of **L1** with $[PdCl_2(PhCN)_2]$ afforded after workup complex **2a** (ca. 40%),[48] which is characterised by a ^{31}P NMR signal at 11.9 ppm. Again all ^1H NMR data are consistent with a twofold molecular symmetry. The formation of a monomeric species was inferred from the FAB mass spectrum which displays a strong peak at $m/z = 1710.2$ with the appropriate isotopic profile for the expected $[M+H]^+$ ion. The presence in the ^{13}C NMR spectrum of a virtual triplet for the PCH_2 carbon atoms ($J(P,C) + {}^3J(P,C) = 23$ Hz) reflects the presence of *trans*-arranged phosphorus atoms (Scheme 2).[49]

The platinum analogue **3a**, which was obtained from $[PtCl_2(PhCN)_2]$, is characterised by a singlet at 7.8 ppm flanked by Pt satellites. The *trans* configuration was deduced from the $J(P,Pt)$ coupling constant of 2637 Hz, which lies in the range expected for this stereochemistry.[50] The *trans*-spanning behaviour of **2a** and **3a** was further confirmed by X-ray diffraction studies. The compounds are isostructural. Since the structure of **2a** has already been described in a preliminary work, only that of **3a** is reported here (Figure 1). In the solide state, **3a** displays a perfect C_2-symmetrical structure. The P-M-P angle is close to 172°, the P–M vectors being slightly bent towards the cavity. The P–M distances (2.334(1) Å) are slightly longer than those found in other *trans*-$[PtCl_2(PAr_2R)_2]$ complexes.[51, 52] The most interesting feature in each of these structures is undoubtedly the presence of an M–Cl bond that points towards the CD interior. Careful examination of the structure shows that Cl(2) is located between two inwardly pointing H-5 atoms, namely those belonging to the phosphane-substituted glucose units. Assum-



Scheme 2. *trans*-Bonding behaviour of **L1** and **L2**.

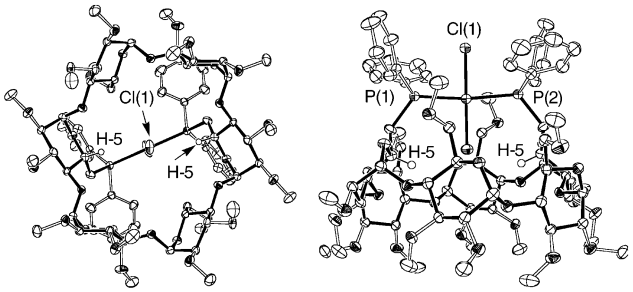


Figure 1. Ortep views of **3a**; side view(left) and bottom (right) view. Ellipsoids are drawn at the 50% probability level. A butanone molecule is included in the cavity, but has been omitted for clarity. Selected bond lengths [Å] and angles [°]: P–Pt 2.234(1), Pt–Cl(1) 2.299(2), Pt–Cl(2) 2.297(2), P(1)-Pt-P(2) 172.17(6), Cl(1)-Pt-Cl(2) 180.00(0), Cl(2)-Pt-P(1/2) 93.92(3), Pt···H-5 2.64.

ing a C(5)–H-5 bond length of 0.95 Å, the calculated H-5···Cl separations are approximately 2.64 Å in both complexes. A clear confirmation for a weak CH···Cl interaction is provided by the ^{1}H NMR spectra, which show that two H-5 atoms have undergone a significant low-field shift of about 0.8 ppm with respect to the free ligand.

Similar complexing properties were found for the unsymmetrical ligand **L2**, from which the *trans*-[MCl_2(**L2**)] complexes **2b** (M = Pd) and **3b** (M = Pt) could be obtained (see Experimental Section). The mass spectra (FAB) of **2a** and **3b** display peaks at $m/z = 1710.4$ and 1799.5, respectively, revealing the presence of the corresponding $[M+H]^+$ ions. The *trans* configuration of **3b** was easily deduced from the ^{31}P NMR spectrum, which exhibits an ABX spectrum (X = Pt) characterised by the following coupling constants: $J(P,P') = 509$ Hz, $J(P,Pt) = 2620$ and 2577 Hz. The stereochemistry of the palladium complex **2b** could not be directly inferred from its ^{31}P NMR spectrum, since the two phosphorus atoms of this complex are accidentally equivalent. However, since the chemical shift of the ^{31}P signal (9.9 ppm in $CDCl_3$) is very close to that found for **2a**, a *trans*-PP arrangement appears likely. It should also be mentioned that the ^{1}H NMR spectra of **2b** and **3b** are very similar. In particular, the three H-5 protons (which were identified by TOCSY/ROESY experiments) of glucose units A, B and C have undergone significant downfield shifts with respect to those of the free ligand (0.7–1.1 ppm for **3b**, Figure 2), as a result of weak interactions between them and an *endo*-oriented M–Cl unit.

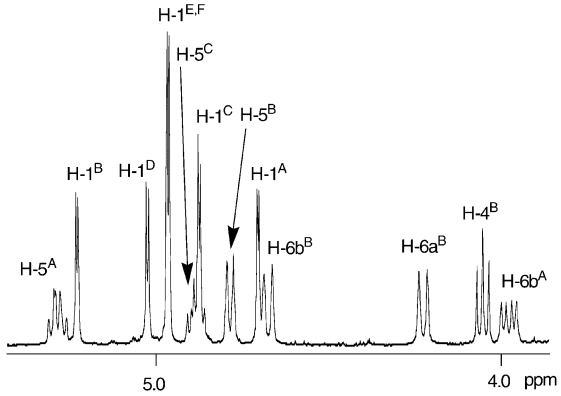
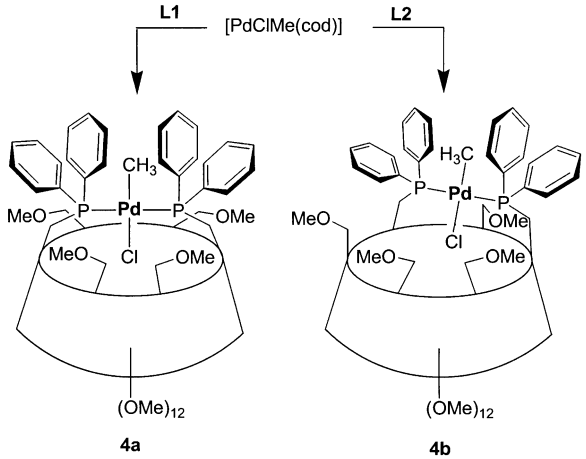


Figure 2. ^{1}H NMR spectrum ($CDCl_3$) of **3b** showing that several H-5 atoms are high-field shifted.

Another illustration of the "chlorophillic" character of **L1** and **L2** was provided by their reactions with [PdClMe(cod)] (cod = cycloocta-1,5-diene), which afforded **4a** and **4b** respectively, in high yields (Scheme 3). The ^{31}P NMR spectrum of the C_2-symmetrical complex **4a** shows a singlet at 19.4 ppm, whereas that of **4b** displays two doublets centred at 14.1 and 20.3 ppm, respectively, and reveals a $J(P,P')$ coupling constant

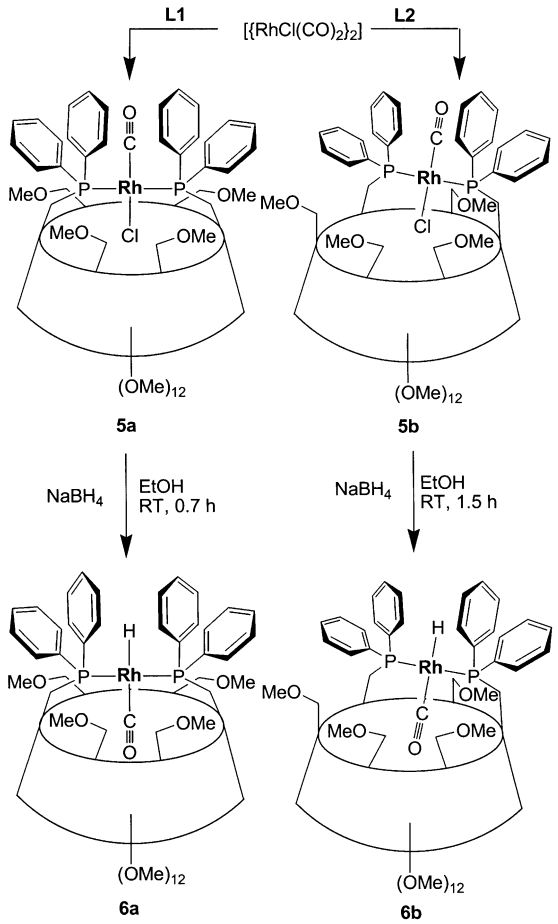


Scheme 3. Controlling the orientation of the "H_3C-Pd-Cl" rod.

of 443 Hz, typical of a *trans* configuration. The monomeric nature of these complexes was inferred from the presence of intense peaks in the FAB mass spectra corresponding to the $[M]^+$ ions ($m/z = 1688.6$). The *trans* arrangement of the phosphorus atoms was further confirmed by the presence of a methyl triplet in the ^{1}H NMR spectra ($^3J(P,H) = 6.0$ Hz for **4a** and 6.4 Hz for **4b**). As for complexes **2a** and **3a**, the two H-5 atoms of the phosphane-functionalised glucose rings of **4a** are significantly low-field shifted relative to their counterparts in free **L1** ($\Delta\delta = 1.35$ ppm). Furthermore, 2D ROESY experiments unambiguously confirmed the spatial proximity of the methyl group and the PPh_2 groups, that is, the *exo* orientation of the Pd–Me bond, a geometrical feature that firmly establishes the preference of the cavity for the Pd–Cl moiety rather than for the less polarised Pd–alkyl group. Additional through-space interactions between the Pd–methyl group and the H-6 atoms as well as the methoxy group of glucose unit B can be detected in the ROESY spectrum of **4b**, indicating a slight tilt of the coordination plane toward glucose ring B. Note that only the H-5 protons of units A and C undergo a significant shift ($\Delta\delta = +1.50$ and $+1.00$ ppm, respectively).

To investigate the hypothesis that the particular orientation of the Cl-Pd-CH_3 rod in **4a** and **4b** has its origin in steric effects, we assessed the binding properties of **L1** and **L2** towards the smaller Cl-Rh-CO unit. Complexes **5a** and **5b** were obtained quantitatively by reaction of $[\{RhCl(CO)_2\}_2]$ with **L1** and **L2**, respectively (Scheme 4). A monomeric structure was assigned to both complexes on the basis of their ^{1}H NMR spectra, which are very similar to those of **4a** and **4b**, respectively. This was confirmed in the case of **5b** by the presence in the FAB mass spectrum of a peak corresponding to the $[M+H]^+$ ion (for **5a** the highest peak corresponds to $[M - Cl - CO]^+$). The *trans* phosphane arrangements could unambiguously be deduced from the corresponding NMR spectra (the ^{13}C NMR spectrum of **5a** displays a typical PCH_2 pattern, while the ^{31}P NMR spectrum of **5b** reveals a large $J(P,P')$ coupling constant, 370 Hz). The infrared spectra of both complexes show, as expected, a strong band in the terminal CO region (1975 cm^{-1} **5a**; 1980 cm^{-1} **5b**). Again in the NMR spectra the H-5 protons of the substituted glucose units show a marked downfield shift relative to their free ligand counterparts, as expected for a weak CH···Cl interaction (**5a**: $\Delta\delta = +0.96$ ppm; **5b**: $\Delta\delta = +1.10$ and $+0.70$ ppm).

Upon treatment of **5a** or **5b** with $NaBH_4$ in ethanol, the hydrido complexes **6a** and **6b**, respectively, were formed. Both ^{1}H NMR spectra show a symmetrical hydride signal (Figure 3) near -5.0 ppm, while the infrared spectra confirm that the CO ligand is still present in the complexes (ν_{CO}: 1978 cm^{-1} **6a**; ν_{CO}: 1969 cm^{-1} **6b**). As clearly revealed by ROESY experiments, the hydride lies outside the cavity; this signal correlates only with the *o*-H atoms of the PPh rings. It is worth mentioning here that the H-5 atoms of the substituted glucose rings remain somewhat deshielded ($\Delta\delta = +0.42$ ppm **6a**; $+0.50$ ppm ($\times 2$) **6b**) in both compounds. This could reflect some noncovalent binding interaction between the H-5 atoms and the CO oxygen atom, although the observed deshielding could also arise from a field effect exerted by the



Scheme 4. *trans*-Binding behaviour of **L1** and **L2** in rhodium(I) complexes.

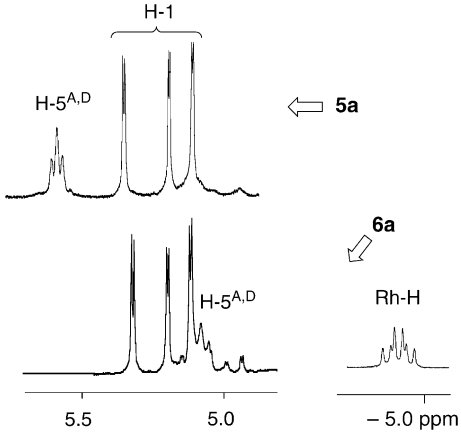
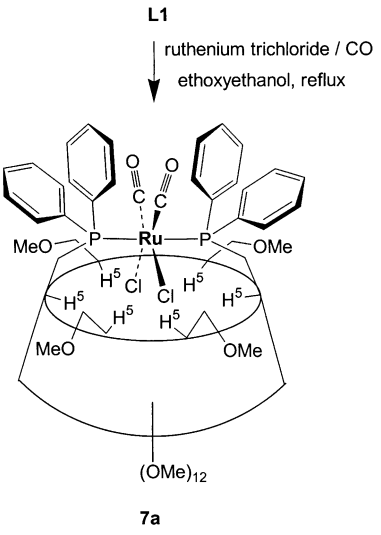


Figure 3. ^{1}H NMR spectra of **5a** (top) and **6a** (bottom) showing the position of the H-5^{A,D} protons.

CO dipole. Molecular models confirm the spatial proximity of these atoms. Finally, we wish to point out that the rate of the reactions leading to **5a** and **5b** are rather slow when compared to other reactions leading to hydrides using $NaBH_4$. This simply illustrates the fact that the metal centre is protected by the cavity against nucleophilic attack. On the other hand the restricted space about the Rh–Cl bond is likely to slow down the stereochemical rearrangements that occur during the substitution reaction. This may notably explain why, in both reactions, some transient species were formed (detected by ^{31}P NMR spectroscopy, see Experimental Section). Despite

the fact that the hydrides **6a** and **6b** are of medium stability, they constitute rare examples of bis(phosphane)hydridorhodium complexes in which the phosphanes are in a *trans* arrangement. The only other known example is [RhH(CO)-$(PCy_3)_2$].[53] Preliminary catalytic studies with **6a** showed that in the oct-1-ene hydroformylation the linear/branch (l/b) selectivity is identical to that obtained with conventional Rh/PPh_3 systems (l/b $\sim$2.7).

The propensity of cavitand **L1** to bind M–Cl moieties seems to be a general trend, even when the chloride is attached to a bulkier metal fragment. Thus reaction of **L1** with $[\{RuCl_2(CO)_2\}_n]$ in boiling ethoxyethanol afforded the octahedral *trans,cis,cis*-complex **7a** in about 70% yield. The



7a

complex is characterised by a singlet at 12.4 ppm in the ^{31}P NMR spectrum. The FAB mass spectrum displays a peak at $m/z = 1763.4$ with an isotopic profile exactly as expected for the $[M+H]^+$ ion. Trace amounts of another, unidentified complex were also detected. The infrared spectrum of **7a** shows two strong carbonyl bands, in keeping with two *cis*-coordinated COs. The ^1H NMR spectrum (Figure 4) is consistent with a C_2-symmetrical molecule and reveals that in this case *two* pairs of symmetrical H-5 atoms are involved in hydrogen bonding with the Cl atoms. The molecular structure of **7a** has already been reported in a preliminary work. Interestingly, the solid-state structure reveals the presence of two rotamers (ratio 80:20), both with their two Ru–Cl bonds pointing towards the cavity. Formally, one may switch from one isomer to the other by rotating the "$RuCl_2(CO)_2$"

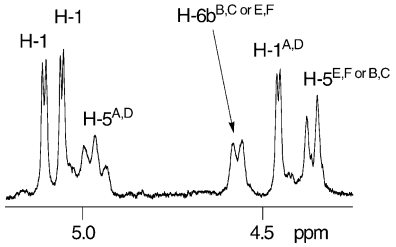


Figure 4. ^1H NMR spectrum (anomeric region) of **7a** revealing the C_2 symmetry of the complex.

fragment by approximately 37° about the P-Ru-P axis. The two isomers could not be resolved in solution, and probably the two chlorine atoms compete for occupying a central position inside the cyclodextrin so as to interact with the H-5 atoms of the A and D units. In the major one (Figure 5) the Cl(2) atom is close to four consecutive H-5 atoms (H···Cl separation ranging from 2.746 to 3.002 Å), while Cl(1) interacts with the two remaining H-5 atoms (2.840 and 2.879 Å). Evidently the weakness of the individual Cl···H-5 interactions allows easy reorientation of the M–Cl bonds within the upper part of the cavity.

Hydrogen bonds between Cl atoms and aliphatic C–H bonds are already known, but these occur usually with Cl^- ions rather than with covalently bonded chlorine.[54] In the chloro complexes reported above, the chlorine atom possesses of course anionic character. It is noteworthy that **7a** does not isomerise in solution under visible light, unlike a related $[RuCl_2(CO)_2P_2]$ complex based on a calixarenediphosphane cavity, which is easily converted into the corresponding *trans,trans,trans*-$[RuCl_2(CO)_2P_2]$ complex.[34] Moreover, the calixarene cavitand favours the inclusion of the CO ligand and not that of a M–Cl bond.

Ligand-exchange processes inside cyclodextrin cavities—reducing the bite angle of the diphosphanes: The above-

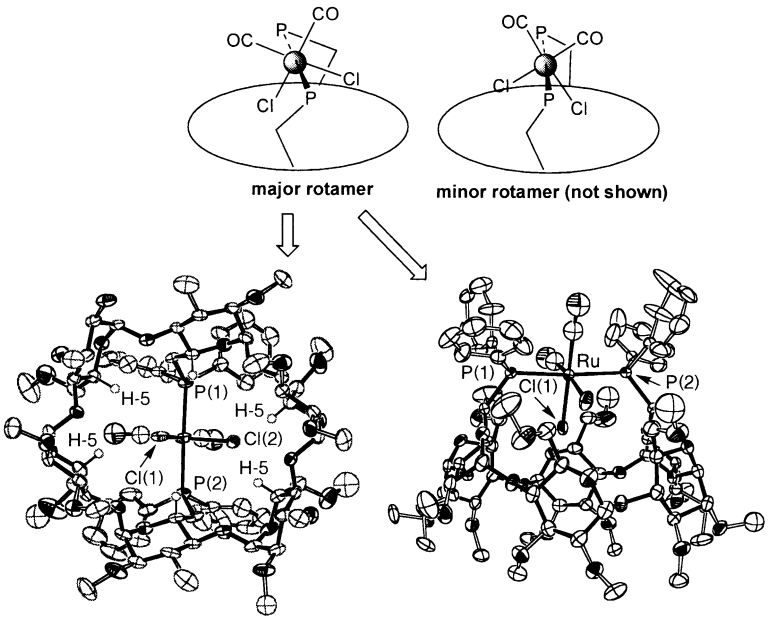
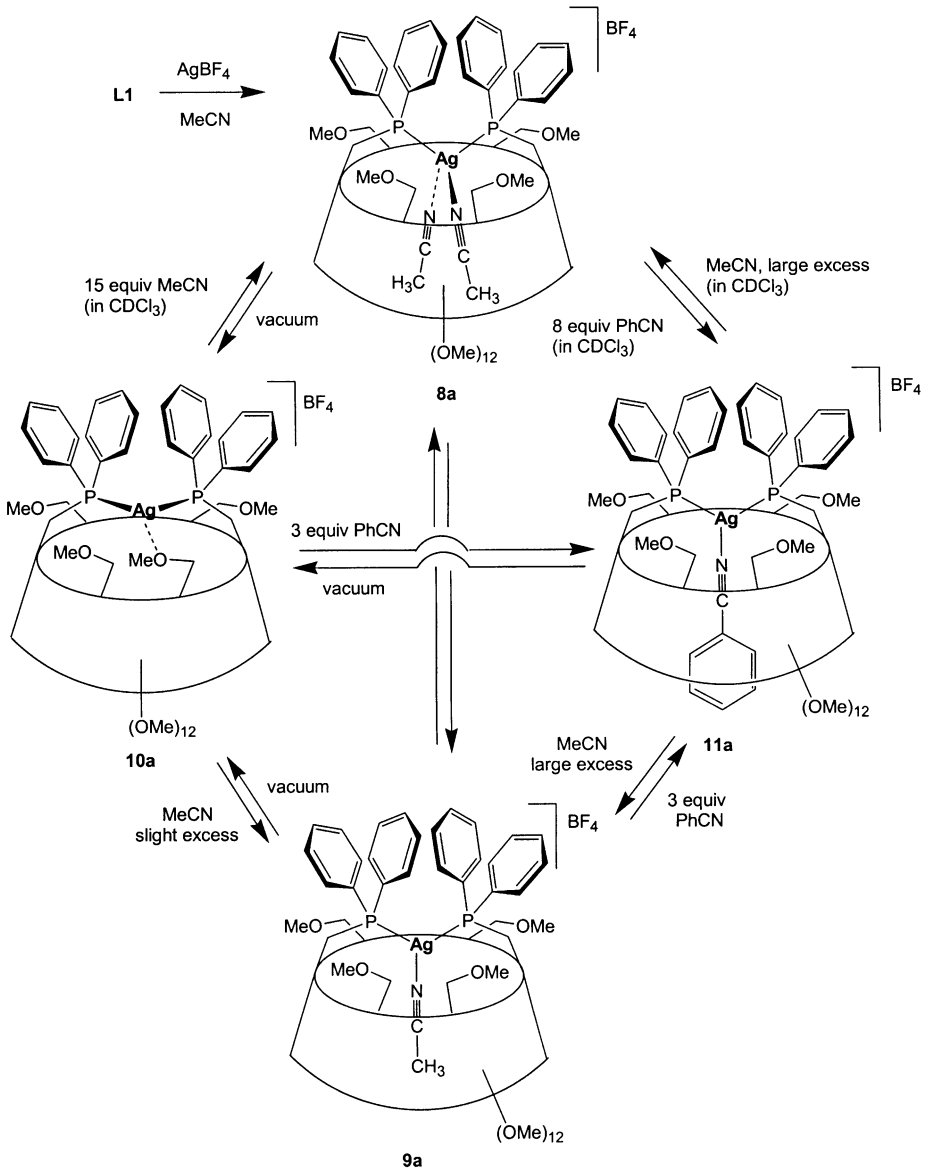


Figure 5. Ortep view of **7a** (major isomer, bottom view) showing two Ru–Cl bonds pointing towards the cavity.

described reactions not only afforded complexes in which the diphosphanes systematically behave as *trans*-spanning ligands, they also lead to complexes in which at least one ligand points to the centre of the cavity. The question whether such architectures are suitable for the study of ligand exchange processes occuring inside the CD cavity was investigated by using Ag^{I}. This ion is known for readily forming trigonal coordination compounds.

Reaction of **L1** with one equivalent of $AgBF_4$ in MeCN leads to the quantitative formation of the complex $[Ag(\mathbf{L1})(CH_3CN)_2]BF_4$ (**8a**, Scheme 5), which is only stable in large excess of MeCN (> 15 equiv) and therefore was not isolated as a solid. The formulation of **8a** was inferred from its ESI-MS spectrum which revealed the presence of a strong peak for the $[M - BF_4 + H_2O]^+$ ion ($m/z = 1741.3$)[55] together with fragmentation peaks resulting from loss of one and two molecules of MeCN. The ^1H, ^{13}C and ^{31}P NMR spectra are all consistent with a C_2-symmetrical complex. The ^{31}P spectrum displays two doublets centred at 7.6 ppm ($^{107}J(Ag,P) = 458$ Hz, $^{109}J(Ag,P) = 529$ Hz). Furthermore, the 2D ROESY spectrum of **8a** in $CDCl_3$ containing 15 equivalents of MeCN shows clearly cross-peaks corresponding to NOEs between the coordinated acetonitrile molecules[56] and all the H-3 CD protons as well as one type of H-5 CD proton, but no through-space correlations between MeCN and protons lying outside the cavity.[57] These observations are fully consistent with coordinated acetonitrile molecules that are located inside the cavity.

Upon evaporation of MeCN, **8a** loses coordinated MeCN to produce complexes **9a** ($\delta = 6.1$ ppm, $^{107}J_{Ag,P} = 417$ Hz, $^{109}J(Ag,P) = 480$ Hz) and **10a** ($\delta = -3.5$ ppm, $^{107}J(Ag,P) = 503$ Hz, $^{109}J(Ag,P) = 581$ Hz) in a 80:20 mixture whose ratio does not decrease significantly after prolonged drying in vacuo at 90 °C. However, full acetonitrile removal with quantitative formation of **10a** could be achieved provided that some drops of acetone were added to the solution prior to evaporation (ketones are known to catalyse ligand-substitution reactions). Complex **10a** was characterised by microanalysis, NMR spectroscopy and FAB mass spectrometry. At room temperature, the ^1H NMR spectrum of **10a**, recorded in $C_2D_2Cl_4$, reveals the presence of two distinctive species (45:55 ratio, characterised by the symbols * and # in Figure 6), both with averaged C_2-symmetry.



Scheme 5. Diphosphane **L1** as first and second coordination sphere ligand.

Upon heating, the signals first broaden, then coalesce near 70 °C, and finally sharpen to produce a spectrum with half the number of signals, in keeping with the fast exchange shown in Figure 6 ((B,E)/(C,F) equilibration[58]). The energy barrier for this process is approximately 67.8 kJ mol^{-1}.[59] Upon cooling down a solution of **10a** in CD_2Cl_2[60] to 0 °C, the room temperature spectrum no longer persists. Two new sets of signals emerge that correspond to two C_1-symmetrical species, reflecting a slow exchange on the ^1H NMR timescale between both pairs of diametrically opposed MeO-6 groups (Figure 7). Overall, the observations described above can be rationalised in terms of ligand fluxionality about a tricoordinate silver ion, the dynamics involving alternating binding of each of the four ether groups located on the primary face. It should be mentioned here that another phosphane multiply-

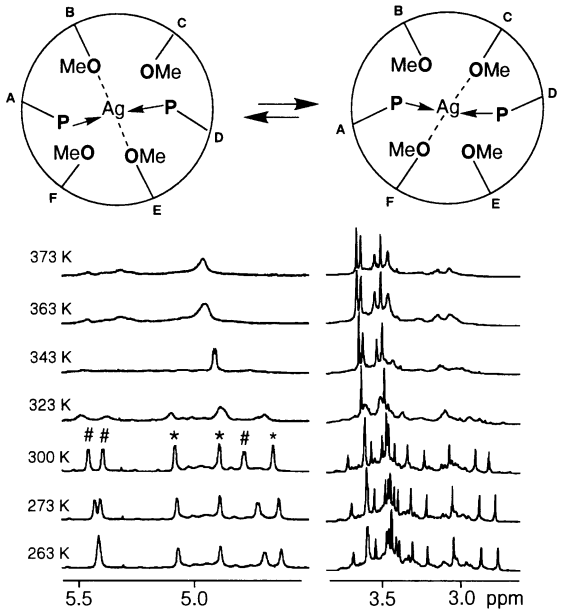


Figure 6. ^{1}H NMR spectra of **10a** in $C_2D_2Cl_4$ (400 MHz) in the range 263–373 K, reflecting the high-energy (B,E)/(C,F) exchange process. The two exchanging species are identified by the symbols * and # (left part, anomeric region; right part, MeO region. For clarity the left part has been magnified).

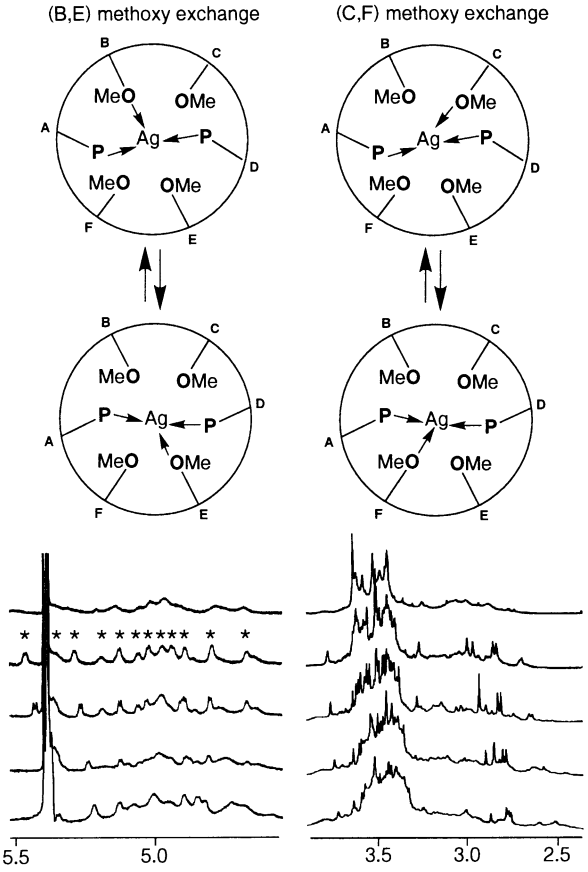


Figure 7. ^{1}NMR spectra of **10a** in CD_2Cl_2 (400 MHz) in the range 213–300 K, reflecting the two low-energy dynamics (left part, anomeric region; right part, MeO region. For clarity the left part has been magnified). The spectrum at 273 K shows distinctively 12 anomeric protons (marked with an *).

substituted by ether groups was recently reported to display hemilabile behaviour in a rhodium complex, but in this case the oxygen donors were not arranged on a macrocycle.[61] In view of the weak binding properties of the primary face ether groups of **10a**, an easy substitution by stronger donors was anticipated.

The addition of 5–10 equivalents of MeCN to a solution of **10a** was monitored by NMR spectroscopy and found to lead reversibly to a mixture of complexes **8a** and **9a** (Scheme 5). A larger excess of MeCN causes **9a** to bind an extra MeCN molecule to give **8a** exclusively. Conversely, reducing the MeCN/CD ratio (by evaporation) regenerated compounds **9a** and **10a**. The C_2 symmetry of the trigonal complex **9a** was confirmed by NMR spectroscopy as well as in the solid state by a single-crystal X-ray diffraction study (Figure 8). As

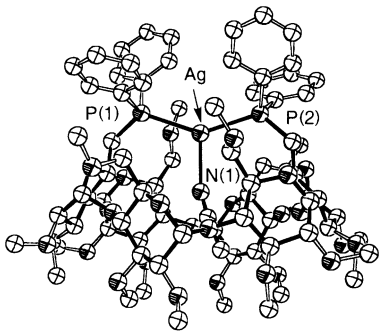


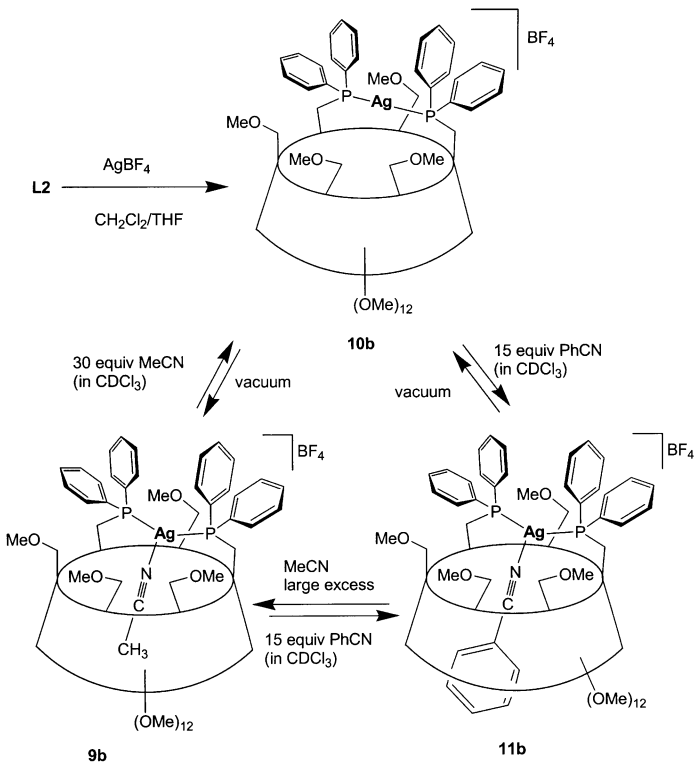
Figure 8. Ortep view of the mononitrile complex **9a**. Selected bond lengths [Å] and angle [°]: Ag–P(1) 2.570(4), Ag–P(2) 2.558(4), Ag–N(1) 2.41(1); P(1)-Ag-P(2) 142.9(1).

anticipated, the two phosphorus atoms point towards the centre of the cavity. The trigonal planar coordination mode forces the coordinated MeCN molecule to be included in the CD cavity, which does not undergo significant shape modification upon complexation. However, compared to the related complex $[Ag(NCMe)(PPh_3)_2]BF_4$,[62] the Ag–P bonds of **9a** are rather long (av 2.56 Å vs 2.44 Å in the PPh_3 complex), reflecting the shortness of the two phosphane arms. Incidently, the stereochemistry of the silver atom significantly deviates from an ideal trigonal geometry, the P-Ag-P angle (142.9(1)°) being considerably larger than 120°. A similar large bite angle has been observed in trigonal planar silver complexes obtained with Venanzi's disphosphane phenanthrene-based ligand.[63] However, the latter is much more flexible than diphosphane **L1** since bite angles close to 90° could be observed with this ligand.[64] Finally, we note that the nitrile rod is slightly bent towards one glucose unit (Ag-N(1)-C(1) 158.3(2)°). This could arise from weak intracavity CH···HC interactions involving the H-3 atoms and the acetonitrile Me group.

The addition of benzonitrile (ca. 8 equiv) to a solution of **8a** in a $CHCl_3$/MeCN mixture (**8a**:MeCN = 1:15) resulted in the *quantitative* formation of complex **11a** ($\delta = 8.7$ ppm, $^{107}J(Ag,P) = 458$ Hz, $^{109}J(Ag,P) = 529$ Hz) in which a single benzonitrile is coordinated to the silver metal, as revealed by the corresponding ESI-MS spectrum ($m/z = 1744.7$ for the $[M - BF_4]^+$ ion). A range of correlations between some H-3 as well as MeO-3 protons[65] and aromatic protons belonging to

the entrapped guest in the 2D ROESY spectrum of **11a** confirmed the inclusion of benzonitrile in the CD cavity. In addition, coupled ROESY/COSY experiments unambiguously establish that the benzonitrile plane keeps an almost fixed orientation, the *o*-H protons of the benzonitrile guest remaining located close to the H-3^{A,D} and H-3^{B,C} inner-cavity protons. Furthermore, as a result of the magnetic field anisotropy created by the included phenyl ring, the MeO-3 and MeO-2 signals in the ^{1}H NMR ($CDCl_3$) spectrum are considerably more spread out in **11a** than in **8a** ($\Delta\delta =$ 0.65 ppm vs 0.2 ppm). Clearly, the CD cavity does not allow the coordination of more than one benzonitrile molecule, but can easily accommodate two smaller ligands such as MeCN. Favourable van der Waals interactions between the interior of the CD torus and the cavity-matching phenyl residue, together with the better electron-donating ability of benzonitrile, are likely to account for the higher stability of **11a** relative to **9a**. The question whether the substitution occurs in an associative or a dissociative mechanism cannot be answered at the present stage. Assistance of the methoxy group during this process cannot be ruled out.

The binding properties of the AC-substituted CD **L2** toward metallo-nitrile fragments were also investigated. Reaction between **L2** and $AgBF_4$ in CH_2Cl_2 afforded compound **10b** quantitatively (Scheme 6), whose FAB mass spectrum displays the signal expected for the $[M - BF_4]^+$ ion ($m/z = 1641.5$). The two phosphorus atoms resonate as two ABX systems in ^{31}P NMR (X = ^{107}Ag and ^{109}Ag, $\delta_A = 3.7$ and $\delta_B = 8.3$ ppm, $J(^{107}Ag,P) = 478$ Hz, $J(^{109}Ag,P) = 556$ Hz, $J(^{107}Ag,P') = 480$ Hz, $J(^{109}Ag,P') = 558$ Hz, $^2J(P,P') = 147$ Hz). Unlike its AD counterpart, **10b** produces a ^{1}H NMR spectrum with sharp signals at room temperature, suggesting nonfluxional ligand behaviour. Molecular models show that the primary MeO groups of glucose unit B is perfectly positioned for binding a silver(I) ion, but we have no formal proof for this coordination.



Scheme 6. Binding properties of the AC-substituted CD **L2**.

Addition of 15 equivalents of CD_3CN to a solution of **10b** in $CDCl_3$ causes both the ^{1}H and ^{31}P NMR spectra, to broaden, suggesting the occurrence of an equilibrium between **10b** and an acetonitrile adduct. Addition of a further 15 equivalents of CD_3CN triggers the complete conversion to **9b**, which presents sharp signals in all NMR spectra (ABX systems (X = ^{107}Ag, ^{109}Ag) in ^{31}P NMR; $\delta_A = 5.1$ and $\delta_B = 7.8$ ppm, $J(^{107}Ag,P) = 475$ Hz, $J(^{109}Ag,P) = 549$ Hz, $J(^{107}Ag,P') = 470$ Hz, $J(^{109}Ag,P') = 544$ Hz, $^2J(P,P') = 137$ Hz). As shown unambiguously by ROESY/TOCSY experiments, the coordinated acetonitrile is here again located inside the cavity.[66] Evaporation of this solution regenerates **10b**. Unlike **9a**, complex **9b** does not coordinate a second acetonitrile despite the fact that there is no steric hindrance for the formation of a tetrahedral $[Ag(\mathbf{L2})_2(CH_3CN)_2]^+$ ion. Molecular models clearly show that in such a hypothetical complex the second coordinated acetonitrile would lie outside the cavity. The present result strongly suggests that formation of the double guest complex **8a** (starting from **10a**) owes its existence to the presence of the cavity. Interestingly, there is no report in the literature on an $[AgP_2(CH_3CN)_2]^+$ species, although transient formation of such complexes has been suggested by Camalli, Venanzi and Pregosin in 1976.[64] It is likely that the cavity walls of **8a** strongly stabilise the dinitrile complex by favouring its recombination after dissociation of one of the nitrile ligands. This *cavity effect* is reminiscent of the observations made by Reinhoudt et al. for another cavitand that ensures a high thermal stability to an incarcerated sulfolene guest.[67]

Finally, we found that, as for the related complex **9a**, addition of PhCN in excess (ca. 15 equiv) to a solution of **9b** resulted in complete acetonitrile substitution and formation of **11b** (see Experimental Section).

Conclusion

In summary, we have shown that the α-cyclodextrin derivative **L1** displays a high propensity to form chelate complexes. The smallest bite angle that was observed with this diphosphane is close to 145°, but in the majority of complexes derived from **L1** the phosphorus atoms are arranged in *trans* positions. Diphosphanes with such a large natural bite angle remain rare. Future work will be aimed at exploiting this *trans*-spanning property in order to control the outcome of catalytic reactions, such as olefin hydroformylation. The second distinctive feature of **L1** concerns its ability to function as an hemilabile ligand. Indeed, together with the four primary methoxy groups, the two P^{III} centres of **L1** form a circularly arranged P_2O_4 12-electron donor set able to complex the Ag^+ ion in a dynamic way, so that alternate binding of the four oxygen atoms takes place. In addition, the particular structure of both **L1** and **L2**, characterised by the presence of P^{III} units lying close to the cavity entrance, leads upon complexation to complexes in which the first coordination sphere is partly entrapped in the CD. Thus, when opposed to complexes

containing a M–Cl bond, both ligands systematically produce complexes in which the M–Cl bond is maintained inside the CD through weak Cl···H-5 interactions. This result illustrates the ability of an α-CD to discriminate between a metal-bonded chloride and other, less polarised M–R bonds. The occurrence of these unusual, noncovalent interactions between a guest and the CD inner walls reflects the absence of stronger competing supramolecular forces, for example, the hydrophobic effect, which usually plays a prevailing role in the formation of CD inclusion complexes. The perhaps most striking result obtained with the funnel complex **10a** is that ligand exchange processes may occur on metal centres confined inside a CD cavity. This has important implications for the development of cavity-based systems displaying both supramolecular and asymmetric catalysis. Finally, the present study provides the first identification of an $[Ag(phosphane)_2(acetonitrile)_2]^+$ species. The unexpected stabilisation of this species probably rests on the fact that the cavity walls strongly favour recombination of the complex after facile dissociation of the nitrile ligands. Future work is aimed at exploiting this *cavity effect*.

Experimental Section

General procedures: All commercial reagents were used as supplied. All manipulations involving phosphanes were performed in Schlenk-type flasks under nitrogen. 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 nitrogen over molecular sieves (4 Å). Routine ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded with FT Bruker AC200 (^{1}H: 200.1 MHz, ^{13}C: 50.3 MHz) and AC300 (^{1}H: 300.1 MHz, ^{31}P: 121.5 MHz) instruments at 25 °C, while 400 MHz and 500 MHz spectra were recorded on an Avance 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz) and an Avance 500 (^{1}H: 500.1 MHz, ^{13}C: 125.8 MHz) Bruker instrument, respectively. ^{1}H NMR spectral data were referenced to residual protiated solvents ($\delta = 7.26$ ppm for $CDCl_3$ and $\delta = 7.16$ ppm for C_6D_6), ^{13}C chemical shifts are reported relative to deuterated solvents ($\delta = 77.00$ ppm for $CDCl_3$ and $\delta = 128.30$ ppm for C_6D_6), and the ^{31}P NMR data are given relative to external H_3PO_4. FAB experiments were carried out on a ZAB HF VG Analytical mass spectrometer with *m*-nitrobenzyl alcohol as matrix, while ESI spectra were recorded on an HP Agilent MSD 1100 mass spectrometer. IR spectra were recorded on a Perkin Elmer 1600 instrument. Elemental analysis were performed by the Service de Microanalyse, Centre de Recherche Chimie, Strasbourg. Melting points were determined with a Büchi 535 capillary meting-point apparatus. Diphenylphosphane[68] and dimesylate **1b**[30] as well as $[PtCl_2(PhCN)_2]$,[69] $[PdCl_2(PhCN)_2]$[69] and [PdClMe(cod)][70] were synthesised according to literature procedures. We have not provided microanalytical data for the nitrile complexes reported in this study, since these species equilibrate with either one or two other species.

Synthesis of ligands and complexes

6^A,6^D-Bis(diphenylphosphinyl)-6^A,6^D-dideoxy-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): A solution of *n*BuLi in hexane (1.6 M, 2.4 mL, 3.770 mmol) was added, at −78 °C, to a solution of Ph_2PH (0.698 g, 3.770 mmol) in Et_2O (20 mL). Upon warming the reaction mixture to room temperature, the solvent was removed in vacuo, affording a yellow residue, which was subsequently dissolved in THF (20 mL). After cooling the resulting red solution down to −78 °C, **1a** (1.000 g, 0.739 mmol) was then added as a powder. After stirring the solution overnight at room temperature, the solvent was evaporated. Excess lithium salt was eliminated with MeOH (10 mL). After drying, the residue was treated with toluene (10 mL) and the resulting suspension filtered through Celite. The solution was evaporated to dryness and the remaining solid was treated with boiling hexane (50 mL). The resulting suspension was subsequently concentrated and cooled down to 0 °C, whereupon the hexane phase was discarded by decantation; this allowed the removal of residual Ph_2PH. This operation was repeated three times to afford **L1** as a white powder (1.100 g, 97%). R_f (CH_2Cl_2/MeOH 94:6, *v*/*v*) = 0.31; m.p. 112–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 2.18, 3.29 (AB, $^2J_{AB} = 10.4$ Hz, 4H; H-6$^{C,F\text{ or }B,E}$), 2.50, 2.67 (br AB, 4H; H-6^{A,D}), 2.76 (s, 6H; CH_3O-6), 2.99 (s, 6H; CH_3O-6), 3.10 (dd, 2H; H-2$^{C,F\text{ or }B,E}$), 3.15 (dd, 2H; H-2$^{B,E\text{ or }C,F}$), 3.22 (dd, 2H; H-2^{A,D}), 3.28, 4.05 (AB, $^2J_{AB} = 10.5$ Hz, 4H; H-6$^{B,E\text{ or }C,F}$), 3.40 (t, 2H; H-4^{A,D}), 3.45 (s, 6H; OCH_3), 3.47 (s, 6H; OCH_3), 3.51 (s, 6H; OCH_3), 3.57 (t, 2H; H-3^{A,D}), 3.58 (t, 2H; H-3$^{C,F\text{ or }B,E}$), 3.59 (t, 2H; H-3$^{B,E\text{ or }C,F}$) 3.61 (s, 6H; OCH_3), 3.63 (s, 6H; OCH_3), 3.64 (t, 2H; H-4$^{C,F\text{ or }B,E}$), 3.64 (t, 2H; H-5$^{C,F\text{ or }B,E}$), 3.65 (s, 6H; OCH_3), 3.71 (t, $^3J = 8.9$ Hz, 2H; H-4$^{B,E\text{ or }C,F}$), 3.79 (m, 2H; $^3J = 9.6$ Hz, 2H; H-5$^{B,E\text{ or }C,F}$), 4.39 (m, $^3J = 8.8$ Hz, 2H; H-5^{A,D}), 4.93 (d, $^3J_{H\text{-}1,H\text{-}2} = 2.9$ Hz, 2H; H-1^{A,D}), 5.01 (d, $^3J_{H\text{-}1,H\text{-}2} = 3.2$ Hz, 2H; H-1$^{B,E\text{ or }C,F}$), 5.03 (d, $^3J_{H\text{-}1,H\text{-}2} = 3.6$ Hz, 2H; H-1$^{C,F\text{ or }B,E}$), 7.22–7.64 ppm (20H; arom. H); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): $\delta = 32.04$ (d, $J_{C,P} = 14.8$ Hz; C-6^{A,D}), 57.69, 57.79, 58.05, 58.22, 58.58 (CH_3O-2, CH_3O-6), 61.53, 61.69, 61.99 (CH_3O-3), 69.40, 71.39 (C-6^{B,C,E,F}), 70.84 (C-4^{A,D}, tentative assignment), 71.66, 72.11 (C-5^{B,C,E,F}), 81.25 (×3), 81.42, 81.83, 81.98, 82.47, 82.79 (C-2, C-3, C-4^{B,C,E,F}), 88.54 (d, $^2J_{C,P} = 10.1$ Hz; C-5^{A,D}), 98.93, 100.40 (×2) (C-1), 128.01 (d, $^3J_{C,P} = 6.6$ Hz; C_{meta}), 128.53 (d, $^3J_{C,P} = 6.6$ Hz; C_{meta}), 131.84 (s; C_{para}), 132.17 (s; C_{para}), 134.29 (d, $^2J_{C,P} = 21.4$ Hz; C_{ortho}), 134.35 (d, $^2J_{C,P} = 21.4$ Hz; C_{ortho}), 140.30 (d, $J_{C,P} = 13.2$ Hz; C_{ipso}), 141.53 ppm (d, $J_{C,P} = 11.5$ Hz; C_{ipso}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): $\delta = -17.8$ ppm (s); elemental analysis (%) calcd for $C_{76}H_{110}O_{28}P_2$ (1533.62): C 59.52, H 7.23; found: C 59.80, H 7.48.

***trans*-*P*,*P*′-Dichloro-{6^A,6^D-bis(diphenylphosphinyl)-6^A,6^D-dideoxy-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}palladium(II) (2a)**: A solution of $[PdCl_2(PhCN)_2]$ (0.025 g, 0.0652 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L1** (0.100 g, 0.0652 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 some oligomeric products, which were then filtered off over Celite. Evaporation of pentane afforded **2a** as a yellow powder, which was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 94:6, *v*/*v*) (0.044 g, 40%). R_f (CH_2Cl_2/MeOH 94:6, *v*/*v*) = 0.31; m.p. 185 °C decomp; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.67$ (br d, $^2J_{H\text{-}6a,H\text{-}6b} = 10.3$ Hz, 2H; H-6a^{A,D}), 2.85 (s, 6H; CH_3O-6), 3.20 (s, 6H; CH_3O-6), 3.47 (s, 6H; OCH_3), 3.49 (s, 6H; OCH_3), 3.52 (s, 6H; OCH_3), 3.61 (s, 6H; OCH_3), 3.65 (s, 6H; OCH_3), 3.78 (s, 6H; OCH_3), 3.06–4.11 (32H; H-2, H-3, H-4, H-5^{B,C,E,F}, H-6a^{B,C,E,F}, H-6b), 4.78 (d, $^3J_{H\text{-}1,H\text{-}2} = 2.7$ Hz, 2H; H-1), 5.01 (d, $^3J_{H\text{-}1,H\text{-}2} = 3.0$ Hz, 2H; H-1), 5.13 (d, $^3J_{H\text{-}1,H\text{-}2} = 3.5$ Hz, 2H; H-1), 5.13 (br t, $^3J = 10.1$ Hz, 2H; H-5^{A,D}), 7.33–7.43 (12H; H_{meta}, H_{para}), 7.55–7.63 (4H; H_{ortho}), 8.07–8.16 ppm (4H; H_{ortho}); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): $\delta = 34.94$ (virtual t, $^1J_{C,P} + {}^3J_{C,P'} = 23.0$ Hz; C-6^{A,D}), 57.50, 57.73 (CH_3O-6), 58.94, 59.13 (×2) (CH_3O-2), 61.13, 61.50, 61.82 (CH_3O-3), 70.02 (C-4^{A,D}), 70.61, 70.80 (C-6^{B,C,E,F}), 71.33, 71.46 (C-5^{B,C,E,F}), 80.28, 80.64, 80.77, 81.23 (×2), 81.69, 81.75, 83.36 (C-2, C-3, C-4^{B,C,E,F}), 89.90 (virtual t, $^2J_{C,P} + {}^4J_{C,P'} = 11.5$ Hz; C-5^{A,D}), 98.27 (×2) (C-1^{B,C,E,F}), 100.77 (C-1^{A,D}), 127.51 (virtual t, $^3J_{C,P} + {}^5J_{C,P'} = 11.5$ Hz; C_{meta}), 128.07 (virtual t, $^3J_{C,P} + {}^5J_{C,P'} = 9.8$ Hz; C_{meta}), 130.10 (s; C_{para}), 130.56 (s; C_{para}), 131.72 (d, $^1J_{C,P} = 10.5$ Hz; C_{ipso}), 133.48 (virtual t, $^2J_{C,P} + {}^4J_{C,P'} = 11.5$ Hz; C_{ortho}), 135.71 ppm (virtual t, $^2J_{C,P} + {}^4J_{C,P} = 13.2$ Hz; C_{ortho}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): $\delta = 11.9$ ppm (s); elemental analysis (%) calcd for $C_{76}H_{110}Cl_2O_{28}P_2Pd$ (1710.95): C 53.35, H 6.48; found C 53.36, H 6.29; MS (FAB): *m*/*z* (%): 1710.2 (33) $[M+H]^+$, 1675.2 (17) $[M-Cl]^+$, 1638.2 (13) $[M-2Cl]^+$.

***trans*-*P*,*P*′-Dichloro-{6^A,6^D-bis(diphenylphosphinyl)-6^A,6^D-dideoxy-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}platinum(II) (3a)**: A solution of $[PtCl_2(PhCN)_2]$ (0.031 g, 0.0656 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L1** (0.100 g, 0.0652 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 small amounts of oligomeric compounds, which were then filtered off over Celite. Evaporation of pentane afforded **3a** as a pale yellow powder, which was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 94:6, *v*/*v*) (0.052 g, 44%). R_f (CH_2Cl_2/MeOH 94:6, *v*/*v*) = 0.31; m.p. 218 °C decomp; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.62$ (br d, $^2J_{H\text{-}6a,H\text{-}6b} = 10.7$ Hz, 2H; H-6a^{A,D}), 2.88 (s, 6H; CH_3O-6), 3.19 (s, 6H; CH_3O-6), 3.46 (s, 6H; OCH_3), 3.48 (s, 6H; OCH_3), 3.52 (s, 6H; OCH_3), 3.60 (s, 6H; OCH_3), 3.64 (s, 6H; OCH_3), 3.78 (s, 6H; OCH_3), 3.05–4.08 (32H; H-2, H-3, H-4, H-5^{B,C,E,F}, H-6a^{B,C,E,F},H-6b), 4.76 (d, $^3J_{H\text{-}1,H\text{-}2} = 2.6$ Hz, 2H;

H-1), 5.00 (d, $^3J_{H\text{-}1,H\text{-}2}=2.9$ Hz, 2H; H-1), 5.13 (d, $^3J_{H\text{-}1,H\text{-}2}=3.4$ Hz, 2H; H-1), 5.18 (br t, $^3J=9.7$ Hz, 2H; H-5^{A,D}), 7.32–7.44 (12H; H_{meta}, H_{para}), 7.58–7.64 (4H; H_{ortho}), 8.09–8.16 ppm (4H; H_{ortho}); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta=36.55$ (virtual t, $^1J_{C,P}+{}^3J_{C,P'}=21.5$ Hz; C-6^{A,D}), 57.53, 57.86 (CH_3O-6), 58.94, 59.20, 59.30 (CH_3O-2), 61.13, 61.50, 61.86 (CH_3O-3), 69.99 (C-4^{A,D}), 70.54, 70.84 (C-6^{B,C,E,F}), 71.39 (×2) (C-5^{B,C,E,F}), 80.28, 80.74 (×2), 81.26 (×2), 81.69 (×2), 83.39 (C-2, C-3, C-4^{B,C,E,F}), 89.10 (virtual t, $^2J_{C,P}+{}^4J_{C,P'}=11.5$ Hz; C-5^{A,D}), 98.21, 98.27 (C-1^{B,C,E,F}), 100.67 (C-1^{A,D}), 127.42 (virtual t, $^3J_{C,P}+{}^5J_{C,P'}=9.8$ Hz; C_{meta}), 127.97 (virtual t, $^3J_{C,P}+{}^5J_{C,P'}=9.8$ Hz; C_{meta}), 130.17 (s; C_{para}), 130.56 (s; C_{para}), 133.55 (virtual t, $^2J_{C,P}+{}^4J_{C,P'}=11.5$ Hz; C_{ortho}), 135.71 ppm (virtual t, $^2J_{C,P}+{}^4J_{C,P'}=11.5$ Hz; C_{ortho}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta=7.8$ ppm (s with Pt satellites, $^1J_{Pt,P}=2637$ Hz); elemental analysis (%) calcd for $C_{76}H_{110}Cl_2O_{28}P_2Pt\cdot 0.5\,C_6H_6$ (1799.61+39.06): C 51.61, H 6.19; found: C 51.64, H 6.08; MS (FAB): *m/z* (%): 1799.7 (0.1) $[M+H]^+$, 1763.8 (0.5) $[M-Cl]^+$.

***trans*-*P*,*P*′-Chloromethyl-{6^A,6^D-bis(diphenylphosphinyl)-6^A,6^D-dideoxy-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}palladium(II) (4a)**: A solution of [PdMeCl(cod)] (0.020 g, 0.0755 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L1** (0.115 g, 0.0755 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 side products, which were then filtered off over Celite. Evaporation of the solvent afforded **4a** (0.080 g, 66%) as a yellow powder. R_f (CH_2Cl_2/MeOH 94:6, *v*/*v*) = 0.31; m.p. 178 °C decomp; ^1H NMR (500 MHz, C_6D_6, 25 °C): $\delta=0.02$ (t, $^3J_{H,P}=6.0$ Hz, 3H; $PdCH_3$), 2.77 (m, 2H; H-6a^{A,D}) 3.20 (s, 6H; OCH_3), 3.22 (s, 6H; OCH_3), 3.30 (s, 6H; OCH_3), 3.31 (s, 6H; OCH_3), 3.33 (s, 6H; OCH_3), 3.39 (s, 6H; OCH_3), 3.86 (s, 6H; CH_3O-6), 3.88 (s, 6H; CH_3O-6), 3.13–4.71 (32H; H-2, H-3, H-4, H-5^{B,C,E,F}, H-6a^{B,C,E,F}, H-6b), 5.05 (d, $^3J_{H\text{-}1,H\text{-}2}=2.6$ Hz, 2H; H-1), 5.22 (d, $^3J_{H\text{-}1,H\text{-}2}=3.1$ Hz, 2H; H-1), 5.40 (d, $^3J_{H\text{-}1,H\text{-}2}=3.5$ Hz, 2H; H-1), 5.98 (br t, $J=9.5$ Hz, 2H; H-5^{A,D}), 6.86–7.25 (12H; H_{meta}, H_{para}), 7.70–7.73 (4H; H_{ortho}), 7.88–7.91 ppm (4H; H_{ortho}); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta=4.51$ ($PdCH_3$), 37.30 (virtual t, $^1J_{C,P}+{}^3J_{C,P'}=24.7$ Hz; C-6^{A,D}), 57.00, 57.36 (CH_3O-6), 59.19, 59.56, 60.05 (CH_3O-2), 60.96, 61.39, 62.11 (CH_3O-3), 70.00 (C-4^{A,D}), 72.27, 72.34 (C-5^{B,C,E,F}), 72.41, 72.50 (C-6^{B,C,E,F}), 81.35, 81.58 (×2), 81.88, 82.30, 82.47, 82.83, 84.17 (C-2, C-3, C-4^{B,C,E,F}), 88.80 (virtual t, $^2J_{C,P}+{}^4J_{C,P'}=9.9$ Hz; C-5^{A,D}), 98.33, 98.43 (C-1^{B,C,E,F}), 101.09 (C-1^{A,D}), 128.00 (virtual t, $^3J_{C,P}+{}^5J_{C,P}=9.8$ Hz; C_{meta}), 128.43 (virtual t, $^3J_{C,P}+{}^5J_{C,P'}=9.8$ Hz; C_{meta}), 129.70 (s; C_{para}), 130.39 (s; C_{para}), 131.11 (d, $^1J_{C,P}+{}^3J_{C,P}=39.6$ Hz; C_{ipso}), 133.54 (virtual t, $^2J_{C,P}+{}^4J_{C,P'}=11.5$ Hz; C_{ortho}), 136.00 (virtual t, $^2J_{C,P}+{}^4J_{C,P'}=13.2$ Hz; C_{ortho}), 137.77 ppm (virtual t, $^1J_{C,P}+{}^3J_{C,P}=39.6$ Hz; C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta=19.4$ ppm (s); elemental analysis (%) calcd for $C_{77}H_{113}ClO_{28}P_2Pd$ (1690.53): C 54.71, H 6.74; found C 54.48, H 6.45; MS (FAB): *m/z* (%): 1688.6 (17) $[M]^+$, 1675.5 (10) $[M-CH_3]^+$, 1653.6 (15) $[M-Cl]^+$, 1638.6 (9) $[M-CH_3-Cl]^+$.

***trans*-*P*,*P*′-Chlorocarbonyl-{6^A,6^D-bis(diphenylphosphinyl)-6^A,6^D-dideoxy-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}rhodium(I) (5a)**: A solution of [{Rh(CO)$_2$Cl}$_2$] (0.013 g, 0.0334 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L1** (0.100 g, 0.0652 mmol) in CH_2Cl_2 (200 mL), under vigorous stirring. After 2 h the reaction mixture was concentrated to 5 mL and pentane (250 mL) was added to precipitate side products, which were filtered off over Celite. Evaporation of the solvent afforded **5a** as an orange-yellow powder (0.070 g, 64%). R_f (CH_2Cl_2/MeOH 94:6, *v*/*v*) = 0.31; m.p. 182 °C decomp; IR (KBr): $\tilde{\nu}=1975.5$ cm^{-1} (C=O); ^1H NMR (500 MHz, C_6D_6, 25 °C): δ (assignment by COSY) = 2.84, 3.65 (2m, 4H; H-6^{A,D}), 3.16 (s, 6H; OCH_3), 3.19 (d, 2H; H-2$^{B,E\text{ or }C,F}$), 3.20 (d, 2H; H-2^{A,D}), 3.21 (d, 2H; H-2$^{C,F\text{ or }B,E}$), 3.22 (s, 6H; OCH_3), 3.25 (s, 6H; OCH_3), 3.28, 4.40 (AB, $^2J=10.6$ Hz, 4H; H-6$^{C,F\text{ or }B,E}$), 3.32 (s, 6H; OCH_3), 3.33 (d, 2H; H-4^{A,D}), 3.39 (s, 6H; OCH_3), 3.44 (s, 6H; OCH_3), 3.61 (d, 2H; H-3$^{C,F\text{ or }B,E}$), 3.65, 4.33 (AB, $^2J=10.6$ Hz, 4H; H-6$^{B,E\text{ or }C,F}$), 3.80 (s, 6H; CH_3O-6), 3.87 (s, 6H; CH_3O-6), 4.08 (t, $^3J=8.8$ Hz, 2H; H-4$^{B,E\text{ or }C,F}$), 4.14 (t, $^3J=9.1$ Hz, 2H; H-3^{A,D}), 4.15 (t, $^3J=8.8$ Hz, 2H; H-4$^{C,F\text{ or }B,E}$), 4.47 (br d, $^3J=9.3$ Hz, 2H; H-5$^{C,F\text{ or }B,E}$), 4.55 (br d, $^3J=9.3$ Hz, 2H; H-5$^{B,E\text{ or }C,F}$), 5.11 (d, $^3J_{H\text{-}1,H\text{-}2}=2.6$ Hz, 2H; H-1^{A,D}), 5.19 (d, $^3J_{H\text{-}1,H\text{-}2}=2.9$ Hz, 2H; H-1$^{B,E\text{ or }C,F}$), 5.36 (d, $^3J_{H\text{-}1,H\text{-}2}=3.3$ Hz, 2H; H-1$^{C,F\text{ or }B,E}$), 5.59 (br t, $^3J=9.7$ Hz, 2H; H-5^{A,D}) 6.95–7.25 (12H; H_{meta}, H_{para}), 7.78–7.82 (4H; H_{ortho}), 8.17–8.21 ppm (4H; H_{ortho}); $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 25 °C): $\delta=35.83$ (virtual t, $^1J_{C,P}+{}^3J_{C,P}=22.4$ Hz; C-6^{A,D}), 57.25, 57.41 (CH_3O-6), 59.14, 59.30, 59.44 (CH_3O-2), 61.25, 61.72, 62.12 (CH_3O-3), 70.78 (C-4^{A,D}), 71.95, 72.32 (C-5^{B,C,E,F}), 72.12, 72.49 (C-6^{B,C,E,F}), 81.15, 81.63, 81.70 (×2), 81.88, 81.78, 82.84, 84.12 (C-2, C-3, C-4^{B,C,E,F}), 89.23 (virtual t, $^2J_{C,P}+{}^4J_{C,P'}=10.4$ Hz; C-5^{A,D}), 98.31, 98.81 (C-1^{B,C,E,F}), 101.37 (C-1^{A,D}), 127.97 (virtual t, $^3J_{C,P}+{}^5J_{C,P'}=9.6$ Hz; C_{meta}), 128.49 (virtual t, $^3J_{C,P}+{}^5J_{C,P}=9.6$ Hz; C_{meta}), 129.69 (s; C_{para}), 130.36 (s; C_{para}), 133.35 (virtual t, $^2J_{C,P}+{}^4J_{C,P'}=12.0$ Hz; C_{ortho}), 134.54 (virtual t, $^1J_{C,P}+{}^3J_{C,P'}=44.2$ Hz; C_{ipso}), 135.58 (virtual t, $^2J_{C,P}+{}^4J_{C,P'}=13.6$ Hz; C_{ortho}), 140.68 ppm (virtual t, $^1J_{C,P}+{}^3J_{C,P'}=42.6$ Hz; C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): $\delta=17.9$ ppm (d, $^1J_{Rh,P}=132$ Hz); elemental analysis (%) calcd for $C_{77}H_{110}ClO_{29}P_2Rh\cdot C_6H_6$ (1699.99+78.11): C 56.07, H 6.58; found: C 56.20, H 6.62; MS (FAB): *m/z* (%): 1679.4 (12) $[M-Cl+O]^+$, 1670.4 (5) $[M-CO]^+$, 1663.4 (3) $[M-Cl]^+$, 1635.5 (19) $[M-CO-Cl]^+$.

***trans*-*P*,*P*′-Hydridocarbonyl-{6^A,6^D-bis(diphenylphosphinyl)-6^A,6^D-dideoxy-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}rhodium(I) (6a)**: Solid $NaBH_4$ (0.030 g, 0.793 mmol) was added to a stirred solution of **5a** (0.032 g, 0.019 mmol) in EtOH (10 mL). The suspension gradually turned orange-brown. After stirring at room temperature for 45 min the mixture was evaporated to dryness. The residue was taken up in benzene (10 mL) and filtered through Celite. Evaporation to dryness yielded **6a** as an orange-brown powder (0.029 g, 93%). IR (KBr): $\tilde{\nu}=1978$ cm^{-1} (C=O); ^1H NMR (500 MHz, C_6D_6, 25 °C): δ (assignments by ROESY and COSY) = −4.96 (dt, $^1J_{H,Rh}=10.5$ Hz, $^2J_{H,P}=15.5$ Hz, 1H; Rh-H), 2.22, 4.00 (AB, $^2J_{AB}=11.0$ Hz, 4H; H-6^{B,E}), 2.73, 3.26 (br AB, $^2J_{AB}=15.3$ Hz, 4H; H-6^{A,D}), 2.81 (s, 6H; OCH_3), 3.04 (s, 6H; OCH_3), 3.12 (s, 6H; OCH_3), 3.13 (2dd, 4H; H-2$^{B,E\text{ and }C,F}$), 3.22 (s, 6H; OCH_3), 3.32 (s, 6H; OCH_3), 3.33 (dd, 2H; H-2^{A,D}), 3.34 (s, 6H; OCH_3), 3.40, 4.17 (2m, $^2J_{AB}=11.2$ Hz, $J=1.6$ Hz, 4H; H-6^{C,F}), 3.56 (dd, 2H; H-4^{A,D}), 3.64–3.74 (3 overlapping dd, 6H; H-3^{B,E,C,F}, H-5^{B,E}), 3.75 (s, 6H; CH_3O-6), 3.86 (s, 6H; CH_3O-6), 4.05 (2dd, 4H; H-4^{B,E,C,F}), 4.10 (dd, 2H; H-3^{A,D}), 4.14 (t, $^3J=9.1$ Hz, 2H; H-5^{C,F}), 4.29 (br d, $^3J=9.7$ Hz, 2H; H-4^{C,F}), 5.07 (br t, $J=11,0$ Hz, 2H; H-5^{A,D}), 5.10 (d, $^3J_{H\text{-}1,H\text{-}2}=2.6$ Hz, 2H; H-1^{C,F}), 5.18 (d, $^3J_{H\text{-}1,H\text{-}2}=2.6$ Hz, 2H; H-1^{A,D}), 5.30 (d, $^3J_{H\text{-}1,H\text{-}2}=3.7$ Hz, 2H; H-1^{B,E}), 6.94–7.18 (12H; H_{meta}, H_{para}), 7.87–7.91 (4H; H_{ortho}), 8.43–8.48 ppm (4H; H_{ortho}); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): $\delta=36.25$ (virtual t, $^1J_{C,P}+{}^3J_{C,P}=19.0$ Hz; C-6^{A,D}), 56.78, 56.88 (CH_3O-6), 58.29, 58.64, 59.11 (CH_3O-2), 61.01, 61.18, 61.98 (CH_3O-3), 70.6 (C-4^{A,D}), 70.84, 71.60, 71.69, 71.77 (C-5^{B,C,E,F} and C-6^{B,C,E,F}), 81.08, 81.40, 81.48, 81.65, 81.81, 82.41 (×2), 83.71 (C-2, C-3, C-4^{B,C,E,F}), 87.39 (virtual t, $^2J_{C,P}+{}^4J_{C,P}=11.2$ Hz; C-5^{A,D}), 98.44, 98.64 (C-1^{B,C,E,F}), 101.01 (C-1^{A,D}), 127.30–131.15 (C_{meta}, C_{para}), 134.27 (virtual t, $^2J_{C,P}+{}^4J_{C,P}=14.4$ Hz; C_{ortho}), 134.47 ppm (virtual t, $^2J_{C,P}+{}^4J_{C,P}=13.6$ Hz; C_{ortho}); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): $\delta=37.6$ ppm (d, $^1J_{Rh,P}=158$ Hz).

During the formation of **6a**, a transient intermediate with the following spectroscopic data was observed: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): $\delta=20.9$ ppm (d, $^1J_{Rh,P}=123$ Hz). Samples of complex **6a** contained variable amounts of benzene which could not be removed at room temperature. This led to unsatisfactory microanalytical data.

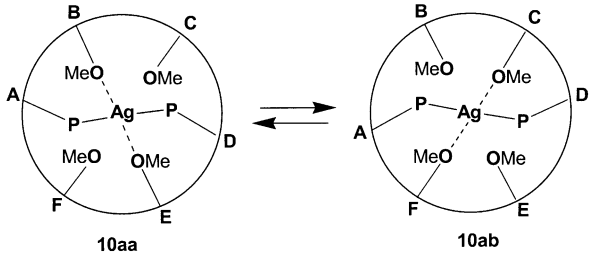
***trans*-*P*,*P*′-*cis*-Dichloro-*cis*-dicarbonyl-{6^A,6D-bis(diphenylphosphinyl)-6^A,6^D-dideoxy-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin}ruthenium(II) (7a)**: CO was bubbled through a solution of commercial trichloride (41.12% Ru, 0.018 g, ca. 0.0750 mmol) in 2-ethoxyethanol (50 mL), whereupon the solution was refluxed under a CO atmosphere until the colour changed to yellow. After cooling down to 90 °C, a solution of **L1** (0.115 g, 0.0755 mmol) in ethoxy-2-ethanol (10 mL) was added. The reaction mixture was stirred for 2 h at room temperature, then the solvent was evaporated to dryness. The greenish-yellow residue was taken up in CH_2Cl_2 (5 mL) and the resulting suspension was filtered through Celite. Addition of pentane (250 mL) to the filtrate caused some products to precipitate, which were then filtered off over Celite. Evaporation of pentane afforded a residue, which was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 94:6, *v*/*v*) to yield **7a** as a yellow powder (0.080 g, 61%). R_f (CH_2Cl_2/MeOH 94:6, *v*/*v*) = 0.31; m.p. 145–147 °C; IR (KBr): $\tilde{\nu}=1986, 2050$ cm^{-1} (C=O); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 2.54 (m, 2H; H-6a^{A,D}), 2.83 (s, 6H; CH_3O-6), 2.95 (dd, $^3J_{H\text{-}1,H\text{-}2}=2,7$ Hz, $^3J_{H\text{-}2,H\text{-}3}=10.0$ Hz, 2H; H-2^{A,D}), 3.06 (t, $^3J_{H\text{-}3,H\text{-}4}={}^3J_{H\text{-}4,H\text{-}5}=9.2$ Hz, 2H; H-4^{A,D}), 3.12 (dd, $^3J_{H\text{-}1,H\text{-}2}=2,9$ Hz, $^3J_{H\text{-}2,H\text{-}3}=9.6$ Hz, 2H; H-2$^{B,E\text{ or }C,F}$), 3.15 (dd, 2H; H-6a$^{C,F\text{ or }B,E}$), 3.17 (dd, 2H; H-2$^{C,F\text{ or }B,E}$), 3.36 (dd, $^2J_{H\text{-}6a,H\text{-}6b}=11.9$ Hz, $^3J_{H\text{-}5,H\text{-}6b}=1.5$ Hz, 2H; H-6b$^{C,F\text{ or }B,E}$), 3.39 (s, 6H; CH_3O-6), 3.43 (s, 6H; OCH_3), 3.47 (s, 6H; OCH_3), 3.50 (s, 6H; OCH_3), 3.60 (s, 6H; OCH_3), 3.65–3.75 (3 overlapping dd, 6H; H-6a$^{B,E\text{ or }C,F}$, H-3^{A,D}, H-4$^{B,E\text{ or }C,F}$), 3.66 (s, 6H; OCH_3), 3.69 (s, 6H; OCH_3), 3.75–3.82 (3 overlapping dd, 6H; H-3$^{B,E\text{ or }C,F}$, H-3$^{C,F\text{ or }B,E}$, H-4$^{C,F\text{ or }B,E}$), 3.93 (m, $^2J_{H\text{-}6b,H\text{-}6a}=11.5$ Hz, 2H; H-6b^{A,D}), 3.97 (dd, $^3J=10.8$ Hz, 2H; H-5$^{B,E\text{ or }C,F}$), 4.36 (dd, $^3J=9.5$ Hz, 2H; H-5$^{C,F\text{ or }B,E}$), 4.45 (d, $^3J_{H\text{-}1,H\text{-}2}=2.7$ Hz, 2H; H-1^{A,D}), 4.57

(br d, $J = 7.0$ Hz, 2H; H-6b$^{B,E\text{ or }C,F}$), 4.97 (br t, $^3J = 9.5$ Hz, 2H; H-5^{A,D}), 5.06 (d, $^3J = 2.9$ Hz, 2H; H-1$^{B,E\text{ or }C,F}$), 5.11 (d, $^3J_{H\text{-}1,H\text{-}2} = 3.1$ Hz, 2H; H-1$^{C,F\text{ or }B,E}$), 7.30–7.40 (12H; H_{meta}, H_{para}), 7.48–7.53 (4H; H_{ortho}), 7.89–7.95 ppm (4H; H_{ortho}); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta = 33.50$ (virtual t, $^1J_{C,P} + {}^3J_{C,P'} = 28.0$ Hz; C-6^{A,D}), 57.10, 58.15 (CH_3O-6), 58.61, 58.84, 59.07 (CH_3O-2), 61.20, 61.27, 61.43 (CH_3O-3), 70.58 (C-4^{A,D}), 71.03, 71.17 (C-6^{B,C,E,F}), 70.67, 71.39 (C-5^{B,C,E,F}), 78.93, 79.95, 80.80 (×2), 81.69, 81.98, 82.83, 83.72 (C-2, C-3, C-4^{B,C,E,F}), 92.21 (virtual t, $^2J_{C,P} + {}^4J_{C,P'} = 9.9$ Hz; C-5^{A,D}), 97.26, 99.32, 102.21 (C-1), 127.94 (virtual t, $^3J_{C,P} + {}^5J_{C,P'} = 11.5$ Hz; C_{meta}), 128.30 (virtual t, $^3J_{C,P} + {}^5J_{C,P'} = 8.2$ Hz; C_{meta}), 129.74 (s; C_{para}), 130.43 (s; C_{para}), 131.35 (virtual t, $^2J_{C,P} + {}^4J_{C,P'} = 9.8$ Hz; C_{ortho}), 132.79 (d, $^1J_{C,P} + {}^3J_{C,P'} = 42.8$ Hz; C_{ipso}), 134.76 (virtual t, $^2J_{C,P} + {}^4J_{C,P'} = 11.5$ Hz; C_{ortho}) 139.94 (virtual t, $^1J_{C,P} + {}^3J_{C,P'} = 46.2$ Hz; C_{ipso}), 193.66 ppm (virtual t, $^2J_{C,P} + {}^2J_{C,P'} = 23.0$ Hz; CO); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 12.4$ (s); elemental analysis (%) calcd for $C_{78}H_{110}Cl_2O_{30}P_2Ru \cdot 0.5\ CH_2Cl_2$ (1761.62+42.47): C 52.26, H 6.20; found: C 52.18, H 6.43; MS (FAB): *m/z* (%): 1763.4 (8) $[M+H]^+$, 1735.4 (30) $[M - CO+H]^+$, 1706.4 (20) $[M - 2CO]^+$, 1699.4 (35) $[M - Cl - CO]^+$.

Bis(acetonitrile){6^A,6^D-bis-(diphenylphosphinyl)-6^A,6^D-dideoxy-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 (8a): A solution of $AgBF_4$ (0.027 g, 0.139 mmol) in MeCN (50 mL) was added to a solution of **L1** (0.213 g, 0.139 mmol) in MeCN (200 mL) under vigorous stirring. After 15 min the reaction mixture was concentrated to 5 mL and Et_2O (300 mL) was added, affording a white precipitate which was filtered off (0.190 g). The NMR spectrum in $CDCl_3$ reveals the presence of a mixture of **8a**, **9a** and **10a** ($^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 7.7$ (2d, $^{107}J_{Ag,P} = 458$ Hz, $^{109}J_{Ag,P} = 529$ Hz; **8a**), 6.1 (2d, $^{107}J_{Ag,P} = 417$ Hz, $^{109}J_{Ag,P} = 480$ Hz; **9a**) and −3.5 (2d, $^{107}J_{Ag,P} = 503$ Hz, $^{109}J_{Ag,P} = 581$ Hz; **10a**)). When the spectrum was recorded in pure CD_3CN, only **8a** was detected. ^1H NMR (400 MHz, CD_3CN, 25 °C): $\delta = 2.52$ (d, 2H; $^2J = 10.6$ Hz; H-6b^{A,D}, tentative assignment), 2.78 (s, 6H; CH_3O-6), 2.83 (s, 6H; CH_3O-6), 3.43 (s, 6H; OCH_3), 3.44 (s, 6H; OCH_3), 3.49 (s, 6H; OCH_3), 3.56 (s, 6H; OCH_3), 3.57 (s, 6H; OCH_3), 3.60 (s, 6H; OCH_3), 2.84–3.69 (32H; H-2, H-3, H-4, H-5^{B,C,E,F}, H-6a, H-6b ^{B,C,E,F}), 4.44 (m, 2H; H-5^{A,D}), 4.79 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.6$ Hz, 2H; H-1), 4.95 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.2$ Hz, 2H; H-1), 5.14 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.2$ Hz, 2H; H-1), 7.35–7.80 ppm (20H; arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_3CN): $\delta = 31.02$ (virtual t, $^1J_{C,P} + {}^3J_{C,P'} = 18.7$ Hz, C-6^{A,D}), 58.39 (×2) (CH_3O-6), 59.01, 59.24 (×2) (CH_3O-2), 61.44, 61.54, 61.70 (CH_3O-3), 71.24, 71.67 (C-6^{B,C,E,F}), 72.42, 72.85 (C-5^{B,C,E,F}), 82.03 (×6), 82.55, 82.81, 83.53 (C-2, C-3, C-4), 88.12 (virtual t, $^2J_{C,P} + {}^4J_{C,P'} = 11.5$ Hz; C-5^{A,D}), 98.05, 100.35, 100.97 (C-1), 130.15 (virtual t, $^3J_{C,P} + {}^5J_{C,P'} = 9.8$ Hz; C_{meta}), 130.64 (virtual t, $^3J_{C,P} + {}^5J_{C,P} = 9.8$ Hz; C_{meta}), 132.24, 132.60 (s, C_{para}), 133.23–134.15 ppm (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): $\delta = 7.6$ ppm (2d, $^{107}J_{Ag,P} = 458$ Hz, $^{109}J_{Ag,P} = 529$ Hz); MS (ESI): *m/z* (%): 1741.3 (13) $[M - BF_4 + H_2O]^+$. As deduced from 2D NMR experiments, the Me signals of free and coordinated MeCN are overlapping (1.90–2.10 ppm).

{6^A,6^D-Bis(diphenylphosphinyl)-6^A,6^D-dideoxy-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): This complex was obtained by solvent removal in vacuo of the solution described above (**8a**). Before complete evaporation some drops of acetone were added (yield 0.180 g, 75%). R_f (CH_2Cl_2/MeOH 94:6, *v/v*) = 0.20; m.p. 151 °C decomp; ^1H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): $\delta = 3.11$ (br s, 6H; CH_3O-6), 3.18 (br s, 6H; CH_3O-6), 3.51 (s, 6H; OCH_3), 3.56 (s, 12H; OCH_3), 3.60 (s, 6H; OCH_3), 3.69 (s, 6H; OCH_3), 3.72 (s, 6H; OCH_3), 2.96–4.35 (36H; H-2, H-3, H-4, H-5, H-6), 4.99 (br, 2H; H-1), 5.35 (br, 2H; H-1), 5.50 (br, 2H; H-1), 7.40–7.70 ppm (20H; arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta = 28.50$ (C-6^{A,D}), 57.20, 57.40 (×2), 58.54, 59.89 (CH_3O-2, CH_3O-6), 61.66 (×3) (CH_3O-3), 67.56, 70.50, 70.79, 71.28 (C-5^{B,C,E,F}, C-6^{B,C,E,F}), 80.99 (×4), 82.14 (×5) (C-2, C-3, C-4), 85.82 (C-5^{A,D}), 99.39 (×3) (C-1), 129.35 (×2), 131.05, 131.48, 133.41, 134.33 ppm (arom. C); $^{31}P\{^1H\}$ (121.5 MHz, $C_2D_2Cl_4$, 25 °C): $\delta = 11.37$ (2d, $^{107}J_{Ag,P} = 488$ Hz, $^{109}J_{Ag,P} = 565$ Hz; **10aa**) and 11.60 ppm (2d, $^{107}J_{Ag,P} = 483$ Hz, $^{109}J_{Ag,P} = 559$ Hz; **10ab**); elemental analysis (%) calcd for $C_{76}H_{110}AgBF_4O_{28}P_2$ (1728.30): C 52.82, H 6.41; found: C 53.08, H 6.45; MS (FAB): *m/z* (%): 1657.4 (60) $[M - BF_4 + O]^+$, 1641.4 (100) $[M - BF_4]^+$.

10aa and **10ab** are two equilibrating isomers which both have C_2 symmetry on the NMR timescale. In each of these species two diametrically opposed methoxy groups bind the silver centre, but this exchange can only be evidenced at lower temperature.



Benzonitrile-{6^A,6^D-bis(diphenylphosphinyl)-6^A,6^D-dideoxy-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 (11a): This complex was formed by adding 2–3 equiv of PhCN to a solution of **10a** in $CDCl_3$. It was only characterised in solution. ^1H NMR (400 MHz, $CDCl_3/C_6H_5CN$, 25 °C): δ (assignment by COSY) = 2.28, 3.60 (AB, $^2J_{AB} = 10.2$ Hz, 4H; H-6$^{B,E\text{ or }C,F}$), 2.73 (s, 6H; OCH_3), 2.76, 3.30–3.35 (br AB (×2), 8H; H-6^{A,D}, H-6$^{C,F\text{ or }B,E}$) 2.93 (s, 6H; OCH_3), 2.95 (t, 2H; H-3$^{B,E\text{ or }C,F}$), 2.95 (t, 2H; H-3$^{C,F\text{ or }B,E}$), 3.00 (d, 2H; H-2$^{C,F\text{ or }B,E}$), 3.03 (s, 6H; OCH_3), 3.05 (d, 2H; H-5$^{C,F\text{ or }B,E}$), 3.05 (d, 2H; H-2$^{B,E\text{ or }C,F}$), 3.32 (s, 6H; OCH_3), 3.35 (d, 2H; H-2^{A,D}), 3.37 (s, 6H; OCH_3), 3.40 (d, 2H; H-5$^{B,E\text{ or }C,F}$), 3.50 (s, 6H; OCH_3), 3.50 (br, 2H; H-4^{A,D}), 3.52 (s, 6H; OCH_3), 3.55 (d, 2H; H-4$^{B,E\text{ or }C,F}$), 3.65 (d, 2H; H-4$^{C,F\text{ or }B,E}$) 3.70 (s, 6H; OCH_3), 3.75 (t, 2H; H-3^{A,D}), 4.70 (m, 2H; H-5^{A,D}), 4.84 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.2$ Hz, 2H; H-1$^{C,F\text{ or }B,E}$), 4.88 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.6$ Hz, 2H; H-1^{A,D}), 5.16 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.3$ Hz, 2H; H-1$^{B,E\text{ or }C,F}$), 7.35–7.90 ppm (20H; arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3/C_6H_5CN$): $\delta = 30.94$ (virtual t, $^1J_{C,P} + {}^3J_{C,P'} = 16.5$ Hz; C-6^{A,D}), 57.59, 58.18 (CH_3O-6), 58.90 (×2), 59.17 (CH_3O-2), 61.13 (×2), 61.69 (CH_3O-3), 70.08 (×2) (C-6^{B,C,E,F}), 71.30, 71.89 (C-5^{B,C,E,F}), 79.46, 80.74, 80.84, 80.95, 81.26, 81.36, 81.65, 82.18 (×2) (C-2, C-3, C-4), 86.90 (C-5^{A,D}), 98.31, 99.19, 100.60 (C-1), 112.24 (C_{ipso} nitrile), 118.80 (CN) (free nitrile at 118.53), 128.92–133.18 ppm (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3/C_6H_5CN$): $\delta = 8.7$ ppm (2d, $^{107}J_{Ag,P} = 458$ Hz, $^{109}J_{Ag,P} = 529$ Hz); MS (ESI): *m/z* (%): 1744.7 (22) $[M - BF_4]^+$.

6^A,6^C-Bis(diphenylphosphinyl)-6^A,6^C-dideoxy-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): A solution of *n*BuLi in hexane (1.6 M, 2.3 mL, 3.69 mmol) was added, at −78 °C, to a solution of Ph_2PH (0.683 g, 3.690 mmol) in Et_2O (20 mL). Upon warming the reaction mixture to room temperature, the solvent was removed in vacuo, affording a yellow residue which was subsequently dissolved in THF (20 mL). After cooling this red solution down to −78 °C, **1b** (1.000 g, 0.739 mmol) was added as a powder. After stirring the solution overnight at room temperature, THF was evaporated. Excess lithium salt was eliminated with MeOH (10 mL). After drying, the residue was treated with toluene (10 mL) and the resulting suspension filtered through Celite. The solution was evaporated to dryness and the remaining solid was treated with boiling hexane (50 mL). The resulting suspension was subsequently concentrated and cooled down to 0 °C, whereupon the hexane phase was discarded by decantation; this allowed the removal of residual Ph_2PH. This operation was repeated three times to afford **L2** as a white powder (0.930 g, 82%). R_f (CH_2Cl_2/MeOH 9:1, *v/v*) = 0.55; m.p. 102–104 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.76$ (s, 3H; CH_3O-6), 3.02 (s, 3H; CH_3O-6), 3.20 (s, 3H; CH_3O-6), 3.40 (s, 3H; CH_3O-6), 3.44 (s, 3H; CH_3O-2), 3.46 (s, 9H; CH_3O-2), 3.47 (s, 6H; CH_3O-2), 3.61 (s, 12H; CH_3O-3), 3.62 (s, 3H; CH_3O-3), 3.64 (s, 3H; CH_3O-3), 2.42–3.81 (34H; H-2, H-3, H-4, H-5^{B,D,E,F}, H-6), 4.12–4.28 (2 overlapping m, 2H; H-5^{A,C}), 4.84 (d, $^3J_{H\text{-}2,H\text{-}1} = 2.9$ Hz, 1H; H-1), 4.85 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.1$ Hz, 1H; H-1), 5.02–5.04 (3d, 3H; H-1), 5.06 (d, $^3J_{H\text{-}2,H\text{-}1} = 3.1$ Hz, 1H; H-1), 7.17–7.45 ppm (20H; arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta = 31.52$ (d, $J_{C,P} = 14.8$ Hz; C-6$^{A\text{ or }C}$), 31.81 (d, $J_{C,P} = 14.8$ Hz; C-6$^{C\text{ or }A}$), 57.66, 57.76, 57.86, 57.92, 58.12, 58.35, 58.77 (×3), 59.04 (CH_3O-2, CH_3O-6), 61.50, 61.63, 61.72 (×2), 61.79 (×2) (CH_3O-3), 69.66 (×2), 70.18 (×2) (C-6^{B,D,E,F}), 71.10, 71.20 (×2), 71.49 (C-5^{B,D,E,F}), 81.13 (×8), 81.26, 81.69, 81.95 (×2), 82.05, 82.11 (×2), 82.28, 82.34, 82.61 (C-2, C-3, C-4), 87.62 (2d, $^2J_{C,P} = 9.9$ Hz; C-5^{A,C}), 99.09, 99.26, 100.01(×2), 100.31, 100.50 (C-1), 128.05–128.43 (4d; C_{meta}), 128.69, 128.96, 130.60, 130.82 (4s; C_{para}), 132.66 (d, $^2J_{C,P} = 16.5$ Hz; C_{ortho}), 132.74 (d, $^2J_{C,P} = 18.1$ Hz; C_{ortho}) 133.22 (d, $^2J_{C,P} = 19.8$ Hz; C_{ortho}), 133.28 (d, $^2J_{C,P} = 19.8$ Hz; C_{ortho}), 139.66 (d, $J_{C,P} = 11.5$ Hz; C_{ipso}), 139.89 (d, $J_{C,P} = 11.5$ Hz; C_{ipso}), 140.30 (d, $J_{C,P} = 13.5$ Hz; C_{ipso}), 140.58 ppm (d, $J_{C,P} = 14.6$ Hz; C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = -22.7$ and −22.3 ppm (2s); elemental analysis

(%) calcd for $C_{76}H_{110}O_{28}P_2$ (1533.62): C 59.52, H 7.23 ; found: C 59.80, H 7.48.

***trans-P,P′*-Dichloro-{6^A,6^C-bis(diphenylphosphinyl)-6^A,6^C-dideoxy-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}palladium(II) (2b)**: A solution of $[PdCl_2(PhCN)_2]$ (0.025 g, 0.0652 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L2** (0.100 g, 0.0652 mmol) in CH_2Cl_2 (200 mL), under vigorous stirring. After 30 min the reaction mixture was concentrated to 5 mL and pentane (250 mL) was added to precipitate oligomeric material, which was then filtered off over Celite. Evaporation of pentane afforded a yellow powder, which was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 94:6, *v*/*v*), yielding pure **2a** (0.045 g, 41 %). R_f (CH_2Cl_2/MeOH 9:1, *v*/*v*) = 0.55; m.p. 178 °C decomp; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (br d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 12.7 Hz, 1H; H-6a^F), 2.54 (br d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 10.2 Hz, 1H; H-6a^D), 2.70 (m, 1H; H-6a^C), 2.83 (br d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 13.0 Hz, 1H; H-6b^F), 3.10 (s, 3H; CH_3O-6), 3.12 (s, 3H; CH_3O-6), 3.24 (s, 3H; CH_3O-6), 3.27 (dd, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, $^3J_{H\text{-}3,H\text{-}2}$ = 10.2 Hz, 1H; H-2^E), 3.43 (s, 3H; OCH_3), 3.44 (s, 3H; OCH_3), 3.45 (s, 3H; OCH_3), 3.47 (s, 3H; OCH_3), 3.48 (s, 3H; OCH_3), 3.50 (s, 3H; OCH_3), 3.54 (s, 3H; OCH_3), 3.59 (s, 3H; OCH_3), 3.60 (s, 3H; OCH_3), 3.63 (s, 3H; OCH_3), 3.67 (s, 3H; OCH_3), 3.69 (s, 3H; OCH_3), 3.77 (s, 3H; OCH_3), 2.94 – 3.79 (23H; H-2^{A,B,C,D,F}, H-3^{A,C,D,E,F}, H-4^{A,C,D,E,F}, H-5^{D,E,F}, H-6a^{A,E}, H-6b^{C,D,E}), 3.83 (dd, $^3J_{H\text{-}4,H\text{-}3}$ = 8.4 Hz, $^3J_{H\text{-}2,H\text{-}3}$ = 10.1 Hz, 1H; H-3^B), 3.99 (br d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 15.9 Hz, 1H; H-6b^A), 4.06 (dd, $^3J_{H\text{-}3,H\text{-}4}$ = 8.3 Hz, $^3J_{H\text{-}5,H\text{-}4}$ = 9.2 Hz, 1H; H-4^B), 4.36 (br d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.3 Hz, 1H; H-6a^B), 4.72 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.5 Hz, 1H; H-1^A), 4.83 (br d, ^3J = 8.8 Hz, 1H; H-5^B), 4.86 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1^C), 4.87 (br d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.3 Hz, 1H; H-6b^B), 4.90 (m, 1H; H-5^C), 4.97 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1^E), 4.98 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.8 Hz, 1H; H-1^F), 5.22 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 1H; H-1^D), 5.24 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1^B), 5.34 (m, 1H; H-5^A), 6.93 – 6.98 (m, 2H; arom. H), 7.18 – 7.54 (12H; arom. H), 7.80 – 7.86 (m, 2H; H_{ortho}), 7.93 – 8.00 (m, 2H; H_{ortho}), 8.16 – 8.22 ppm (m, 2H; H_{ortho}); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 29.67 (d; C-6$^{A\text{ or }C}$), 31.42 (d; C-6$^{C\text{ or }A}$), 57.46, 58.22, 58.32, 58.41, 58.74, 58.94, 59.13 (×3), 59.76 (CH_3O-6, CH_3O-2), 61.23 (×2), 61.33, 61.59, 61.79, 61.89 (CH_3O-3), 67.43, 70.71, 71.23, 72.38 (C-5^{B,C,E,F}), 68.77, 69.95, 70.61, 72.05 (C-6^{B,C,E,F}), 80.00, 80.10 (×2), 80.18, 80.38, 80.64, 80.74, 80.80, 81.10, 81.15, 81.59 (×2), 81.75, 81.98, 82.28, 82.44, 83.03, 83.13 (C-2, C-3, C-4), 89.29 (virtual t, C-5$^{A\text{ or }C}$), 90.60 (virtual t, $^2J_{C,P}$ + $^4J_{C,P'}$ = 11.5 Hz; C-5$^{C\text{ or }A}$), 97.23, 98.31, 98.63, 100.01, 101.03 (×2) (C-1), 127.15 (virtual t, $^3J_{C,P}$ + $^5J_{C,P'}$ = 9.8 Hz; C_{meta}), 127.87 (virtual t, $^3J_{C,P}$ + $^5J_{C,P'}$ = 10.5 Hz; C_{meta}), 128.24 (virtual t, $^3J_{C,P}$ + $^5J_{C,P'}$ = 10.5 Hz; C_{meta}), 128.56 (virtual t, $^3J_{C,P}$ + $^5J_{C,P'}$ = 9.8 Hz; C_{meta}), 129.97 (s; C_{para}), 130.46 (s; C_{para}), 130.89 (s; C_{para}), 131.28 (s; C_{para}), 131.97 (virtual t, $^2J_{C,P}$ + $^4J_{C,P'}$ = 13.2 Hz; C_{ortho}), 133.64 (virtual t, $^2J_{C,P}$ + $^4J_{C,P'}$ = 13.2 Hz; C_{ortho}), 134.99 (virtual t, $^2J_{C,P}$ + $^4J_{C,P'}$ = 11.5 Hz; C_{ortho}), 136.92 ppm (virtual t, $^2J_{C,P}$ + $^4J_{C,P'}$ = 14.6 Hz; C_{ortho}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 9.9 ppm (s); elemental analysis (%) calcd for $C_{76}H_{110}Cl_2O_{28}P_2Pd$ (1710.95): C 53.35, H 6.48; found: C 53.23, H 6.55; MS (FAB): *m*/*z* (%): 1710.4 (100) $[M]^+$, 1675.4 (80) $[M-Cl]^+$, 1638.4 (42) $[M-2Cl]^+$.

By recording the ^{31}P NMR spectrum in C_6D_6, the signal splits into two peaks, one at 10.3, the other at 10.5 ppm, which probably are part of an AB system with a very strong roof effect.

***trans-P,P′*-Dichloro-{6^A,6^C-bis(diphenylphosphinyl)-6^A,6^C-dideoxy-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}platinum(II) (3b)**: A solution of $[PtCl_2(PhCN)_2]$ (0.037 g, 0.0783 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L2** (0.120 g, 0.0783 mmol) in CH_2Cl_2 (200 mL), under vigorous stirring. After 30 min the reaction mixture was concentrated to 5 mL and pentane (250 mL) was added to precipitate some oligomeric compounds, which were then filtered off over Celite. Evaporation of pentane afforded a pale yellow powder, which was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 94:6, *v*/*v*), yielding pure **3b** (0.053 g, 38 %). R_f (CH_2Cl_2/MeOH 9:1, *v*/*v*) = 0.55; m.p. 170 – 172 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (assignment by TOCSY and ROESY) = 2.34 (br d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 12.8 Hz, 1H; H-6a^F), 2.46 (br d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 10.8 Hz, 1H; H-6a^D), 2.65 (m, 1H; H-6a^C), 2.77 (dd, $^3J_{H\text{-}5,H\text{-}6a}$ = 1.8 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 12.8 Hz, 1H; H-6b^F), 2.95 – 3.04 (4 overlapping signals, 4H; H-2^{A,C,F}, H-6a^A), 3.05 – 3.11 (3 overlapping signals, 3H; H-6b^C, H-4^A, H-2^D), 3.11 (s, 3H; CH_3O-6), 3.12 (s, 3H; CH_3O-6), 3.15 (dd, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, $^3J_{H\text{-}3,H\text{-}2}$ = 9.7 Hz, 1H; H-2^E), 3.23 (s, 3H; CH_3O-6), 3.26 (dd, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, $^3J_{H\text{-}3,H\text{-}2}$ = 10.1 Hz, 1H; H-2^B), 3.40 (dd, 1H; H-5^F), 3.42 (s, 3H; OCH_3), 3.43 (s, 3H; OCH_3), 3.44 (dd, 1H; H-4^C), 3.45 (s, 3H; OCH_3), 3.47 (s, 3H; OCH_3), 3.48 (s, 3H; OCH_3), 3.51 (s, 3H; OCH_3), 3.54 (s, 3H; OCH_3), 3.55 (2 overlapping signals, 2H; H-3^E, H-4^F), 3.58 – 3.67 (5 overlapping signals, 5H; H-3^{C,D,F}, H-5^D, H-6b^D), 3.59 (s, 3H; OCH_3), 3.60 (s, 3H; OCH_3), 3.64 (s, 3H; OCH_3), 3.67 (s, 3H; OCH_3), 3.68 (s, 3H; OCH_3), 3.69 – 3.77 (3 overlapping signals, 3H; H-3^A, H-4^{D,E}), 3.78 (s, 3H; OCH_3), 3.83 (dd, $^3J_{H\text{-}4,H\text{-}3}$ = 8.5 Hz, $^3J_{H\text{-}2,H\text{-}3}$ = 10.1 Hz, 1H; H-3^B), 3.99 (dd, $^3J_{H\text{-}5,H\text{-}6a}$ = 6.7 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 15.1 Hz, 1H; H-6b^A), 4.06 (dd, $^3J_{H\text{-}3,H\text{-}4}$ = 8.5 Hz, $^3J_{H\text{-}5,H\text{-}4}$ = 9.2 Hz, 1H; H-4^B), 4.23 (dd, $^3J_{H\text{-}5,H\text{-}6a}$ = 1.2 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 12.0 Hz, 1H; H-6a^B), 4.68 (dd, $^3J_{H\text{-}5,H\text{-}6b}$ = 1.5 Hz, $^2J_{H\text{-}6a,H\text{-}6b}$ = 12.0 Hz, 1H; H-6b^B), 4.71 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.5 Hz, 1H; H-1^A), 4.79 (br d, ^3J = 9.3 Hz, 1H; H-5^B), 4.88 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 1H; H-1^C), 4.89 (dt, ^3J = 5.8 Hz, ^3J = 9.3 Hz, 1H; H-5^C), 4.97 (2d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 2H; H-1^{E,F}), 5.03 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, 1H; H-1^D), 5.23 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1^B), 5.28 (dt, ^3J = 6.8 Hz, ^3J = 9.2 Hz, 1H; H-5^A), 6.96 (br t, J = 8.2 Hz, 2H; arom H), 7.21 – 7.51 (12H; arom. H), 7.78 (br t, J = 8.5 Hz, 2H; H_{ortho}), 8.00 (m, 2H; H_{ortho}), 8.25 ppm (br t, J = 7.7 Hz, 2H; H_{ortho}); H-5^E and H-6^E not assigned; ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 28.50 (d; C-6$^{A\text{ or }C}$), 31.50 (d; C-6$^{C\text{ or }A}$), 57.40, 58.22, 58.28, 58.38, 58.68, 58.91, 59.10 (×3), 59.72 (CH_3O-6, CH_3O-2), 61.10, 61.20, 61.30, 61.50, 61.69, 61.82 (CH_3O-3), 67.33, 70.35, 71.20, 72.31 (C-5^{B,C,E,F}), 68.71, 69.66, 70.61, 72.61 (C-6^{B,C,E,F}), 79.95 (×3), 80.08, 80.31, 80.54, 80.70 (×2), 81.00, 81.10, 81.59 (×2), 81.72, 81.92, 82.18, 82.41, 83.03, 83.16 (C-2, C-3, C-4), 89.60 (d, C-5$^{A\text{ or }C}$), 90.60 (d, C-5$^{C\text{ or }A}$), 97.13, 98.21, 98.41, 99.88, 100.96, 101.13 (C-1), 126.80 – 137.00 ppm (arom. C); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 2.1, 7.8 ppm (2d with Pt satellites, $^1J_{Pt,P}$ = 2620 Hz, $^1J_{Pt,P'}$ = 2577 Hz, $^2J_{P,P'}$ = 509 Hz; P, P′); elemental analysis (%) calcd for $C_{76}H_{110}Cl_2O_{28}P_2Pt \cdot 0.5\ C_6H_6$ (1799.61 + 39.06): C 51.61, H 6.19; found: C 51.64, H 6.08; MS (FAB): *m*/*z* (%): 1799.5 (2) $[M+H]^+$, 1763.5 (3) $[M-Cl]^+$, 1727.6 (2.5) $[M-2Cl]^+$.

***trans-P,P′*-Chloromethyl-{6^A,6^C-bis(diphenylphosphinyl)-6^A,6^C-dideoxy-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}palladium(II) (4b)**: A solution of [PdMeCl(cod)] (0.020 g, 0.0755 mmol) in CH_2Cl_2 (30 mL) was added to a solution of **L2** (0.116 g, 0.0755 mmol) in CH_2Cl_2 (200 mL), under vigorous stirring. After 15 min the reaction mixture was concentrated to 5 mL and pentane (250 mL) was added to precipitate side products, which were then filtered off over Celite. Evaporation of pentane afforded **4b** as a yellow powder (0.090 g, 71 %). R_f (CH_2Cl_2/MeOH 9:1, *v*/*v*) = 0.50; m.p. 165 °C decomp; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ (assignment by COSY) = −0.04 (t, $^3J_{H,P}$ = 6.4 Hz, 3H; $PdCH_3$), 2.65, 3.34 (AB, $^2J_{AB}$ = 13.3 Hz, 2H; H-6), 2.79, 4.14 (AB, $^2J_{AB}$ = 10.6 Hz, 1H; H-6), 2.87, 3.92 (AB, 2H; H-6$^{A\text{ or }C}$), 2.90, 3.14 (AB, 2H; H-6$^{C\text{ or }A}$), 3.05 (dd, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, $^3J_{H\text{-}3,H\text{-}2}$ = 9.8 Hz, 1H; H-2), 3.26 (s, 15H; OCH_3), 3.27 (s, 3H; OCH_3), 3.29 (s, 3H; OCH_3), 3.30 (s, 3H; OCH_3), 3.32 (s, 3H; OCH_3), 3.42 (s, 3H; OCH_3), 3.61 (s, 3H; OCH_3), 3.63 (s, 3H; OCH_3), 3.64 (s, 3H; OCH_3), 3.68 (s, 3H; OCH_3), 3.69 (s, 3H; OCH_3), 3.85 (s, 3H; OCH_3), 3.88 (s, 3H; OCH_3), 3.10 – 4.23 (23H; H-2, H-3, H-4, H-5, H-6), 4.38, 5.09 (AB, ^3J = 8.4 Hz, $^2J_{AB}$ = 9.3 Hz,1H; H-6), 5.03 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.5 Hz, 1H; H-1), 5.05 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1), 5.05 (m, 1H; H-5, tentative assignment), 5.07 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.5 Hz, 1H; H-1), (br d, 1H; H-6), 5.24 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1), 5.25 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H; H-1), 5.26 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 1H; H-1), 5.43 (dt, $^3J_{H\text{-}4,H\text{-}5}$ = 5.3 Hz, $^3J_{H\text{-}6,H\text{-}5}$ = 9.4 Hz, 1H; H-5$^{A\text{ or }C}$), 5.94 (br dt, $^3J_{H\text{-}4,H\text{-}5}$ = 7.2 Hz, $^3J_{H\text{-}6,H\text{-}5}$ = 8.9 Hz, 1H; H-5$^{C\text{ or }A}$), 6.90 – 7.10 (8H; arom. H), 7.26 – 7.47 (6H; arom H), 7.69 (br t, J = 8.7 Hz, 2H; H_{ortho}), 8.34 (br t, J = 8.6 Hz, 2H; H_{ortho}), 8.41 ppm (br t, J = 9.0 Hz, 2H; H_{ortho}); ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6): δ = 7.70 ($PdCH_3$), 35.13 (d, $J_{C,P}$ = 26.4 Hz; C-6$^{A\text{ or }C}$), 35.13 (d, $J_{C,P}$ = 19.8 Hz; C-6$^{C\text{ or }A}$), 57.13, 57.36, 57.69, 57.95, 58.28, 58.51, 58.64, 59.03, 59.19, 60.05 (CH_3O-6, CH_3O-2), 61.29, 61.46 (×2), 61.65 (×2), 61.85 (CH_3O-3), 68.77, 71.26, 72.11, 72.97 (C-5^{B,C,E,F}), 70.14, 70.64, 71.98, 73.85 (C-6^{B,C,E,F}), 80.60 (×4), 81.12, 81.22, 81.35, 81.58, 81.85, 81.98, 82.17, 82.96, 83.12, 83.45 (×3), 83.88, 84.01 (C-2, C-3, C-4), 91.00 (d, $J_{C,P}$ = 6.6 Hz; C-5$^{A\text{ or }C}$), 91.34 (d, $J_{C,P}$ = 9.9 Hz; C-5$^{C\text{ or }A}$), 97.65, 98.96, 99.06, 100.37, 101.45, 101.55 (C-1), 127.77 – 137.83 ppm (arom. C); ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 14.1, 20.3 ppm (2d, $^2J_{P,P'}$ = 443 Hz; P, P′); elemental analysis (%) calcd for $C_{77}H_{113}ClO_{28}P_2Pd$ (1690.53): C 54.71 H 6.74; found: C 54.32, H 6.45; MS (FAB): *m*/*z* (%): 1688.6 (7) $[M]^+$, 1675.6 (15) $[M-CH_3]^+$, 1653.7 (15) $[M-Cl]^+$, 1638.6 (9) $[M-CH_3-Cl]^+$.

***trans-P,P′*-Chlorocarbonyl-{6^A,6^C-bis(diphenylphosphinyl)-6^A,6^C-dideoxy-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}rhodium(I) (5b)**: A solution of $[\{Rh(CO)_2Cl\}_2]$ (0.016 g, 0.0408 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L2** (0.125 g, 0.0815 mmol) in CH_2Cl_2 (200 mL), under vigorous stirring. After 2 h the reaction mixture was concentrated to 5 mL and pentane (250 mL) was added to precipitate some unidentified products, which were then filtered off over Celite. Solvent evaporation afforded **5b** as a yellow powder

(0.100 g, 72%). R_f (CH_2Cl_2/MeOH 9:1, *v*/*v*) = 0.55; m.p. 175 °C decomp; IR (KBr): $\tilde{\nu}$ = 1979.9 cm^{-1} (C=O); ^1H NMR (200 MHz, C_6D_6): δ = 2.41 (d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 10.5 Hz, 2H; H-6a), 2.64 (d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 13.2 Hz, 1H; H-6a), 2.76–3.01 (2 overlapping m, 2H; H-6a^{A,C}), 3.03 (dd, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, $^3J_{H\text{-}3,H\text{-}2}$ = 9.9 Hz, 1H; H-2), 3.22 (s, 3H; OCH_3), 3.24 (s, 9H; OCH_3), 3.25 (s, 3H; OCH_3), 3.29 (s, 3H; OCH_3), 3.30 (s, 3H; OCH_3), 3.30 (s, 3H; OCH_3), 3.41 (s, 3H; OCH_3), 3.55 (s, 3H; OCH_3), 3.63 (s, 3H; OCH_3), 3.66 (s, 3H; OCH_3), 3.69 (s, 3H; OCH_3), 3.75 (s, 3H; OCH_3), 3.82 (s, 3H; OCH_3), 3.88 (s, 3H; OCH_3), 3.09–4.21 (24H; H-2, H-3, H-4, H-5, H-6), 4.45 (t, $^2J_{H\text{-}6b,H\text{-}6a}$ = 8.9 Hz,1H; H-6a), 4.99–5.07 (2 overlapping signals, 2H; H-5, H-6b, tentative assignment), 5.00 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1), 5.05 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, 1H; H-1), 5.06 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.8 Hz, 1H; H-1), (br d, 1H; H-6), 5.17 (m, 1H; H-5$^{A\text{ or }C}$), 5.23 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 1H; H-1), 5.24 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 1H; H-1), 5.32 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H; H-1), 5.58 (br q, ^3J = 8.3 Hz, 1H; H-5$^{C\text{ or }A}$), 6.88–7.43 (12H; H_{ortho}, H_{meta}), 7.80–7.86 (m, 2H; H_{ortho}), 7.93–8.02 (br m, 2H; H_{ortho}), 8.32–8.38 (m, 2H; H_{ortho}), 8.52–8.58 ppm (br m, 2H; H_{ortho}); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6): δ = 34.53 (d, $J_{C,P}$ = 18.1 Hz; C-6$^{A\text{ or }C}$), 35.81 (d, $J_{C,P}$ = 11.5 Hz; C-6$^{C\text{ or }A}$), 57.06, 57.49, 57.72, 58.15, 58.31, 58.41, 58.67, 58.83, 59.23, 60.05 (CH_3O-6, CH_3O-2), 61.29, 61.39, 61.49, 61.59, 61.69, 61.88 (CH_3O-3), 68.96, 71.26, 72.18, 73.00 (C-5^{B,C,E,F}), 69.95, 70.14, 71.98, 74.24 (C-6^{B,C,E,F}), 80.53 (×3), 80.70, 81.12 (×2), 81.22, 81.45, 81.65, 81.91, 82.17, 82.96 (×2), 83.03, 83.39, 83.45, 83.81, 84.04 (C-2, C-3, C-4), 90.96 (d, $J_{C,P}$ = 9.9 Hz; C-5$^{A\text{ or }C}$), 91.17 (d, $J_{C,P}$ = 11.5 Hz; C-5$^{C\text{ or }A}$), 97.91, 98.86 (×2), 100.40, 101.58, 101.65 (C-1), 127.67–137.87 (arom. C), 138.80 (d, $J_{C,P}$ = 41.2 Hz; C_{ipso}), 143.14 ppm (d, $J_{C,P}$ = 42.9 Hz; C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 8.4, 20.3 ppm (2dd, $^1J_{Rh,P}$ = $^1J_{Rh,P'}$ = 126 Hz, $^2J_{P,P'}$ = 370 Hz; P, P′); elemental analysis (%) calcd for $C_{77}H_{110}ClO_{29}P_2Rh$ (1699.99): C 54.40 H 6.52; found: C 54.32, H 6.45; MS (FAB): *m*/*z* (%): 1700.7 (3) $[M+H]^+$, 1670.7 (32) $[M-CO]^+$, 1635.8 (5) $[M-CO-Cl]^+$.

***trans*-*P*,*P*′-Hydridocarbonyl-{6^A,6^C-bis(diphenylphosphinyl)-6^A,6^C-dideoxy-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}rhodium(I) (6b)**: Solid $NaBH_4$ (0.040 g, 1.0573 mmol) was added to a stirred solution of **5b** (0.065 g, 0.0382 mmol) in EtOH (10 mL). The resulting suspension gradually turned orange-brown. After stirring for 1 h, the mixture was evaporated to dryness. The residue was taken up in toluene (10 mL) and filtered through Celite. Evaporation to dryness of the solution yielded **6b** (orange brown) along with small amounts of an isomeric compound (0.060 g, 94%). IR (nujol): $\tilde{\nu}$ = 1969.0 cm^{-1} (C=O); ^1H NMR (500 MHz, C_6D_6, 25 °C): δ (assignment by COSY) = -5.48 (dt, $^1J_{H,Rh}$ = 10.2 Hz, $^2J_{H,P}$ = 17.9 Hz, 1H; Rh-H), 2.53, 4.20 (AB, ^3J = 2.5 Hz, $^2J_{AB}$ = 11.2 Hz, 2H; H-6), 2.67 (s, 3H; CH_3O-6), 2.94, 3.31 (AB, $^2J_{AB}$ = 12.1 Hz, 2H; H-6), 3.11 (dd, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, $^2J_{H\text{-}3,H\text{-}2}$ = 9.8 Hz, 1H; H-2), 3.18 (s, 3H; OCH_3), 3.18 (s, 3H; OCH_3), 3.20 (s, 3H; OCH_3), 3.23 (s, 3H; OCH_3), 3.29 (s, 6H; OCH_3), 3.36 (s, 3H; OCH_3), 3.37 (s, 3H; OCH_3), 3.62 (s, 3H; OCH_3), 3.67 (s, 3H; OCH_3), 3.69 (s, 3H; OCH_3), 3.70 (s, 3H; OCH_3), 3.70 (s, 3H; OCH_3), 3.75 (s, 3H; OCH_3), 3.81 (s, 3H; OCH_3), 4.15, 4.80 (br AB, $^2J_{AB}$ = 9.5 Hz, 2H; H-6), 3.18–4.29 (27H; H-2, H-3, H-4, H-5^{B,D,E,F}, H-6), 4.95, 4.97 (2 overlapping m, 2H; H-5^{A,C}), 5.01 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.1 Hz, 1H; H-1), 5.10 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.6 Hz, 1H; H-1), 5.13 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 1H; H-1), 5.14 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 1H; H-1), 5.19 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, 1H; H-1), 5.25 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1), 6.94–7.39 (12H; arom. H), 7.75–7.78 (m, 2H; H_{ortho}), 8.05–8.11 (4H; H_{ortho}), 8.36–8.40 ppm (m, 2H; H_{ortho}); NMR $^{31}P\{^1H\}$ (121.5 MHz, C_6D_6): δ = 33.6, 39.24 ppm (2dd, $^1J_{Rh,P}$ = $^1J_{Rh,P'}$ = 158 Hz, $^2J_{P,P'}$ = 280 Hz, P, P′).

In the course of reaction, a transient intermediate with the following characterising data was observed: NMR $^{31}P\{^1H\}$ (121.5 MHz, C_6D_6): δ = 15.1, 24.9 ppm (2dd, $^1J_{Rh,P}$ = $^1J_{Rh,P'}$ = 118 Hz, $^2J_{P,P'}$ = 326 Hz, P, P′). Samples of complex **6b** contained variable amounts of benzene which could not be removed at room temperature. This led to unsatisfactory microanalytical data.

Acetonitrile-{6^A,6^C-bis(diphenylphosphinyl)-6^A,6^C-dideoxy-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 (9b): Addition of a large excess of MeCN (ca. 30 equiv) to a solution of **10b** (see below) in $CDCl_3$ afforded **9b** quantitatively. It is worth mentioning that whatever the amount of MeCN in excess used in this reaction, only one new species was detected. Solvent evaporation regenerated **10b**. ^1H NMR (300 MHz, $CDCl_3/CD_3CN$): δ = 2.13 (d, ^2J = 10.9 Hz, 1H; H-6), 2.17 (s, 3H; CH_3O-6), 2.44 (dd, ^3J = 3.0 Hz, ^2J = 11.4 Hz, 1H; H-6), 2.73 (d, ^2J = 10.6 Hz, 1H; H-6), 2.91 (s, 3H; CH_3O-6), 2.98 (s, 3H; CH_3O-6), 3.38 (s, 6H; OCH_3), 3.42 (s, 3H; OCH_3), 3.42 (s, 3H; OCH_3), 3.43 (s, 3H; OCH_3), 3.44 (s, 3H; OCH_3), 3.49 (s, 3H; OCH_3), 3.50 (s, 3H; OCH_3), 3.52 (s, 3H; OCH_3), 3.53 (s, 3H; OCH_3), 3.54 (s, 3H; OCH_3), 3.54 (s, 3H; OCH_3), 3.55 (s, 3H; OCH_3), 2.82–3.73 (31H; H-2, H-3, H-4, H-5^{B,D,E,F}, H-6), 4.29–4.39 (2 overlapping m, 2H; H-5^{A,C}), 4.54 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.2 Hz, 1H; H-1), 4.67 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.7 Hz, 1H; H-1), 4.92 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 1H; H-1), 5.01 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.5 Hz, 1H; H-1), 5.04 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.5 Hz, 1H; H-1), 5.12 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1), 7.08–7.64 ppm (m, 20H; arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_3CN): δ = 30.10 (d, $^1J_{C,P}$ + $^3J_{C,P'}$ = 19.8 Hz; C-6$^{A\text{ or }C}$), 30.98 (d, $^1J_{C,P}$ + $^3J_{C,P'}$ = 19.8 Hz; C-6$^{C\text{ or }A}$), 57.75, 58.21 (×2), 58.34, 58.67, 58.84, 59.20 (×2), 59.75, 60.21 (CH_3O-6, CH_3O-2), 61.26 (×2), 61.33, 61.85 (×2), 62.15 (CH_3O-3), 70.37, 71.39 (×2), 72.83 (C-6^{B,D,E,F}), 71.82, 72.44, 72.57, 73.46 (C-5^{B,C,E,F}), 78.34, 80.73, 80.93, 81.81, 82.04 (×4), 82.17 (×3), 82.31, 82.63, 82.70, 82.80, 82.96, 83.06, 84.11 (C-2, C-3, C-4), 88.72 (d, $^2J_{C,P}$ + $^4J_{C,P'}$ = 10.7 Hz; C-5$^{A\text{ or }C}$), 88.92 (d, $^2J_{C,P}$ + $^4J_{C,P'}$ = 10.7 Hz; C-5$^{C\text{ or }A}$), 97.38, 98.76, 100.17, 100.30, 100.86, 101.25 (C-1), 129.67–135.15 ppm (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3/CD_3CN$): δ = 5.1, 7.8 ppm (ABX, $^{107}J_{Ag,P}$ = 475 Hz, $^{109}J_{Ag,P}$ = 549 Hz, $^{107}J_{Ag,P'}$ = 470 Hz, $^{109}J_{Ag,P'}$ = 544 Hz, $^2J_{P,P'}$ = 137 Hz; P, P′).

{6^A,6^C-Bis(diphenylphosphinyl)-6^A,6^C-dideoxy-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 $AgBF_4$ (0.020 g, 0.103 mmol) in THF (50 mL) was added to a solution of **L1** (0.157 g, 0.103 mmol) in CH_2Cl_2 (200 mL) under vigorous stirring. After 15 min the reaction mixture was concentrated to 5 mL and Et_2O (250 mL) was added, affording **10b** as a white precipitate, which was filtered off (0.080 g, 46%). R_f (CH_2Cl_2/MeOH 9:1, *v*/*v*) = 0.40; m.p. 125 °C decomp; ^1H NMR (300 MHz, $CDCl_3$): δ (assignment by COSY) = 2.09, 3.67 (AB, $^2J_{AB}$ = 10.0 Hz, 2H; H-6), 2.10 (s, 3H; CH_3O-6), 2.75, 2.93 (AB, $^2J_{AB}$ = 11.5 Hz, 2H; H-6), 2.81, 3.40 (AB, $^2J_{AB}$ = 10.9 Hz, 2H; H-6), 2.86 (s, 3H; CH_3O-6), 3.01 (s, 3H; CH_3O-6), 3.43 (s, 3H; OCH_3), 3.45 (s, 6H; OCH_3), 3.46 (s, 3H; OCH_3), 3.47 (s, 3H; OCH_3), 3.48 (s, 3H; OCH_3), 3.57 (s, 3H; OCH_3), 3.58, 4.55 (AB, $^2J_{AB}$ = 9.0 Hz, 2H; H-6), 3.59 (s, 3H; OCH_3), 3.60 (s, 3H; OCH_3), 3.61 (s, 3H; OCH_3), 3.66 (s, 3H; OCH_3), 3.68 (s, 3H; OCH_3), 3.75 (s, 3H; OCH_3), 2.73–3.87 (23H; H-2, H-3, H-4, H-5, H-6), 4.30 (2br d, ^3J = 8.8 Hz, 2H; H-5), 4.37 (br d, ^3J = 9.6 Hz, 1H; H-5), 4.58 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H; H-1), 4.72 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.4 Hz, 1H; H-1), 4.83–4.94 (2 overlapping m, 2H; H-5^{A,C}, tentative assignment), 4.95 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1), 4.99 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H; H-1), 5.03 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1), 5.10 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1), 7.23–7.55 (18H; arom. H), 7.82–7.89 ppm (m, 2H; H_{ortho}); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 30.45 (d, $J_{C,P}$ = 16.5 Hz; C-6$^{A\text{ or }C}$), 32.09 (d, $J_{C,P}$ = 16.5 Hz; C-6$^{C\text{ or }A}$), 57.23, 57.79 (×2), 58.05, 58.18 (×2), 58.32, 58.61, 59.20, 59.26 (CH_3O-6, CH_3O-2), 61.17 (×2), 61.50, 61.76, 62.02, 62.15 (CH_3O-3), 69.79, 70.05, 70.19 (×2), 70.40, 70.51 (×2), 71.26 (C-6^{B,D,E,F}, C-5^{B,C,E,F}), 79.75, 79.95, 80.11, 80.64, 80.70, 81.00 (×3), 81.45, 81.52 (×3), 81.88, 82.31, 82.74, 82.90 (×2), 83.00 (C-2, C-3, C-4), 89.54 (d, $J_{C,P}$ = 11.5 Hz; C-5$^{A\text{ or }C}$), 90.85 (d, $J_{C,P}$ = 11.5 Hz; C-5$^{C\text{ or }A}$), 98.14, 99.13 (×2), 99.95, 101.00, 101.22 (C-1), 128.50–135.09 ppm (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 3.7, 8.3 ppm (ABX, $^{107}J_{Ag,P}$ = 478 Hz, $^{109}J_{Ag,P}$ = 556 Hz, $^{107}J_{Ag,P'}$ = 480 Hz, $^{109}J_{Ag,P'}$ = 558 Hz, $^2J_{P,P'}$ = 147 Hz; P, P′); elemental analysis (%) calcd for $C_{76}H_{110}AgBF_4O_{28}P_2$ (1728.30): C 52.82, H 6.41; found: C 52.53, H 6.30; MS (FAB): *m*/*z* (%): 1657.5 (37) $[M-BF_4+O]^+$, 1641.5 (100) $[M-BF_4]^+$.

Benzonitrile-{6^A,6^C-bis(diphenylphosphinyl)-6^A,6^C-dideoxy-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 (11b): Complex **11b** was obtained after addition of an excess of PhCN (ca. 15 equiv) to a solution of **10b** in $CDCl_3$. Note that whatever the amount of PhCN in excess used, only one new species was detected. Solvent evaporation regenerated **10b**. ^1H NMR (300 MHz, $CDCl_3/C_6H_5CN$): δ = 2.13 (d, ^2J = 8.8 Hz, 1H; H-6), 2.17 (s, 3H; CH_3O-6), 2.91 (s, 3H; CH_3O-6), 3.01 (s, 3H; CH_3O-6), 3.40 (s, 6H; OCH_3), 3.45 (s, 12H; OCH_3), 3.47 (s, 3H; OCH_3), 3.49 (s, 3H; OCH_3), 3.55 (s, 3H; OCH_3), 3.56 (s, 6H; OCH_3), 3.62 (s, 3H; OCH_3), 3.65 (s, 3H; OCH_3), 2.76–4.27 (33H; H-2, H-3, H-4, H-5^{B,D,E,F}, H-6), 4.64 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1), 4.70–4.87 (2 overlapping m, 2H; H-5^{A,C}), 4.73 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.1 Hz, 1H; H-1), 4.99 (2d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 2H; H-1), 5.01 (d, 1H; H-1), 5.12 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.5 Hz, 1H; H-1), 7.22–7.67 (18H; arom. H), 7.80–7.86 ppm (m, 2H; H_{ortho}); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3/C_6H_5CN$, 25 °C): δ = 30.19 (d, $J_{C,P}$ = 21.0 Hz, C-6$^{A\text{ or }C}$), 31.82 (d, $J_{C,P}$ = 16.5 Hz; C-6$^{C\text{ or }A}$), 57.28, 57.78, 57.84, 58.05, 58.09, 58.25, 58.30, 58.58, 59.28, 59.37, (CH_3O-6 and CH_3O-2), 61.14 (×2), 61.40, 61.47, 61.87 (×2) (CH_3O-3), 69.93, 70.16 (×2), 71.28 (C-

$6^{B,D,E,F}$), 70.34 (×2), 70.77, 71.46 (C-$5^{B,C,E,F}$), 79.91, 80.03, 80.06 (×2), 80.39, 80.72 (×2), 81.00, 81.29, 81.37, 81.44, 81.65 (×2), 82.15, 82.38, 82.56, 82.65, 82.80 (C-2, C-3, C-4), 89.31 (d, $^2J_{C,P}=11.3$ Hz; C-$5^{A\ or\ C}$), 90.42 (d, $^2J_{C,P}=12.8$ Hz; C-$5^{C\ or\ A}$), 98.14, 99.02, 99.18, 99.78, 100.90, 101.08 (C-1), 128.64–134.72 ppm (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3/C_6H_5CN$): $\delta=4.3$, 8.0 ppm (ABX, $^{107}J_{Ag,P}=^{107}J_{Ag,P'}=500$ Hz, $^{109}J_{Ag,P}=^{109}J_{Ag,P'}=580$ Hz, $^2J_{P,P'}=142$ Hz; P, P′). The 2D ROESY spectrum of **11b** unambiguously shows that the inward pointing H-3^B proton correlates with the *o*- and *m*-protons of the included benzonitrile.

Crystal structure analysis of $3a\cdot C_4H_8O$: Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a butanone solution of the complex. Crystal data: $M_r=1871.67$, hexagonal, space group $P6_522$, $a=b=14.8955(3)$, $c=67.009(15)$ Å, $\alpha=90°$, $\beta=90°$, $\gamma=120°$, $V=12875.8(7)$ Å^3, $Z=6$, $\rho=1.448$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å), $\mu=1.813$ mm^{-1}. Data were collected on a Bruker SMART 1000 CCD system at 133(2) K. The structure was solved by direct methods and refined on F_o^2 by full-matrix least squares (program SHELXL-97,[71]). The complex crystallises with imposed twofold symmetry; a disordered butanone molecule is positioned inside the cyclodextrin cavity. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included using a riding model. The absolute configuration (and thus the enantiomeric space group assignment) was determined by a Flack x parameter of −0.016(6). Refinement proceeded to $wR2=0.1093$ for all 12553 reflections and $R1=0.0485$ for data with $I>2\sigma(I)$. CCDC-202109 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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[56] Coordinated MeCN molecules could not be differentiated from uncoordinated ones.

[57] This includes H-1, H-2, H-4, H-6, MeO-3 and MeO-6 protons. Molecular models show that coordinated MeCN molecules not entrapped inside the cavity would result in strong steric interactions with some of the MeO-6 and H-6 protons.
[58] Because of the C_2 symmetry, the B and C glucose units are respectively equivalent to the E and F moities.
[59] The value was calculated using the following formula: $\Delta G^* = RT_c(22.96 + \ln T_c/\delta\nu)$ [J mol^{-1}].
[60] The whole variable-temperature NMR study required the use of two distinct solvents, CD_2Cl_2 (-60 to 20 °C) and $C_2D_2Cl_4$ (20–100 °C). The coalescence temperature for the two low-energy processes is close to the boiling point of CD_2Cl_2 and hence the corresponding activation barriers could not be determined accurately.
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