Université Louis Pasteur

THESE

Présentée à l'UFR de Chimie
pour obtenir le grade de

Docteur de l'Université Louis Pasteur de Strasbourg

par

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Métallo-cavitands dérivés de cyclodextrines

Soutenue le 7 mars 2003 devant la commission d'examen :

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A mes parents

Remerciements

Tout d'abord j'aimerais exprimer ma profonde gratitude à Dominique Matt de m'avoir permis d'effectuer ma thèse au sein de son laboratoire, de m'avoir confié en même temps cette thématique fascinante qu'est l'étude des phosphanes dérivés de cyclodextrines, et sans oublier son encadrement excellent tout au long de ce travail.

J'adresse également un très grand merci à Dominique Armspach qui, par son enthousiasme et sa disponibilité, non seulement m'avait aidé à me familiariser avec le monde des cylodextrines et à l'apprécier, mais a aussi assuré un parfait encadrement au cours de ces trois années de thèse. Je n'oublierai pas les diverses discussions scientifiques et extra-scientifiques, toujours très enrichissantes, que j'ai pu mener avec "les deux Dominique".

Ma particulière reconnaissance est due au Ministère de la Culture, de l'Enseignement Supérieur et de la Recherche du Grand-Duché de Luxembourg, sans le support financier duquel cette thèse aurait été beaucoup moins évidente à réaliser.

Je suis très sensible à l'honneur que m'ont fait Messieurs Patrick Pale, Edwin Constable et Jean-Bernard Regnouf-de-Vains en acceptant de juger le présent travail et de faire partie du jury de thèse.

Les études décrites dans ce mémoire n'auraient pas pu être rèalisées sans les nombreuses contributions des différents services communs de la Faculté de Chimie. Tout particulièrement je voudrais remercier Madame Michelle Martignaux et Messieurs Jean-Daniel Sauer et Roland Graff de la RMN ainsi que Monsieur Raymond Huber de la spectrométrie de masse. Un grand merci aussi aux différents cristallographes qui se sont investis dans la résolution des structures moléculaires (pas toujours évidente pour des dérivés de cyclodextrines) : Messieurs Peter G. Jones de Braunschweig, Loïc Toupet de Rennes, Richard Welter et André DeCian de Strasbourg.

Je ne manquerai pas d'exprimer ma reconnaissance aux différents membres, stagiaires et invités que j'ai pu côtoyer au sein du Laboratoire de Chimie Inorganique Moléculaire, Catherine Jeunesse, Stéphane Steyer, Manuel Lejeune, Laurent Poorters, Pierre Kuhn et Jörg Glöde.

Finalement, une mention toute spéciale revient à mes parents et grands-parents pour leur soutien financier et tout particulièrement à mes parents pour leur support et de m'avoir encouragé à prendre cette voie.

Contents

Abbreviations

COD	cycloocta-1,5-diene
COSY	COrrelation SpectroscopY
δ	chemical shift
DMAP	4-(dimethylamino)pyridine
DMBA	dimethylbenzylamine
DMF	dimethylformamide
ee	enantiomeric excess, $\lvert R\text{-}S \rvert /(R+S)$
ESI MS	Electro-Spray Ionisation Mass Spectrometry
FAB MS	Fast Atom Bombardment Mass Spectrometry
IR	Infra Red absorption spectroscopy
$^{n}J_{A,B}$	coupling constant (Hz) between nuclei A and B through n bonds
Ms	mesyl / $-SO_2CH_3$
NBD	Norbornadiene / bicyclo[2,2,1]hepta-2,5-diene
NMR	Nulear Magnetic Resonance
ROESY	Rotating frame Overhauser Effect SpectroscopY
THF	tetrahydrofurane
THT	tetrahydrothiophene
TOCSY	TOtal Correlation SpectroscopY
TOF	Turnover Frequency
Tr	trityl / triphenylmethyl
sTr	supertrityl / tris(*p*-*tert*-butylphenyl)methyl
VT NMR	Variable temperature Nuclear Magnetic Resonance

Résumé

Cette thèse est consacrée à la synthèse multi-étapes d'une série de ligands basés sur une plateforme de type α-cyclodextrine ainsi qu'à l'étude de leurs propriétés complexantes et catalytiques. Deux des cyclodextrines, **L1** et **L2**, sont substituées par deux bras phosphites, $-C_6H_4$-*o*-$OP(OPh)_2$, greffés respectivement sur les positions A,D et A,C. Quatre autres CD comportent des entités PPh_2 directement ancrées sur le bord primaire: **L3** (disubstitution A,D), **L4** (disubstitution A,C), **L5** (trisubstitution A,C,E) et **L8** (monosubstitution). Enfin, deux monophosphines, **L6** et **L7**, très encombrées, ont été obtenues par pontage des unités AB et AC, respectivement, par le dianion PPh^{2-}.

Malgré leur longueur importante, les deux diphosphites **L1** et **L2** forment facilement avec $[Rh(NBD)(THF)_2]BF_4$ des complexes chélate où l'atome métallique fait partie d'un très grand macrocycle (29 ou 24 chaînons, respectivement). Le complexe rhodié obtenu avec **L2** catalyse l'hydrogénation asymétrique du diméthylitaconate avec un excès énantiomérique remarquable (83.6%).

La phosphine **L3**, de symétrie C_2, forme avec Ag^+ un complexe chélate (P,P,O^{Me}). Ce dernier présente un comportement hémilabile en solution caractérisé par une coordination alternée de chacun des 4 groupes MeO du bord supérieur. L'addition de divers nitriles provoque la formation d'espèces où le (ou les) nitrile(s) coordiné(s) sont piégés à l'intérieur de la cavité. Cette dernière contribue de façon remarquable à la stabilité du complexe $[AgP_2(CH_3CN)_2]^+$, un type de complexe dont l'existence n'avait pas encore été démontrée.

Autre propriété inattendue: lorsqu'on fait réagir les diphosphines **L3** ou **L4** avec des entités chlorées, L_nMCl, on obtient systématiquement des chélates *trans* où l'entité M–Cl pointe vers l'intérieur de la cavité. Cette orientation particulière résulte d'une interaction faible entre le chlore coordiné et deux protons H-5 de la cavité, une interaction encore jamais observée à l'intérieur d'une cyclodextrine.

Dans les monophosphines **L6** et **L7**, obtenues par pontage diastéréospécifique, le doublet libre du phosphore est dirigé vers l'axe de la CD. Cette propriété permet de synthétiser des complexes auto-inclus.

Mots-clés : cyclodextrine, métallo-cavitand, chélates, diphosphines chirales, hydroformylation, hydrogénation asymétrique, phosphine, phosphite

Synopsis

The present thesis deals with the multi-step synthesis of a series of ligands based on an α-cyclodextrin platform as well as the study of their coordination and catalytic properties. Two of the cyclodextrins, **L1** and **L2**, are functionalised with two phosphite sidearms, $-C_6H_4$-*o*-$OP(OPh)_2$, tethered to the A,D and A,C positions, respectively. Four other CDs bear PPh_2 entities which have been directly anchored to the primary face: **L3** (AD-disubstitution), **L4** (AC-disubstitution), **L5** (ACE-trisubstitution) and **L8** (monosubstitution). Finally, two sterically hindered monophosphines, **L6** and **L7**, have been obtained by bridging units AB and AC, respectively, with the PPh^{2-} dianion.

Despite their length, both diphosphites **L1** and **L2** readily form cationic chelate complexes with $[Rh(NBD)(THF)_2]BF_4$, in which the metal is part of a large macrocyle (29 and 24 members, respectively). The rhodium complex obtained with **L2** catalyses the asymmetric hydrogenation of dimethylitaconate with a remarkable enantiomeric excess (83.6%).

The C_2-symmetrical diphosphine **L3** forms a (P,P,O^{Me}) chelate complex with Ag^+ which displays hemilabile behaviour, the four primary MeO groups alternatively binding the metal centre. Addition of various nitriles affords complexes in which the coordinated nitrile(s) is (are) always trapped inside the cavity. The latter highly contributes to the stability of the $[AgP_2(CH_3CN)_2]^+$ complex, a type of complex that had so far never been detected.

Another unexpected property was uncovered when reacting diphosphines **L3** and **L4** with chloro complexes, L_nMCl, which gave rise systematically to *trans* chelates, in which the M–Cl fragment is directed towards the cavity interior. The particular orientation of the M–Cl bond results from weak interactions between the coordinated chloride and two inner-cavity H-5 protons. Such interactions inside a CD are unprecedented.

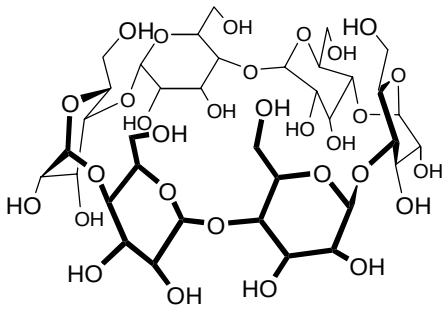
In both monophosphines, **L6** and **L7**, synthesised by diastereospecific capping, the phosphorus lone pair is pointing towards the CD axis. This feature allows formation of self-inclusion complexes.

Keywords : cyclodextrin, metallo-cavitand, chelates, chiral diphosphines, hydroformylation, asymmetric hydrogenation, phosphine, phosphite

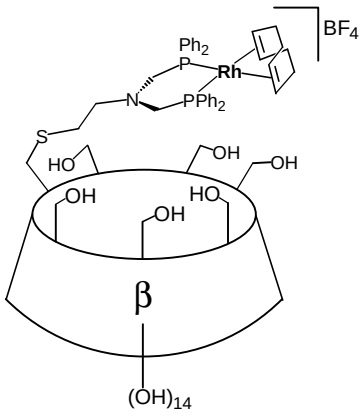
General Introduction

General Introduction

The chemistry of multifunctional ligands built on a molecular cavity has undergone a tremendous development over the last ten years.[1-5] This is mainly due to the fact that a number of valuable, cavity-shaped building blocks (*e.g.* calixarenes[6-8] or glycoluril derivatives[9,10]) have become cheap and/or readily available. A challenging idea that has recently emerged is to couple the properties of receptor molecules with those of transition metal centres. Cavitands which incorporate a catalytic centre are anticipated to lead to selective reactions, provided the receptor is able to orientate properly the substrate which undergoes the catalytic transformation.



α-cyclodextrin



Reetz' hydroformylation catalyst

Cyclodextrins as well as their chemically modified derivatives are chiral receptor molecules, generally made up of six to eight circularly arranged α-(+)-glucopyranose units, that have been widely used as enzyme mimics. Apart from the work of Reetz, only little has been attempted to extend their application field to transition metal-catalysed reactions such as the hydroformylation or the asymmetric hydrogenation of olefins. Reetz' catalysts[11,12] are exclusively based on monofunctionalised cyclodextrin derivatives bearing a rather flexibly anchored diphosphine moiety. The selectivities obtained with Reetz' catalysts in the rhodium-based hydroformylation do not vary significantly from those obtained with classic systems, which is probably a result of insufficient interactions between the metal coordination sphere and the cavity. Therefore it appeared useful to us to rigidify the catalytic centre with respect to the cavity entrance. We chose to achieve this goal by using chelating ligands in which the

individual binding sites are tethered to distinct glucose units. Such ligands were expected to produce metal-capped cyclodextrins.

The present thesis is divided into five chapters:

- Chapter I gives a literature overview of the chemistry of capped cyclodextrins
- Chapter II deals with the synthesis and coordination properties of the first cyclodextrin-based diphosphites
- Chapter III describes two cyclodextrins bearing two short phosphine arms. These are suited for the preparation of chelate complexes having the first coordination sphere partly included in the cyclodextrin cavity
- In chapter IV the preparation and coordination chemistry of the first C_3-symmetrical triphosphine built on a cavity are described
- Chapter V deals with the first cyclodextrins containing "PPh" capping units

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Chapter I. Capped cyclodextrins

I. Capped cyclodextrins

I.1. Introduction

This chapter deals with a particular class of chemically modified compounds, namely capped cyclodextrins (CDs). CDs are a family of naturally occurring, water-soluble oligosaccharides forming a bucket-shaped macrocycle and made up of α-(+)-glucopyranose units which adopt a $^4C_1$ chair conformation. The most common members which are produced on an industrial scale contain 6, 7 or 8 units and are named α-, β- or γ-CD, respectively (Figure 1). As a result of their conical shape, they display a large and a narrow cavity entrance. The former, bearing the secondary hydroxyl groups, is called the secondary rim (or face), whereas the latter, bearing the primary hydroxyl groups, is referred to as the primary rim (or face).

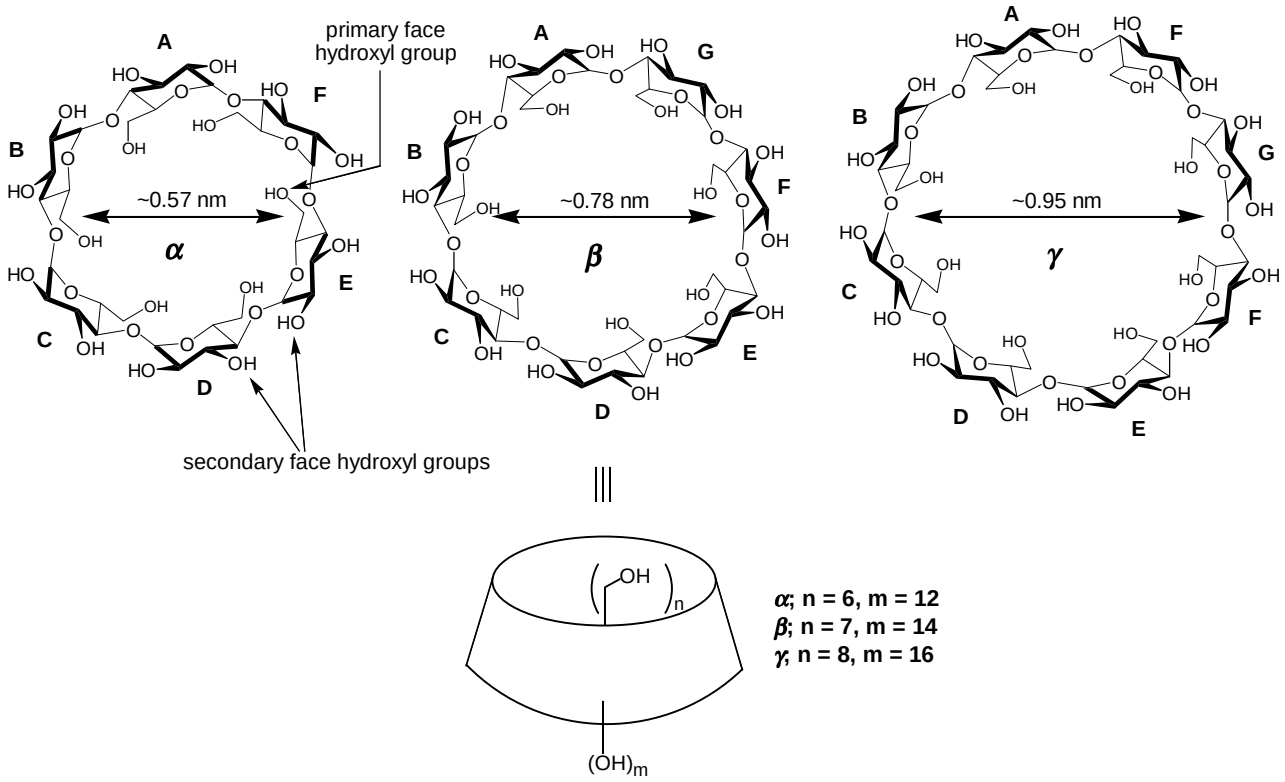
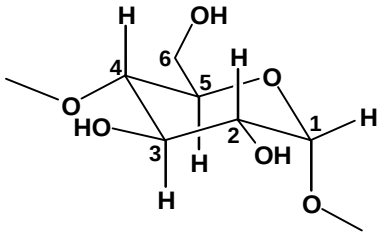


Figure 1. Schematic representations of the most commonly used CDs

I.1.1. Historical background

In 1891 Villiers reported the isolation of 3 g of a mixture of two crystalline compounds obtained after degradation of 1000 g of starch by *Bacillus amylobacter*, which he called "cellulosine", because like cellulose, the substances displayed some resistance to acidic hydrolysis and were non-reducing.[1] Only twelve years later Schardinger[2] described the formation of a similar mixture also obtained from digested starch using specific micro-organisms, in 25-30% yield. The formation of adducts, having different colours, with iodine, allowed to distinguish between both compounds.[3-5] He called the major product α-dextrin and the minor one β-dextrin. Later on, Pringsheim[6,7] discovered the ability of the dextrins as well as their acetates to form complexes with certain organic compounds. It was not until 1936 that Freudenberg *et al.* attributed a cyclic structure[8] to Schardinger's dextrins and found that they are composed of α-(1→4)-linked D-(+)-glucopyranose units.[9-11] They also managed to obtain pure samples of both cyclodextrins for the first time. At the end of the 1940s, γ-cyclodextrin was discovered[12] and a few years later, through considerable efforts to further purify the different cyclodextrins and to optimise their enzymatic production, the groups of French and Cramer managed to shed some light on their chemical and physical properties.[13,14] Macrocycles containing more than 8 units have also been isolated, but because they do not form well-defined molecular cavities, their use is quite limited.



The cavity's interior is lined up with the O-4 oxygen atoms, the H-3 hydrogen atoms at the secondary rim as well as the H-5 hydrogen atoms near the primary rim, thus conferring it a hydrophobic character. CDs are therefore prone to form inclusion complexes with various organic compounds in aqueous solution. This feature combined with the hydrolytic property of the surrounding hydroxyl groups has led to the thorough study, especially by Bender and Cramer, of the catalytic behaviour of CDs in reactions such as the hydrolysis of aryl esters[15-17] and pyrophosphates,[18] or decarboxylation

reactions.[19] It was found that the high stereoselectivities observed during the catalytic process are a result of substrate encapsulation. Their work provided the first examples of enzyme model reactions and paved the way for the elaboration of the forthcoming artificial enzyme systems.

I.1.2. Towards CD-capping

The application of native CDs in an area such as the design of supramolecular catalysts, including enzyme mimics, is rather limited. The alcohol functions are the only chemical functionalities available and the intramolecular hydrogen network the latter form around each rim provides native CDs with a rigid structure that is not easily subjected to topological changes. Thus, control over the binding strength towards organic guests having various shapes and chemical functions is far from being straightforward. Furthermore, native CDs are only soluble in water or very polar organic solvents, making their use in common organic solvents quite limited. Synthetic chemists have therefore been prompted to alter the physical and chemical properties of native CDs by either anchoring regiospecifically organic moieties onto the primary rim which leads to mono- or multiply-functionalised CD-derivatives, or simply by modifying one, two, or all three types of alcohol functions present in the macrocycle in the same way (persubstitution).[20] The latter strategy (*i.e.* permethylation, peracylation,…) is often used to tune the solubilities of CDs in given organic solvents or to modify the binding abilities towards particular organic guests in aqueous solution. The former allows the introduction of entities providing the CD with, for instance, additional hydrophobic area or a guest-rigidifying character, in which case the grafted moiety inhibits or reduces the rotational freedom of the bound guest. It can also serve as a coordinating site for metals, which may act as catalytic centres, either in metallo-enzyme mimics or in catalysis involving phosphorus- or nitrogen-containing ligands (*vide infra*). Such entities, grafted onto one of the CD rims, have been termed “caps” by Breslow, suggesting that the anchored moiety sits above the cavity entrance. The first “caps” were attached to only *one* glucose unit, leaving them rather flexible (flexible caps). Soon after, Tabushi introduced, for the first time, CD derivatives equipped with so-called “rigid caps”. In these systems, an organic fragment links two glucose units at one end of the CD, thus forming a bridge (see Figure 2). Such caps, which may induce

significant cavity distortions, have been believed to provide better complementarity between the receptor and bound guests than their flexible counterparts and, in this respect, lead to higher binding constants or higher catalytic reaction rates. A useful application of these capped systems concerns the selective difunctionalisation of the primary and the secondary rim, upon nucleophilic substitution of the cap.

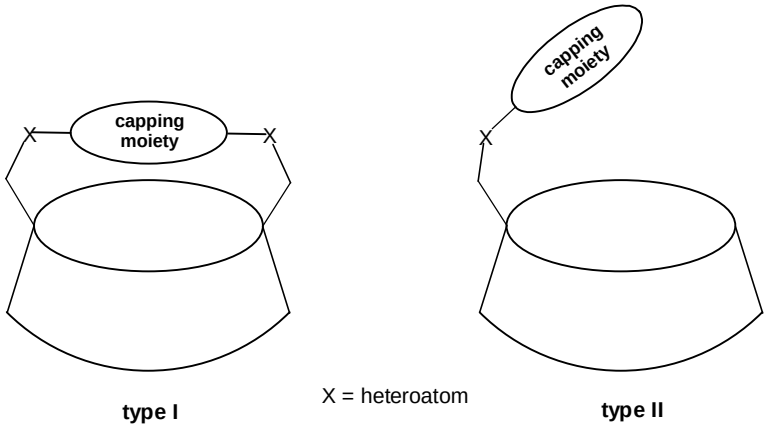


Figure 2. Schematic representations of a CD cavity equipped with a **rigid** (type I) or a **flexible** cap (type II)

I.1.3. Scope of this review

In this review we will discuss all studies involving CD derivatives bearing *bridging* caps that have been described so far and which include guest complexation, catalytic reactivity and photochemical studies. The review is composed of two main parts, the first one dealing with purely organic caps and the second one with caps comprising one or more metal centres. Where possible, comparisons in terms of guest binding strength or catalytic rates, with flexibly-capped analogues will be made. It will be apparent that in many studies rigid capping of the CD indeed leads to a more promising outcome. Unless otherwise specified the term "cap" designates herein a unit that bridges one of the CD entrances (type I cap).

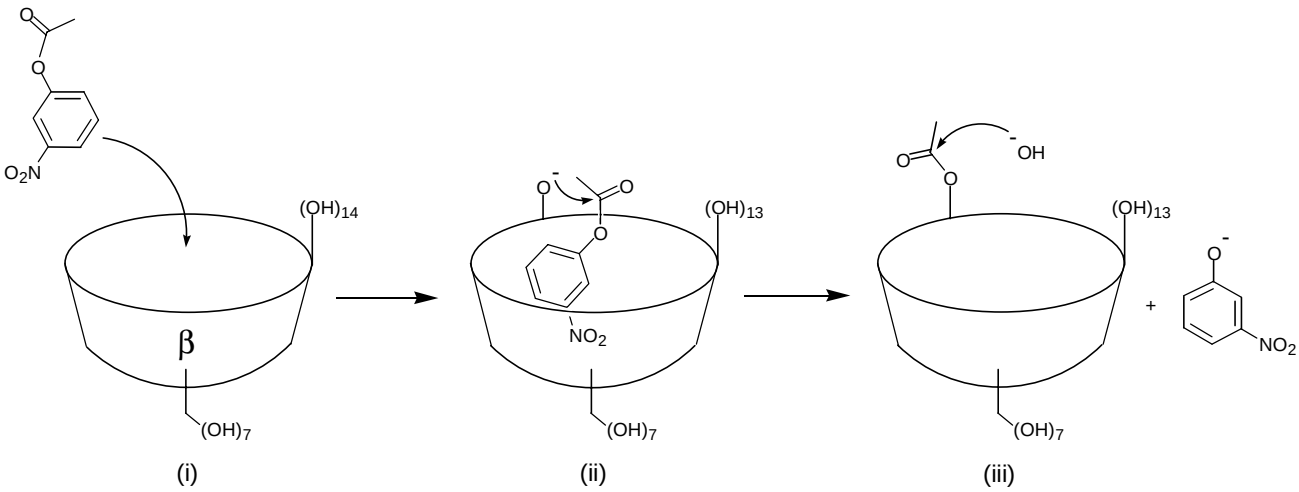
I.2. Caps bearing no metal centres

I.2.1. Enhancing the binding abilities by formation of inter-glucose bridges

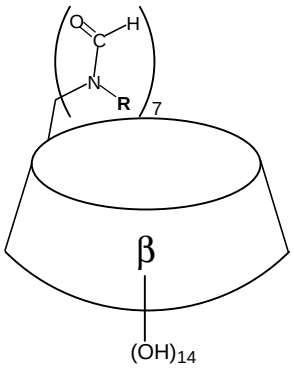
Breslow found that introducing flexible *N*-methyl- or *N*-ethylformamido moieties onto the primary rim of a *β*-CD (**ℜ-1** and **ℜ-2**)* produced significant rate

* The numbering of the compounds described in this chapter and in the first section of chapter II is preceded by an "ℜ" (ℜ = review)

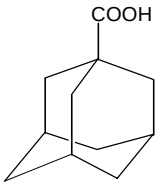
enhancements[21] (up to 18 times faster) for acetyl transfers from either *m*-nitrophenylacetate or *m-tert*-butylphenylacetate to one of the secondary hydroxyl



Scheme 1. Step-by-step representation of the CD-catalysed *m*-nirtophenylacetate hydrolysis (carried out in buffered aqueous solution, pH 9-12 usually): (i) trapping of the substrate through the secondary face entrance, (ii) nucleophilic attack of a CD-alkoxide followed by the expulsion of the nitrophenolate fragment, (iii) regeneration of the CD-alkoxide after nucleophilic hydroxide attack on the CD-acetyl group



ℜ-1, R = CH_3
ℜ-2, R = CH_2CH_3

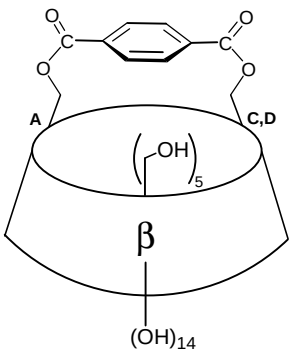


ℜ-3

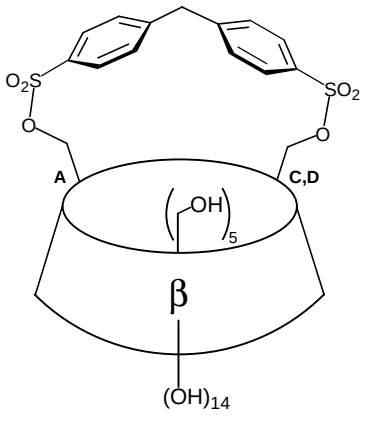
groups (Scheme 1) with respect to non-modified CDs.[19] Apparently the methyl and ethyl residues of the pendant groups provide a hydrophobic floor, which reduces rotational freedom of a bound substrate and allows better positioning of integrated functional groups than in an unmodified CD. Interestingly, the overall binding constants were not enhanced and even reduced in some cases due to the smaller cavity size. On

the other hand, competition experiments with adamantane-1-carboxylic acid (**ℜ-3**), a compound known to fit well the reduced cavity size, established a more than 20 times stronger binding of the latter with **ℜ-1** or **ℜ-2** compared to native *β*-CD. In fact, both receptors, the modified and the unmodified CDs, operate in a similar fashion. The unmodified CDs were found to bind a first guest so as to provide a cavity floor before trapping a second one. The binding constant of the ternary complex turned out to be 100 times higher than the binary one, thus demonstrating the utility of a cap in **ℜ-1** and **ℜ-2**.

The concept of enhancing the hydrophobic area of the cavity, in other words, decreasing the hydrophobic surface exposed to water, was further investigated by Tabushi *et al.* A way to circumvent the problem of cavity intrusion by pending functional groups attached to the CD was to rigidly cap the macrocycle. This was achieved for the first time in 1976 with the synthesis of disulfonate-bridged *β*-CDs, **ℜ-4** and **ℜ-5**.[22] 1-Anilino-8-naphtalenesulfonate turned out to be bound 11 and 24 times stronger by these CDs, respectively, than by native *β*-CD. **ℜ-4** binds adamantane-1-carboxylic acid over 3 times stronger than do Breslow's "flexibly capped" CDs **ℜ-1** and **ℜ-2** (although both compounds were claimed to be pure, Breslow later found[23] that they were actually mixtures of both A,C and A,D regioisomers). Soon afterwards, a similarly capped *α*-CD was prepared by Tabushi.[24]



ℜ-4

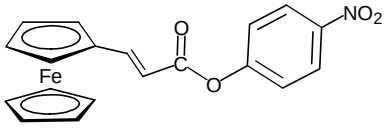


ℜ-5

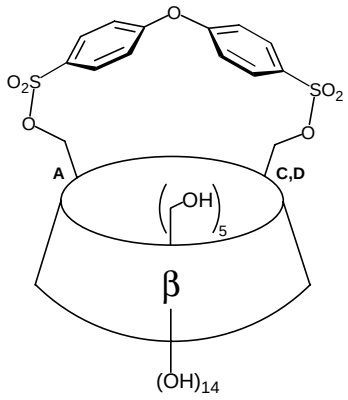
Fujita *et al.* observed a dramatic selectivity inversion in the ester hydrolysis of *m*- and *p*-nitrophenylacetate[25] when the regioisomer mixture **ℜ-5**[22] was used instead of native *β*-CD,[17] flexibly-capped **1**,[21] or various monofunctionalised *β*-CDs.[25] With the latter compounds, the *meta* isomer is converted *ca.* 5 times faster, while **ℜ-5** displays a

marked *para* selectivity ($k_c/K_d \cong 10$; k_c = hydrolysis rate, K_d = dissociation constant). In a detailed study, they found that **ℜ-5** binds the *para* isomer much better than the *meta* isomer, but the nucleophilic attack of the alkoxide on the entrapped ester proceeds at comparable rates for both isomers. Thus the observed *para* selectivity of **ℜ-5** is essentially due to the higher binding constant of the *para* isomer. With *β*-CD, both isomers give rise to similar binding strengths. Hence, the observed *meta* selectivity of native *β*-CD and **ℜ-1** arises from a shorter distance between the reacting hydroxyl group and the bound *meta* ester with respect to the bound *para* ester.

When ferrocenylacrylic ester **ℜ-6** was hydrolysed using capped **ℜ-7**, the reaction rate was somewhat higher than with native *β*-CD[17] and over 4 times higher than with flexibly-capped **ℜ-1** (10^6 times the rate of the non-catalysed reaction).[26] It is possible that intrusion of the *N*-methyl residue of flexibly capped **ℜ-1** into the cavity takes place during the catalytic process, lowering the energy level of the inclusion complex with respect to the unsubstituted *β*-CD complex. It is worth mentioning that, for the first time, these rates approached those obtained with some natural enzymes. The authors of this work also suggested that the intermediate immediately formed after nucleophilic attack on the ester carbonyl has the aryl fragment being partially lifted out of the cavity and thus less well bound than the substrate in the initial host-guest complex.

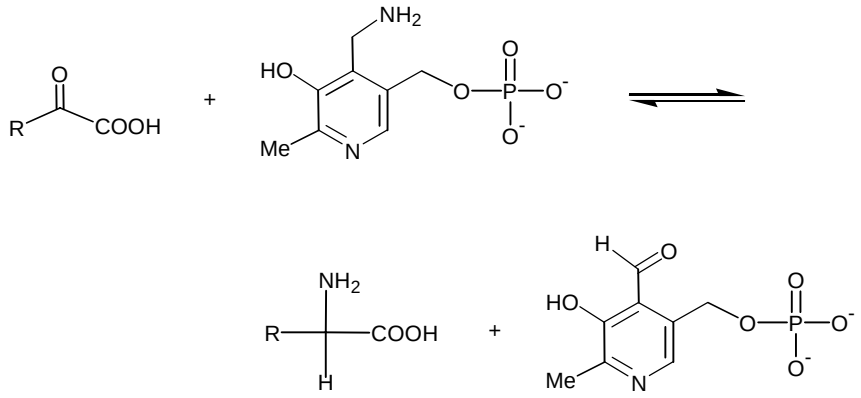


ℜ-6

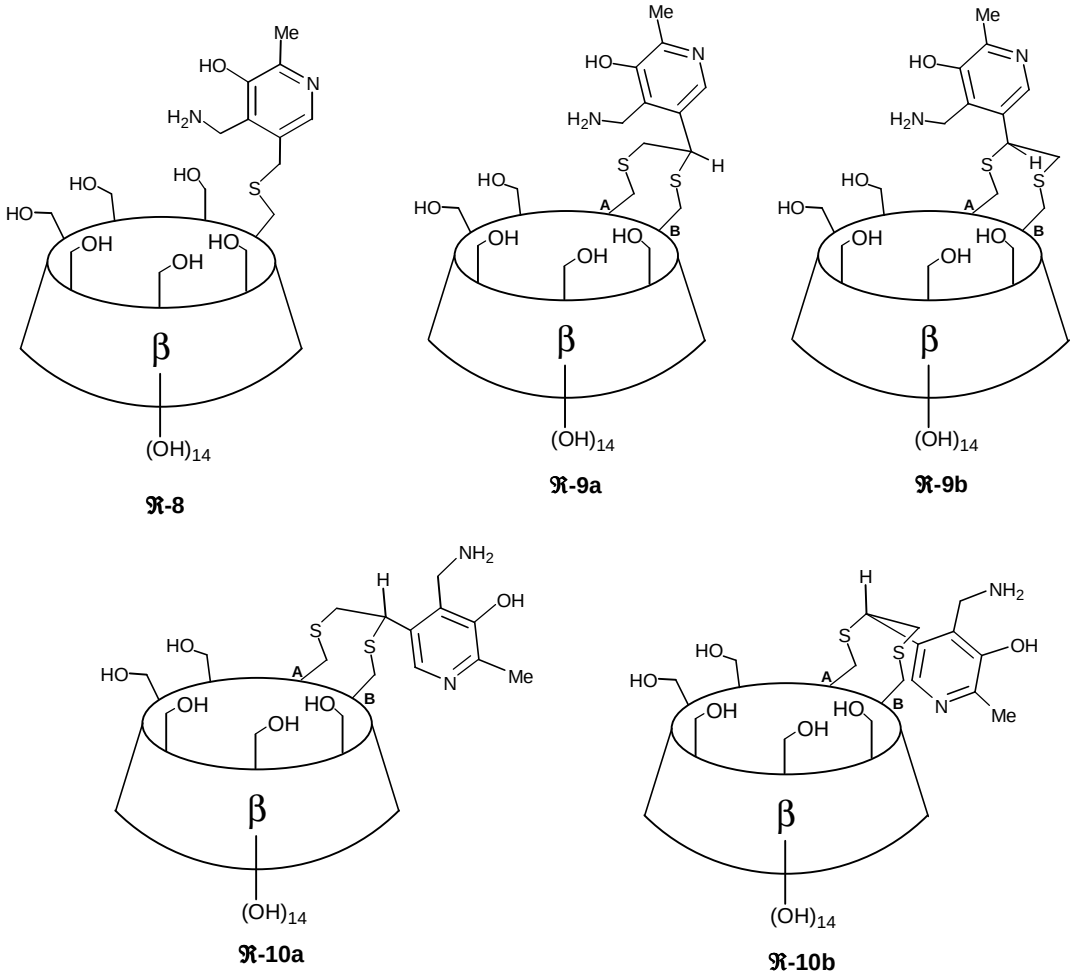


ℜ-7

A quite interesting transaminase model was designed by Breslow *et al.* These enzymes transform *α*-ketoacids into amino acids while producing pyridoxal phosphate from pyridoxamine phosphate (Scheme 2). A pyridoxamino residue was either singly (**ℜ-8**) or doubly linked (**ℜ-9**, **ℜ-10**) to *β*-CD.[27] In the isomers **ℜ-9a**, **ℜ-9b** the

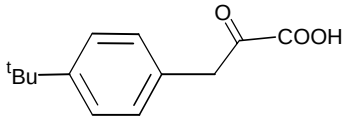


Scheme 2. Enzymatic transamination

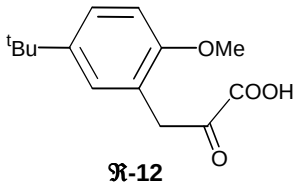


pyridoxal group is *endo* oriented with respect to the cavity while in **ℜ-10a**, **ℜ-10b** it points toward the exterior. A competition experiment with a mixture of phenylpyruvic acid / pyruvic acid (1:100 ratio) resulted in a 1:1 ratio of phenylalanine and alanine when using **ℜ-8**, thus reflecting a 100-fold increase in reactivity for phenylpyruvic acid

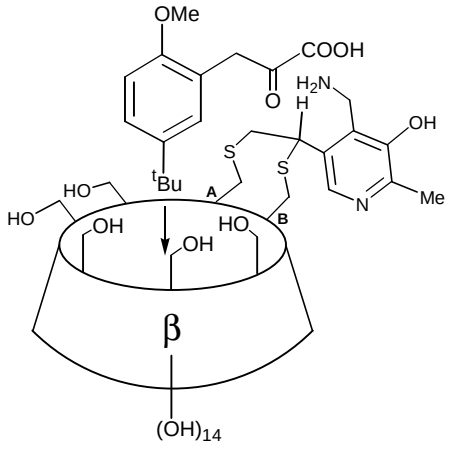
as a result of better binding of the aromatic guest by the CD cavity. An analogous experiment using the *endo* pair **ℜ-9** produced only a 50-fold increase, while with the *exo* pair **ℜ-10**, phenylpyruvic acid was only about 21 times more active. 4-*t*-Butylphenylpyruvic (**ℜ-11**) acid was found to be 150 times more reactive than phenylpyruvic acid with flexible **ℜ-8**. The reactivity increase dropped to 30 in the presence of either the *endo* or the *exo* pair. This trend was interestingly inverted when the *t*-Bu group was moved to the *meta* position and a methoxy function added. Thus, a 2-methoxy-5-*t*-butylpyruvic acid (**ℜ-12**) / pyruvic acid mixture (1:10 ratio) in the presence of the flexible transaminase revealed only a 2-fold selectivity in favour of the aromatic substrate. The selectivity was only slightly enhanced when the *endo* pair was used (2.8-fold), but with the *exo* pair it rose to 40. Apparently the high reactivity of the *exo* pair in the last experiment originates from the fact that a geometry in which the pyridoxamine group points away from the cavity and can parallel the cavity axis, is required if the *t*-Bu group is in *meta* position. Compound **ℜ-8** and **ℜ-10** can of course both adopt such a configuration, but the *restricted* flexibility of **ℜ-10** as a result of the double linkage strongly favours the required geometry. This study nicely illustrates how a rigidified functional group linked to a CD may efficiently induce selectivity .



ℜ-11

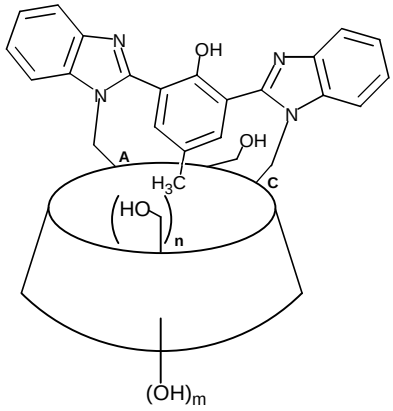


ℜ-12

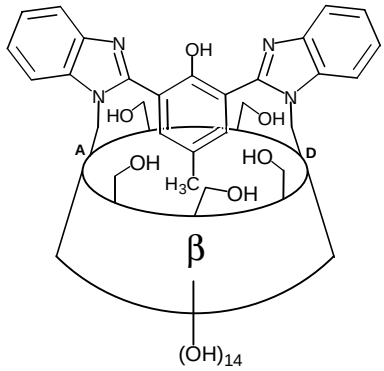


ℜ-10 • 12

In a recent study Fujita *et al*. attempted to improve the resolution of NMR resonances of functionalised CDs by introducing a large aromatic moiety. Reacting A,C and A,D-ditosylated β-CD derivatives with 2,2'-(1,3-phenylene)-bis-benzimidazole led to the formation of the capped CD hosts **ℜ-13** and **ℜ-14**,[28] respectively. The analogous A,C-capped α-CD derivative **ℜ-15**, has also been reported.[29] It turned out that all signals in the ^{1}H and ^{13}C NMR spectra, including those of the aromatic bridge, are well spread out for both compounds, reflecting a strong differentiation of all glucose units. Complete assignment was achieved by means of the COSY and NOESY spectra. The strong differentiation of the two protons in *ortho* position with respect to the methyl group in A,C-bridged **ℜ-13** and **ℜ-15** (> 1 ppm) as well as through-space correlations suggest that the methylphenyl residue is inclined towards the cavity interior. In **ℜ-14** the methylphenyl unit is assumed to be located deeply inside the cavity as deduced from an NMR study. Accordingly, while adamantane-1-carboxylate was moderately bound in **ℜ-13** ($5 \cdot 10^4$ M^{-1}), no inclusion complex could be detected with **ℜ-14**.

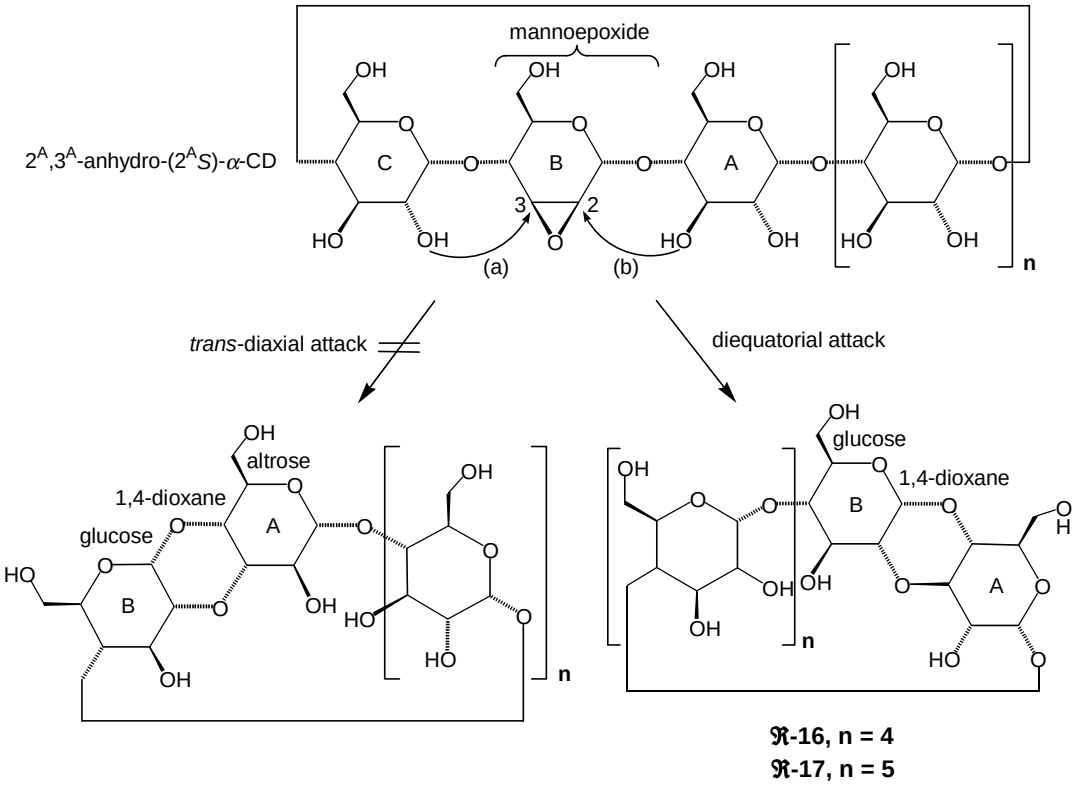


ℜ-13, n = 4, m = 14
ℜ-15, n = 3, m = 12



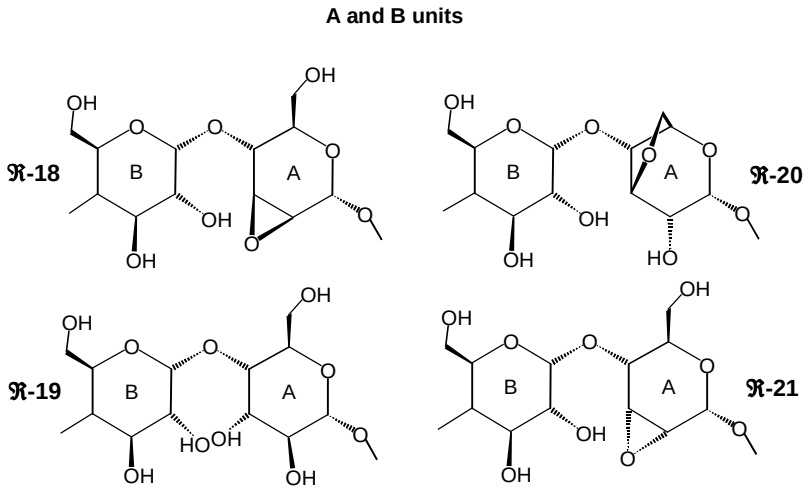
ℜ-14

Usually nucleophilic attack on 2,3-*manno*-epoxides of cyclodextrins, such as 2^{A},3^{A}-anhydro-(2^{A}*S*)-α-CD, occurs in the favourable *trans*-diaxial fashion on the C-3 atom, leading to the formation of an altropyranose ring. However, as was found by Fujita *et al*., if the nucleophile is a hydroxyl from a neighbouring glucose unit in α-CD, the attack takes place exclusively on the C-2 atom (diequatorial epoxide opening, Scheme 3), giving 3^{A},2^{B}-anhydro-α-CD, **ℜ-16**,[30] which displays the *shortest* possible bridge between two adjacent glucose units. This effect was rationalised in terms of



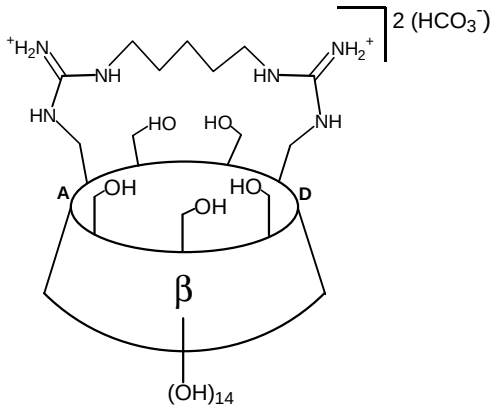
Scheme 3. Two possible epoxide ring opening pathways

sterically hindered *trans*-diaxial ring opening. A detailed molecular dynamics simulation study[31] suggested that the product resulting from C-2 attack was indeed thermodynamically favoured as well as kinetically favoured as a result of its more rigid structure compared to that displayed by the hypothetical product resulting from the diaxial attack. An X-ray study confirmed the theoretical results[31] and gave evidence for the less pronounced conical shape of the macrocycle **ℜ-16** (tilt angles for the $3^{A},2^{B}$-

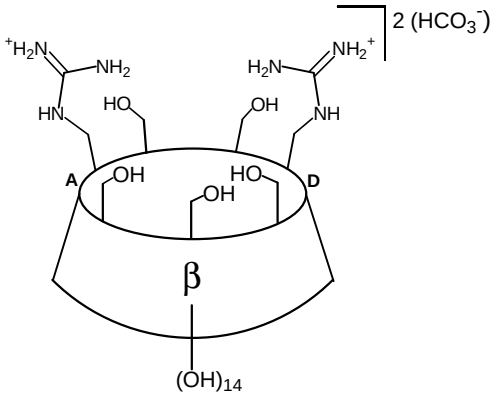


anhydro ring system $\tau \approx 60°$ *vs.* >100° for non-distorted CDs[32]). Interestingly, a study on the binding strengths of methylorange by a series of β-CDs having a distorted cavity, **ℜ-17**-**ℜ-21**, revealed that the only host leading to a binding constant as well as binding free energy higher (up to 2.75 times higher at 10°C) than those of the parent β-CD, is **ℜ-17**, which contains the extra interglucosidic ether function.[33] It was assumed that the slightly smaller cavity size of **ℜ-17** with respect to the other hosts leads to a significant gain in free enthalpy upon inclusion of methylorange.

Aiming at the encapsulation of phosphotyrosine derivatives at the surface of human growth factor receptors, Smith *et al*. synthesised a β-CD derivative, A,D-bridged with a doubly positively charged cap, **ℜ-22a**.[34] It was anticipated that the rigid cap is able to bind phosphotyrosine more strongly than the "flexibly capped" analogue **ℜ-22b**.[35]

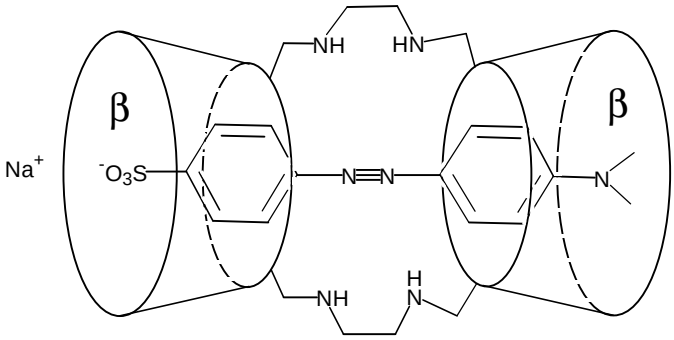


ℜ-22a

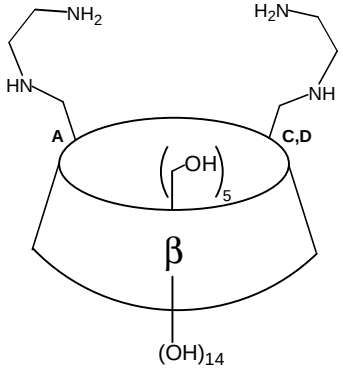


ℜ-22b

Ligase-type enzyme models are suitable for either simultaneous binding of two functionalised substrates or binding of ditopic ones. "Double recognition" may be achieved with molecules having two receptor units. This feature has been successfully realised by Tabushi in the so-called *duplex cyclodextrin* **ℜ-23**,[36] which comprises two β-CDs linked by ethylene diamino groups at A,D or A,C positions (starting from a mixture of A,D- and A,C-capped β-CDs **ℜ-4**, six different regioisomers of the duplex cyclodextrin were obtained). Fluorescence studies showed that **ℜ-23** binds methyl orange 6 times more tightly than does the β-CD tetramine **ℜ-24**, thus demonstrating the simultaneous encapsulation of the guest by the double cavity-system.

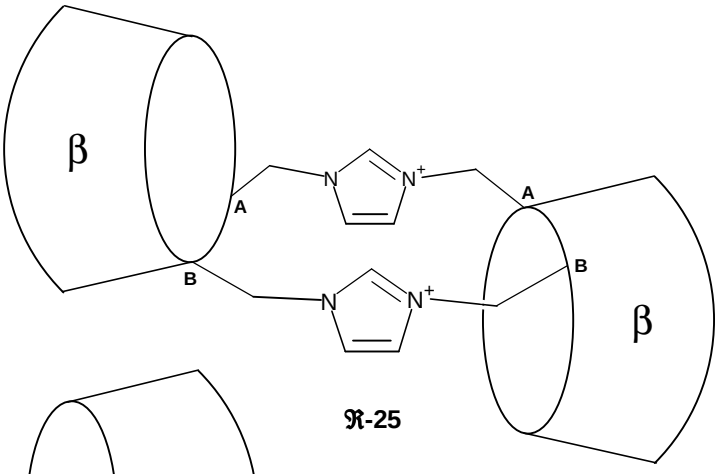


ℜ-23 · methylorange

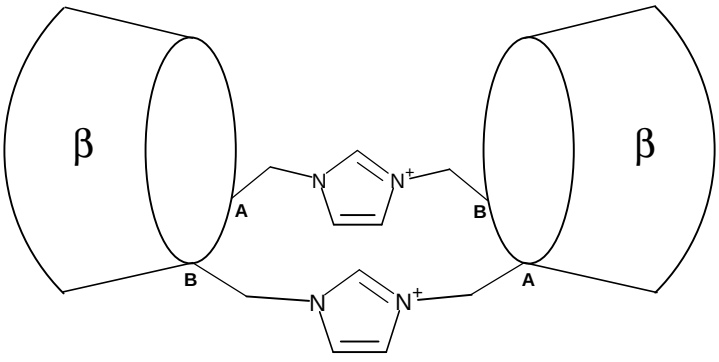


ℜ-24

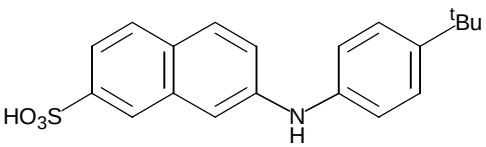
Doubly-linked CD dimers have also been reported by Breslow *et al*. In an attempt to improve the binding of CDs towards certain guests, as well as to overcome flexibility problems associated with some inclusion complexes, they synthesised occlusive CD-dimers linked in A,B positions, along with their aversive counterparts.[37] It has been clearly established that **ℜ-25**, because of its aversive character cannot bind cooperatively ditopic guests such as **ℜ-27**, unlike the occlusive dimer **ℜ-26**,



ℜ-25

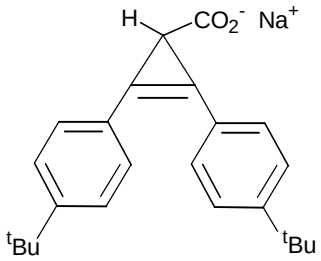


ℜ-26

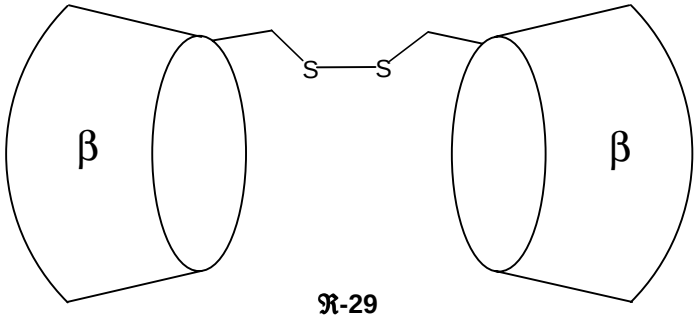


ℜ-27

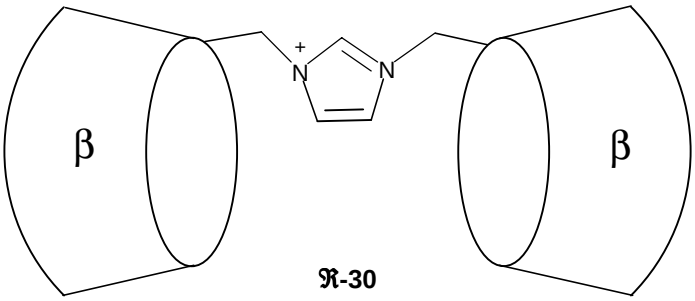
which leads to stronger overall binding. Nevertheless the binding constants for guests **ℜ-27** or **ℜ-28** turned out to be significantly lower than those observed with singly-linked dimers **ℜ-29** and **ℜ-30**. No explanation has been found yet for these lower affinities. However, when dimer **ℜ-31**, which bears neutral linkers of different lengths, was used to entrap a substrate having an appropriate shape such as **ℜ-33**, a binding constant of 10^{10} M^{-1} was found[38] using a competition fluorescence method. Even stronger binding was observed with **ℜ-34**, to such an extent that the exact constant value could not be determined by the same competition method. A lower limit has been fixed at $4 \cdot 10^{11}$ M^{-1}, a value that lies in the range of very strong antigen-antibody complexes. The aversive **ℜ-32**, as expected, did not produce outstanding binding abilities. This study illustrates that recognition of a substrate with appropriate geometry can be dramatically improved if the host possesses a rigid structure, induced by double linkage.



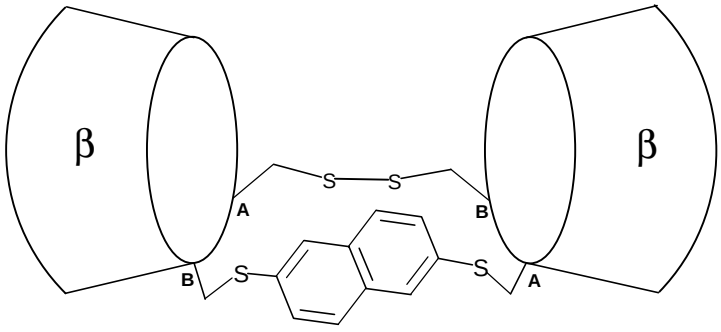
ℜ-28



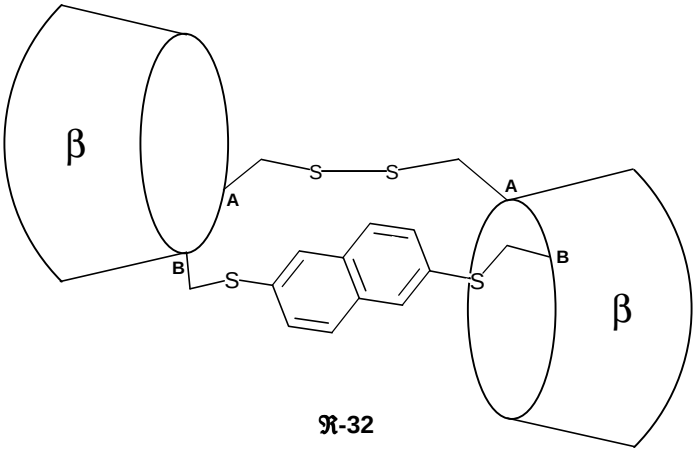
ℜ-29



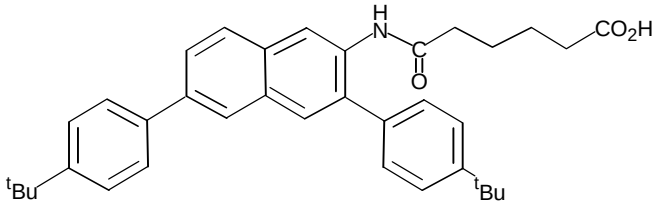
ℜ-30



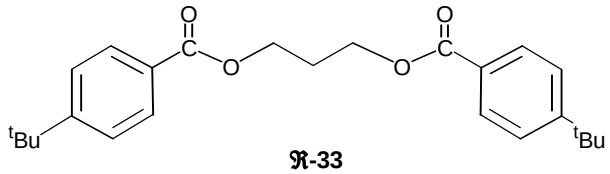
ℜ-31



ℜ-32



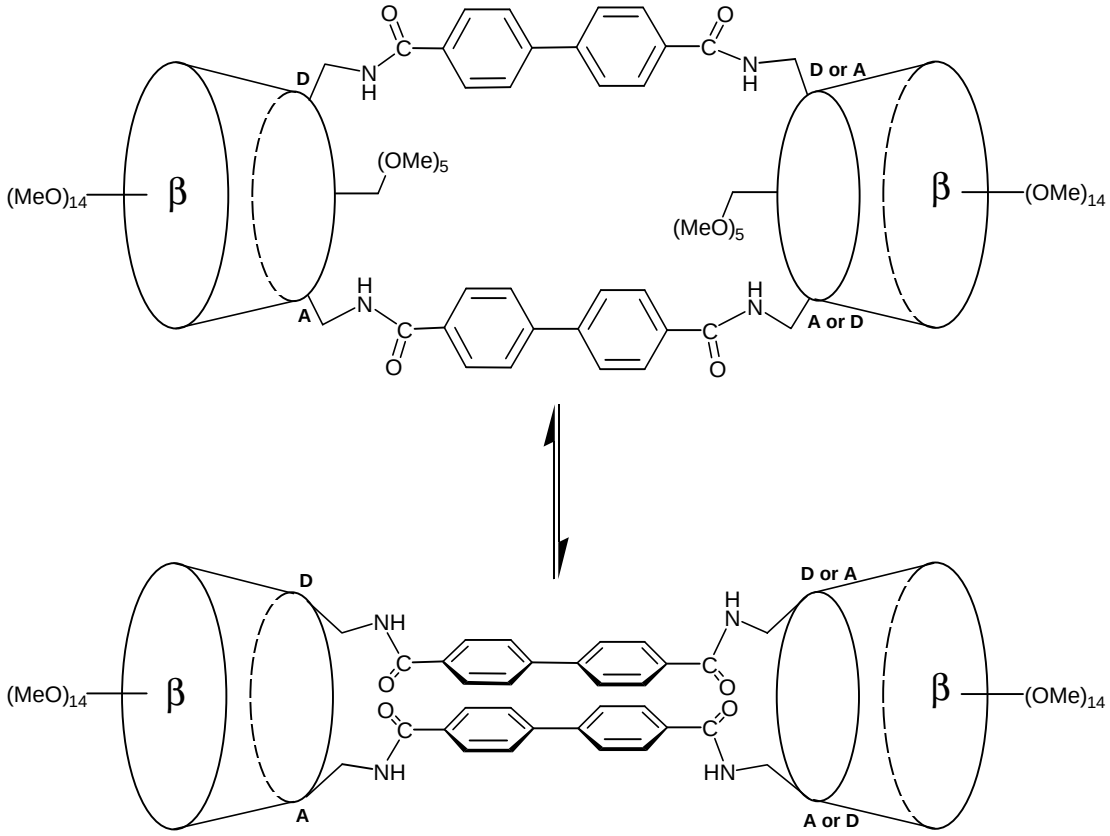
ℜ-34



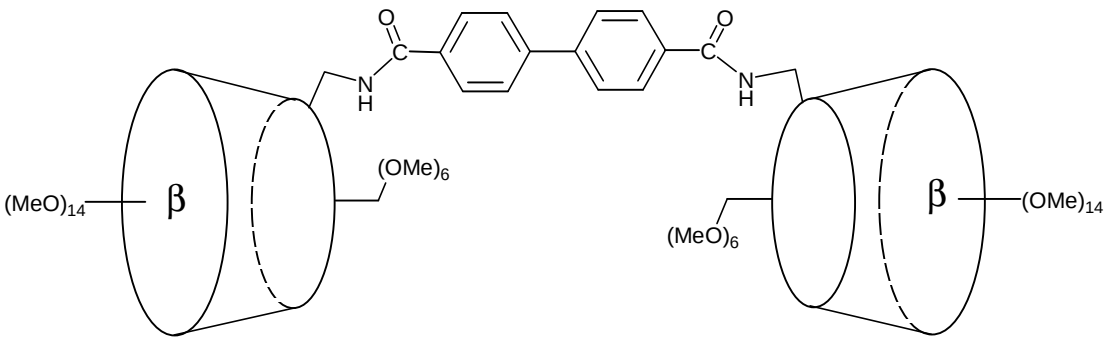
ℜ-33

The binding abilities of another doubly-bridged CD-dimer as well as a CD-trimer have been studied by Kuroda *et al.* (compounds **ℜ-35** and **ℜ-36**, respectively).[39] Their synthesis was achieved by connecting A- and D-substituted, permethylated *β*-CD derivatives in a head-to-head fashion with two biphenyl linkers. The isomers resulting from each coupling reaction, *i.e.* $(A\text{-bp-D})_2$ and (A-bp-D)(A-bp-D) (**ℜ-35**) and $(A\text{-bp-D})_3$ and (A-bp-A)(D-bp-D)(A-bp-D) (**ℜ-36**), could not be separated and were thus used as mixtures. Fluorescence studies carried out with **ℜ-35** in water gave rise to excimer emisson at room temperature. Upon heating to 348 K, the intensity of the latter dropped to 1/10 of the initial value, which suggests the presence in solution of the equilibrium drawn in Scheme 4. Support for this assumption came from the observation that in organic solution (*i.e.* MeOH or $CHCl_3$) the excimer emission is cancelled and the fluorescence of **ℜ-35** resembles that of the singly-linked dimer **ℜ-37**. Hence, the driving force for the stacking behaviour of the biphenyl moieties seems to be mainly due to the hydrophilic character of the medium. In keeping with this feature, **ℜ-35** binds the anthracene derivative **ℜ-38** less strongly than its singly-linked counterpart **ℜ-37** (K =

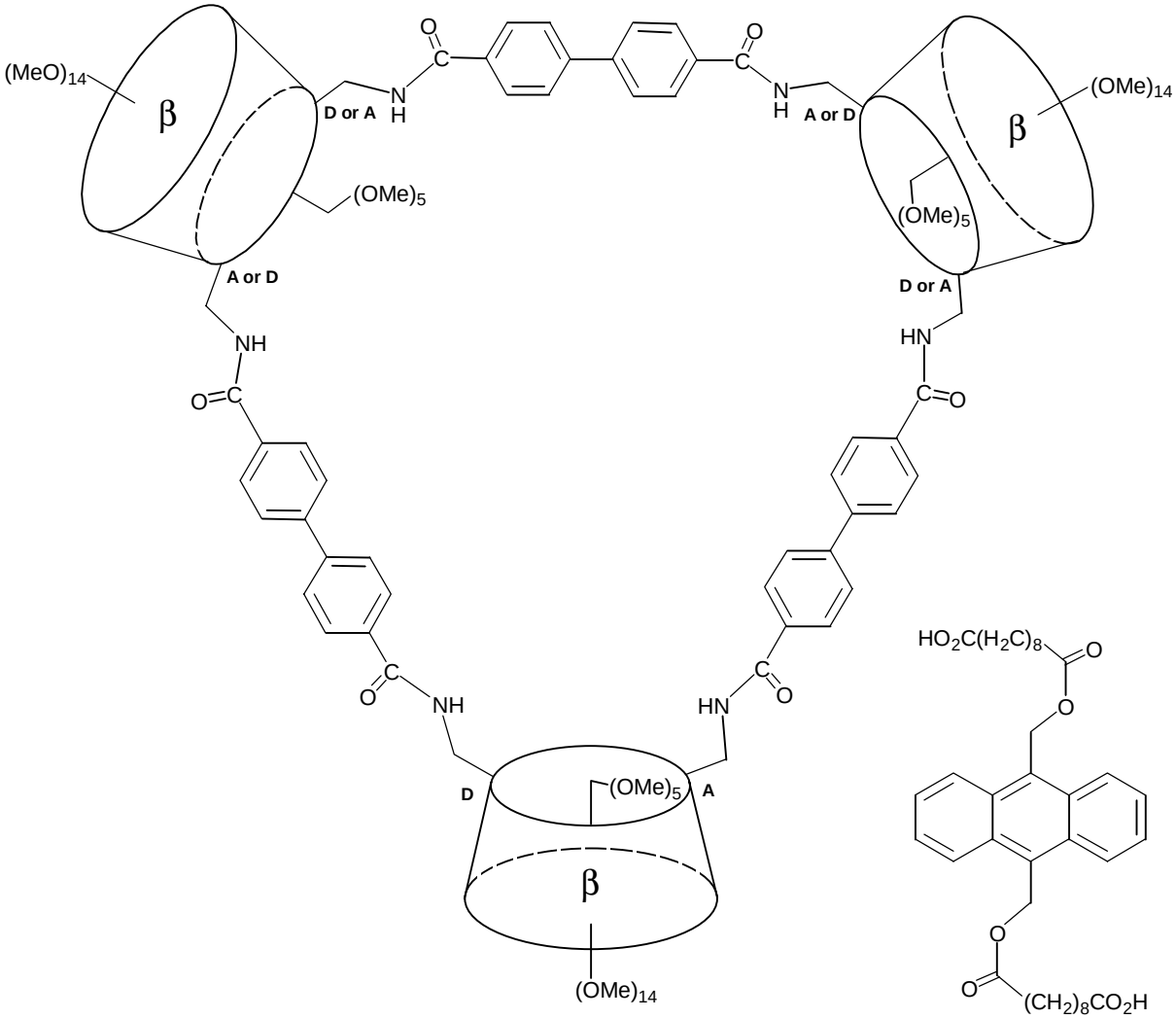
5200 *vs.* 8600 M^{-1}, respectively). The dislocation of the stacked biphenyl groups prior to guest-encapsulation takes up an extra amount of energy. The tightest binding, being at the same time entropically favoured over the one into **ℜ-37** as a result of the double connection between CD receptors, occurred with the trimeric host **ℜ-36** (K = 27000 M^{-1}). This property was also attributed to the presence of an additional binding site in this trimer.



Scheme 4. Equilibrium in **ℜ-35** (occlusive and aversive isomer mixture) between the "open" and the "stacked" conformation



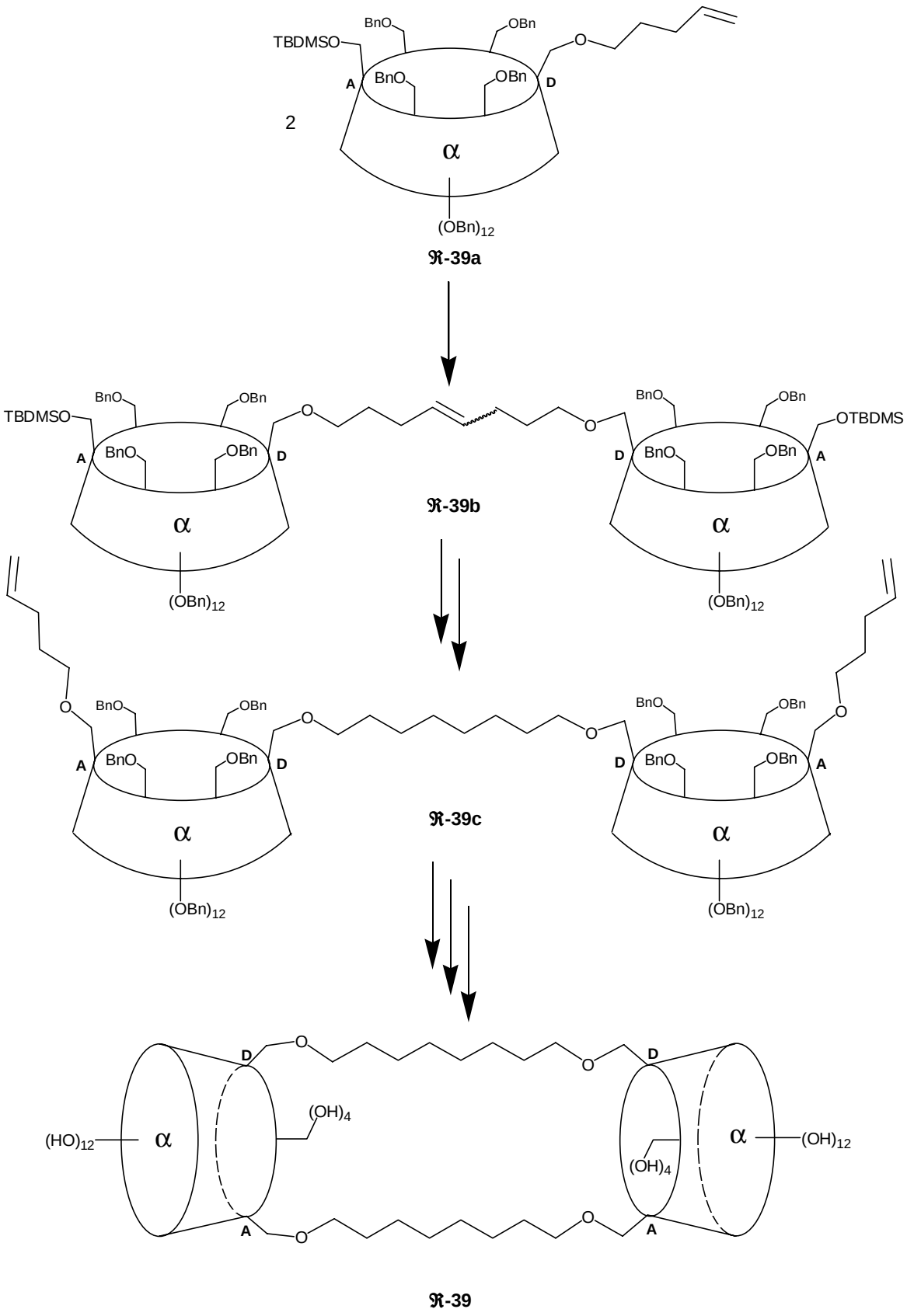
ℜ-37



ℜ-36 (isomer mixture) **ℜ-38**

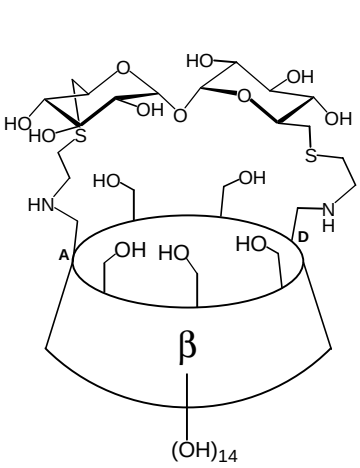
An novel synthetic strategy has recently been reported by Sinaÿ *et al.* for the preparation of a doubly-linked CD dimer, **ℜ-39**.[40] Thus, the α-CD derivative **ℜ-39a** was first converted into the double CD **ℜ-39b** by olefin metathesis (Scheme 5). Subsequent hydrogenation, followed by removal of the TBDMS groups and alkylation of the resulting alcohol groups afforded diolefin **ℜ-39c**. Ring-closing metathesis, followed by double bond hydrogenation and cleavage of the benzyl groups led to dimer **ℜ-39** in a fairly good overall yield (49%).

An alternative to the generally used aromatic caps has been reported by Cucinotta *et al.* who prepared the trehalose-capped β-CD derivative, **ℜ-40** (21% yield).[41,42] The use of the trehalose moiety provides an enhancement of the chiral and hydrophobic inner-cavity environment. ROESY and circular dichroism experiments show that at basic pH (so as to maintain the amino groups unprotonated) the plane of an included

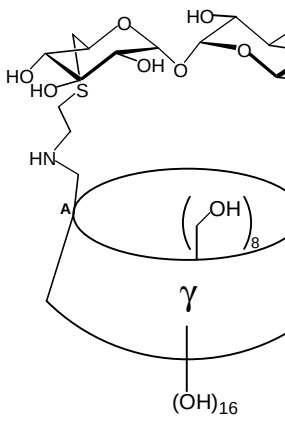


Scheme 5. Synthesis of a doubly-linked CD-dimer via ring-closing metathesis

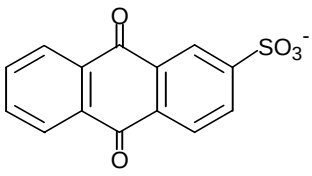
anthraquino-2-sulfonate (**ℜ-41**) anion parallels the CD axis, with the sulfonate group pointing outside the cavity. When the inclusion takes place at slightly acidic pH, the protonated amino groups give rise to electrostatic interactions with the negatively charged SO_3^- function, thus leading to an upside-down arrangement of the guest with respect to the previous one. Interestingly, this binding mode leads to an almost 4.5 times higher binding constant than the purely hydrophobic binding mode and a 6-fold binding enhancement with respect to unsubstituted *β*-CD. Fujita *et al*. also described the synthesis of a series of similarly designed, so-called molecular sugar bowls.[43] Thus compounds **ℜ-42**-**ℜ-44** were obtained in moderate yields (13–16%) starting from A,C-, A,D- and A,E-functionalized *γ*-CD's. **ℜ-44** displays C_2-symmetry, while **ℜ-42**, with the shortest N···N separation, shows the strongest asymmetry. No studies dealing with inclusion complexes have been reported to date.



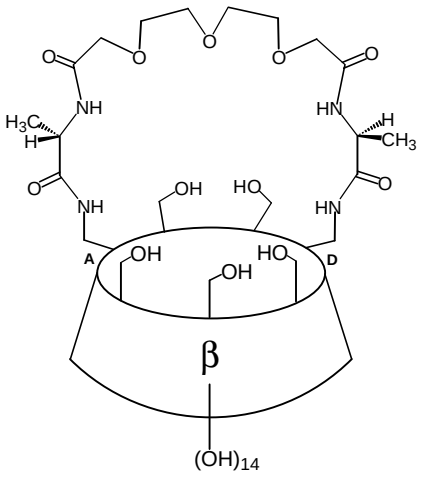
ℜ-40



ℜ-42, X = C
ℜ-43, X = D
ℜ-44, X = E



ℜ-41



ℜ-45

Chiral bridges derived from aminoacids have also been used to cap CDs. Thus, Marchelli *et al*. reacted an A,D-diamino-*β*-CD derivative with *N*,*N*'-3,6,9-trioxaundecanoyl-(L,L)-bis-aniline, to produce **ℜ-45** in 17% yield.[44] Its chiral recognition properties have been tested in capillary electrophoresis. Mixtures of D- and L-dansyl-glutamic as well as D- and L-dansyl-aspartic acid have been successfully separated.

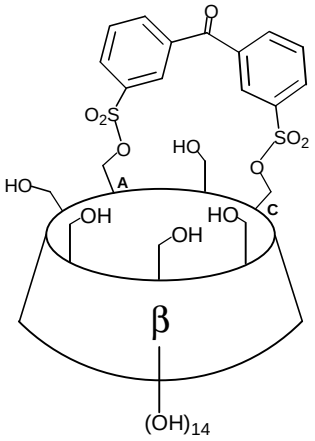
I.2.2. CD-difunctionalisation through regioselective capping of the primary and the secondary rim

I.2.2.1. Primary rim functionalisation

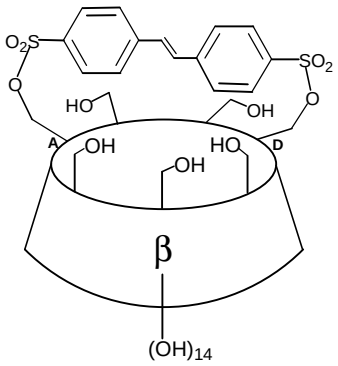
As mentioned above, Tabushi's first rigidly capped *β*-CDs turned out to be a mixture of A,C and A,D derivatives. It became quickly apparent that pure regioisomers were necessary for catalytic applications. Such compounds were first obtained using benzophenone-3,3'-disulfonyl and *trans*-stilbene-4,4'-disulfonyl fragments, the length and rigidity of which are optimal for A,C and A,D capping, respectively (**ℜ-46**, 40% preparative yield; **ℜ-47**, 20% preparative yield).[45,46] Reaction of a second capping reagent with **ℜ-46** afforded the doubly capped species **ℜ-48**, whereas **ℜ-47** underwent no second capping, polymeric material being formed instead. These observations supported the structures proposed for **ℜ-46** and **ℜ-47**. Furthermore, the reaction with bi(phenylsulfonyl) dichloride also proved to be regioselective[47] giving A,D-substituted **ℜ-49** in a preparative yield of 17.5%. Interestingly, the regioselectivities were not affected by the concentration of reactants, except when *trans*-stilbene-4,4'-disulfonylchloride was used (the A,C / A,D ratio approaches 1 at higher concentrations). A,B-capped **ℜ-50** was obtained from *β*-CD (in excess) in 40% preparative yield using *m*-benzenedisulfonylchloride as capping reagent.[48] ^{13}C NMR spectroscopy proved to be a useful tool for the assignment of the A,B regiochemistry. Thus, the C-1, C-4 and C-6 signals of the A and B-substituted glucose units undergo significant shifts with respect to the corresponding signals in the unsubstituted units. Such an effect, called the remote substituent effect, was not observed in A,C and A,D-capped CDs. It should be mentioned though that Breslow only managed to synthesise **ℜ-50** in about 5% yield.[27] Apparently, partial decomposition resulting from the lability of the sulfonate-ester groups occured. Introduction of stabilizing methoxy groups on the capping reagent rose the yield to about 12%. Treatment of the same capping reagent with a *β*-CD in which the secondary face was permethylated, gave only 3.5% of the corresponding A,B derivative **ℜ-51**.[49]

Three modified versions of Tabushi's A,C-bridged **ℜ-46** were obtained by Bradshaw *et al*. as intermediates during the synthesis of CD-oligosiloxane copolymers.[50] They synthesised the secondary rim-permethylated (**ℜ-52**) and

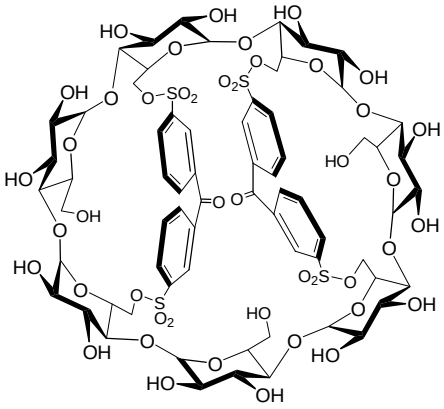
perpentylated (**ℜ-53**) β-CDs, in *ca.* 25% preparative yields. Pure **ℜ-54**, a related α-CD derivative, was obtained in 16% yield.



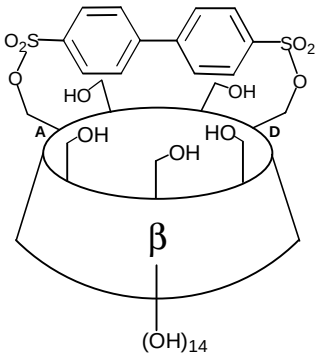
ℜ-46



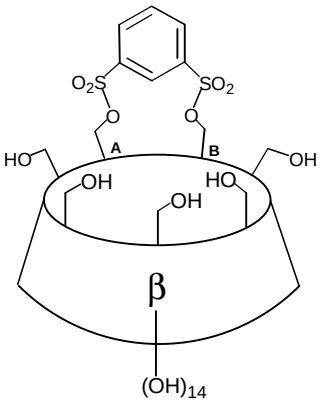
ℜ-47



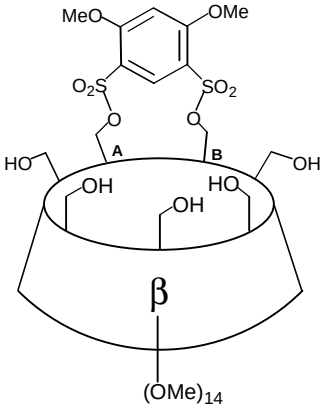
ℜ-48



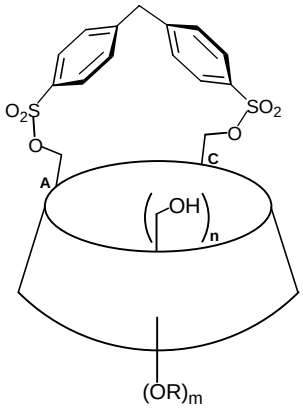
ℜ-49



ℜ-50



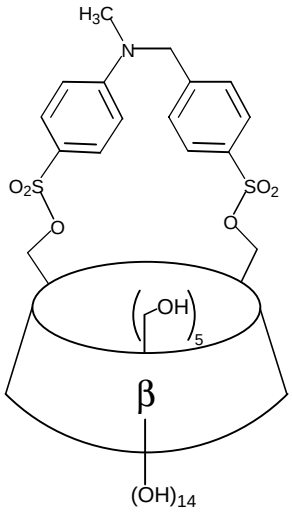
ℜ-51



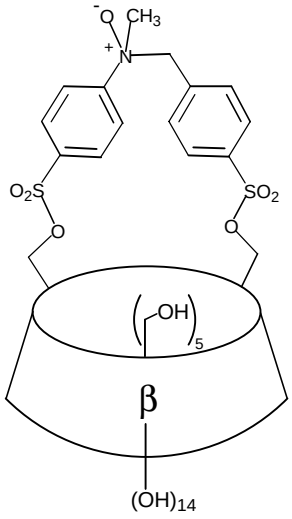
ℜ-52, n = 5; R = CH_3; m = 14
ℜ-53, n = 5; R = C_5H_{11}; m = 14
ℜ-54, n = 4; R = CH_3; m = 12

Tabushi *et al*. also reported the synthesis of the β-CD derivative **ℜ-55** (20% yield), which is bridged with a dissymmetrical cap and was used for the subsequent

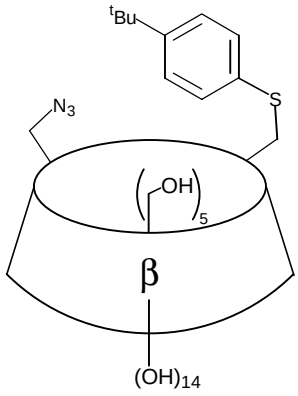
introduction (*vide infra*) of two different functional groups.[51] No data as regards the regioselectivity of the capping reagent or the regioisomer obtained were given though. Upon oxidation of **ℜ-55**, the nitroso compound **ℜ-56** was formed. Treatment of the latter with an excess of NaN_3, followed by reaction with an excess of sodium *p-t*-butylthiophenolate afforded the unsymmetrically substituted compound **ℜ-57** in 59% yield. It was shown that the sulfonate group *para* to the *N*-oxide moiety reacted much faster with N_3^- than the other sulfonate.



ℜ-55



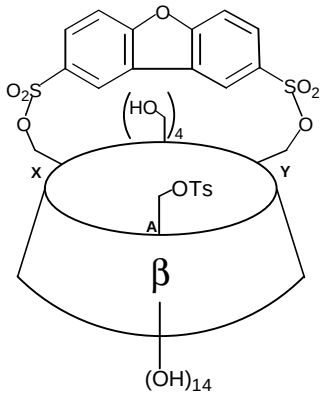
ℜ-56



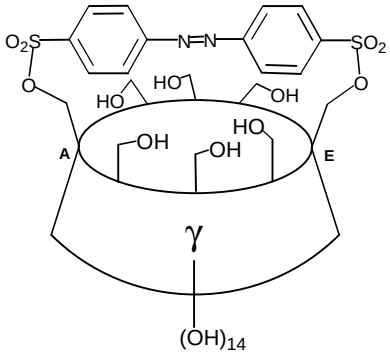
ℜ-57

Applying the capping reaction to monosubstituted CDs may lead to regioselective trifunctionalization. Fujita *et al.* reacted dibenzofuran-2,8-di(sulfonylchloride) with monotosylated *β*-CD,[52] yielding the mixture of products **ℜ-58**-**ℜ-62**, two of which display an A,C,E substitution pattern (23% combined yield). The three other regioisomers were produced in only 4.5% yield.

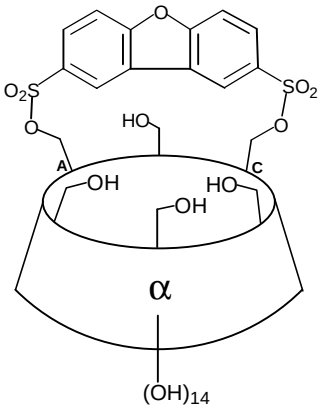
Transannular capping was extended to *γ*-CD by Ueno *et al*. It was not clear at first whether the reaction of *γ*-CD with azobenzene-4,4'-di(sulfonylchloride) afforded an A,D- or A,E-capped species, or even a mixture of both compounds (13% yield).[53,54] Eventually, the ratio was found to be 94:6 in favour of the C_2-symmetrical compound **ℜ-63**.[55] A,B-capped *γ*- and *α*-CD derivatives analogous to the previously reported compound **ℜ-51**[27] were synthesised by Breslow *et al.*,[56] but only a small amount of the *α*-CD derivative was isolated (2.3% yield).



ℜ-58, X = B; Y = D
ℜ-59, X = C; Y = E
ℜ-60, X = D; Y = F
ℜ-61, X = E; Y = G
ℜ-62, X = B; Y = G



ℜ-63



ℜ-64

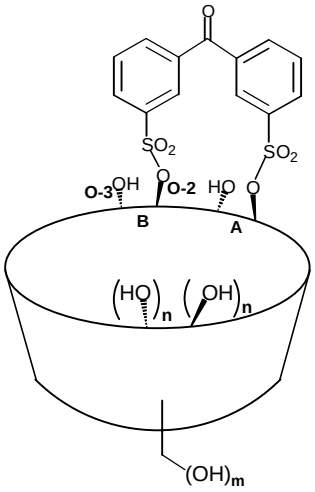
It was not until very recently that a regioselective A,C-difunctionalisation method based on capping was found for α-CDs. Fujita *et al.* reported an 18% yield for product **ℜ-64**, using dibenzofuran-2,8-disulfonylchloride as capping reagent.[57] A,C-substitution was inferred from the strong shielding effect the H-6 protons of the B glucose unit undergo.

I.2.2.2. Secondary rim functionalisation

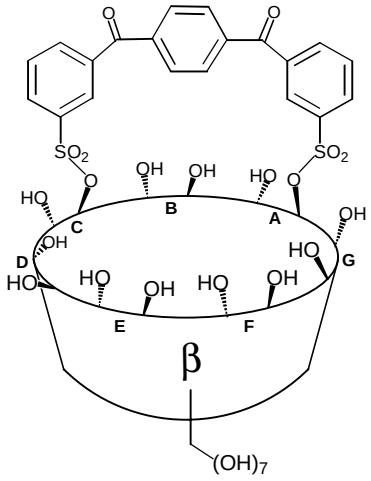
Regiospecific difunctionalisation of the secondary rim has turned out to be a much more difficult task than that of the primary one because of the less pronounced nucleopholic character of the secondary hydroxyl groups. Furthermore, distinction has to be made between the 2- and the 3-hydroxyl groups.

Teranishi *et al.* have recently described synthetic methodologies for the regioselective difunctionalisation of β- and γ-CD with reasonable preparative yields. They are based on the use of imidazolyl leaving groups instead of chlorides. Reaction of benzophenone-3,3'-di(sulfonylimidazole) with γ-CD afforded $2^A,2^B$-capped **ℜ-65** in 30% preparative yield.[58] Amazingly, no 6-*O*-substituted products were detected. It should be mentioned that the 2-hydroxyl groups did not require any kind of activation beforehand. Likewise, treating α- and β-CD with benzophenone-3,3'-di(sulfonylimidazole) afforded the corresponding $2^A,2^B$-bridged species **ℜ-66** and **ℜ-67** in 30% and 33% yield, respectively.[59] Similarly, the $2^A,2^C$-capped compound **ℜ-68** was obtained by reacting β-CD with 1,4-dibenzoylbenzene-3',3''-di(sulfonylimidazole)

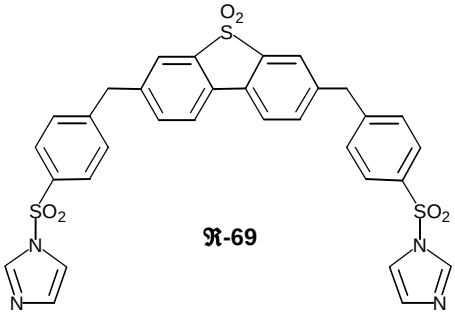
(18% yield).[60] Synthesis of an $2^A,2^D$-capped *β*-CD derivative **ℜ-70** was also achieved, using di(sulfonylimidazole) **ℜ-69** as capping reagent (42% yield).[61] Characteristic ^{1}H NMR and ^{13}C NMR downfield shifts of the H-1, H-2 and H-3 protons (the shifts are more pronounced for H-2 than for the other two protons) of the substituted glucose units as well as of the corresponding C-2 atoms (the C-1 and C-3 atoms are upfield shifted), allowed the assignment of a 2-*O*-substitution pattern in the above described compounds.



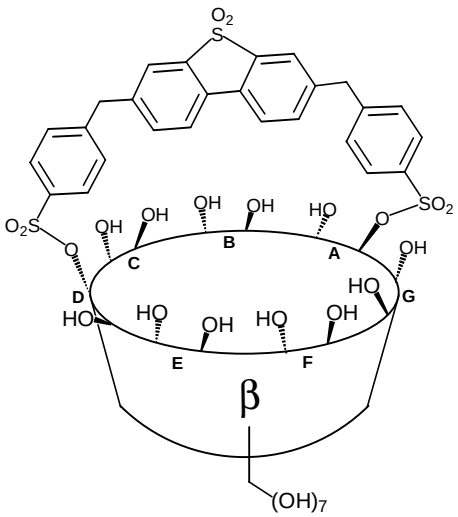
ℜ-65, n = 6; m = 8
ℜ-66, n = 4; m = 6
ℜ-67, n = 5; m = 7



ℜ-68



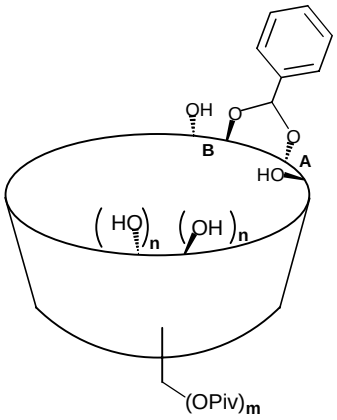
ℜ-69



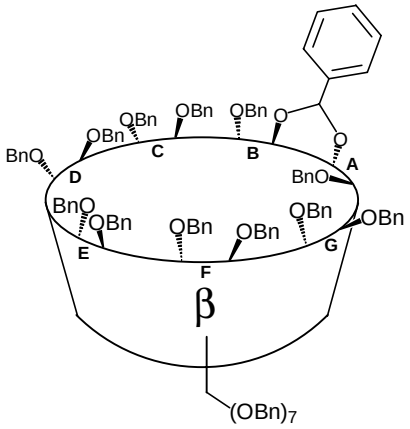
ℜ-70

An example of mixed 2,3-*O*-bridging of contiguous glucose units has been reported by Sakairi *et al.*[62,63] 6-*O*-pivaloyl-protected *α*-, *β*-, and *γ*-CDs were treated with benzaldehyde dimethylacetal using Evans conditions[64] to obtain compounds **ℜ-71**-**ℜ-73** in 37%, 46% and 54% yield, respectively. Removal of the pivaloyl groups and subsequent perbenzylation of **ℜ-72** gave **ℜ-74**, which underwent selective reductive cleavage upon treatment with $LiAlH_4/AlCl_3$ at the 2-*O* position. This preference is possibly a result of the electron-withdrawing character of the anomeric centre. The selective 2,3-*O*-substitution pattern was demonstrated using 2D HOHAHA, PFG-

HMQC and PFG-HMBC NMR techniques on the 2,3-*O*-diacetyl derivative of **ℜ-74**. Alternatively, **ℜ-72** could also be permethylated after de-*O*-pivaloylation and subjected to reductive cleavage at the 2-*O*-position.[65]



ℜ-71, n = 4; m = 6
ℜ-72, n = 5; m = 7
ℜ-73, n = 6; m = 8



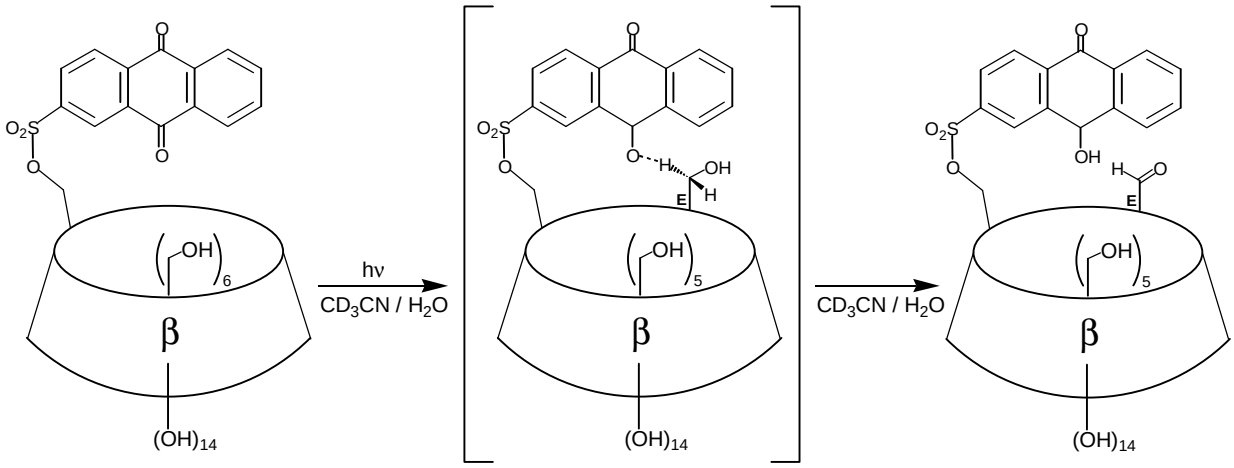
ℜ-74

I.2.3. Photochemical behaviour of capped CDs

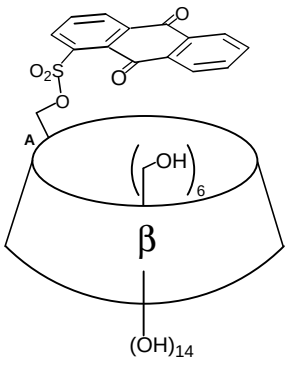
Several reports have dealt with CDs transannularly bridged with moieties prone to undergo various photochemical reactions, such as photoinduced energy or electron transfer from or to encapsulated guests. Modified or improved catalytic activities as well as enhanced binding abilities have also been achieved through photoisomerisation of the CD cap.

Abelt *et al*. studied the reactivity of *β*-CDs flexibly or rigidly capped with anthraquinone units (compounds **ℜ-75**-**ℜ-77**) upon irradiation.[66] The capping reaction between *β*-CD and anthraquinone-2-sulfonyl chloride results in an unseparable mixture of the A,D and A,C (80 : 20 ratio) derivatives **ℜ-77** in a rather low yield (9%). Very similar photochemical behaviour was observed for all four compounds. Irradiation of either one of them in a D_2O/*i*-Pr*O*D-d_7 solution under anaerobic conditions led to the formation of a hydroquinone cap (not drawn) as a result of proton transfer from a primary alcohol group to one of the quinone carbonyl functions, which could subsequently be reverted back to quinone by passing air through the solution. However, upon irradiation of any of the CD derivatives in aqueous CD_3CN, formation of a new product was detected. In the case of **ℜ-75** the presence of an aldehyde function was clearly detected (formation of **ℜ-78**). Molecular modelling suggests that, in the absence of *i*-PrOH, aldehyde formation originats from intramolecular proton transfer from a C-6

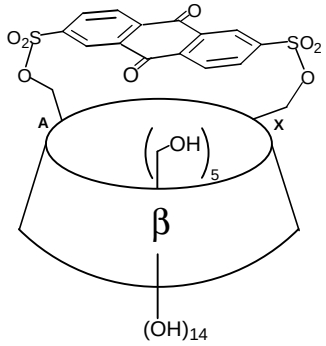
hydroxyl, preferentially in the E position, to the quinone. This behaviour makes such CD hosts unsuitable for photoinduced electron transfer reactions.



ℜ-75 **ℜ-78**



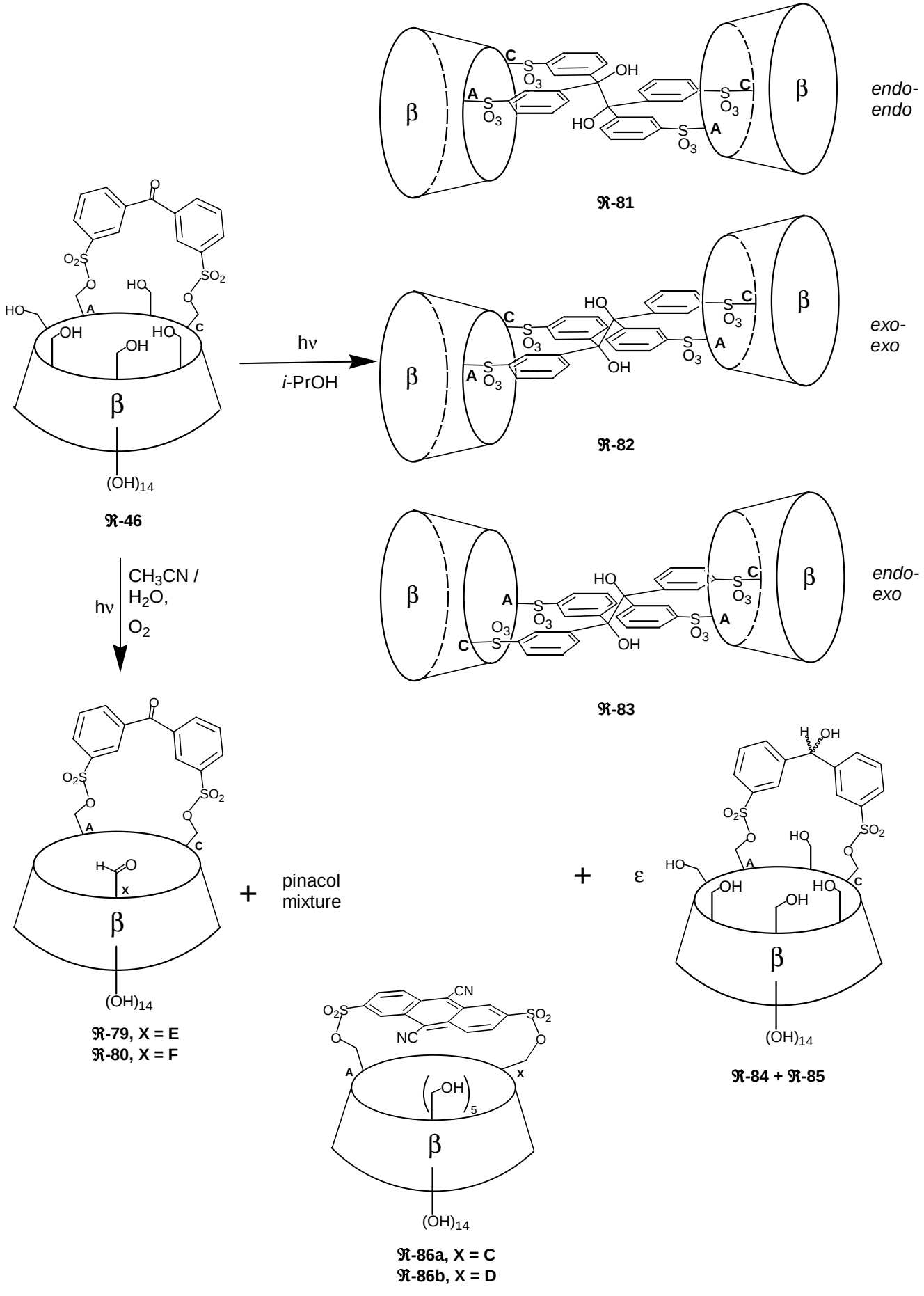
ℜ-76



ℜ-77a, X = C
ℜ-77b, X = D

Similar CD proton abstraction was also observed with Tabushi's *m,m*'-disulfonylbenzophenone-A,C-capped *β*-CD **ℜ-46**.[67] In aqueous acetonitrile media the regioisomeric aldehydes **ℜ-79** and **ℜ-80** were mainly formed, together with a mixture of pinacols, after irradiation and reaction with O_2. According to molecular modelling, deprotonation of the C-6 hydroxyls is promoted in positions E and F. In aqueous *i*-PrOH, which acts as proton donor, three dimeric pinacols, **ℜ-81**-**ℜ-83** were detected as the major products, as in the case of unsubstituted benzophenone, along with little amounts of the two benzhydrol diastereoisomers **ℜ-84** and **ℜ-85**.

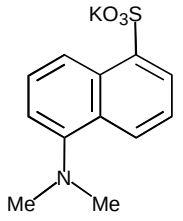
A much lower tendency for CD proton abstraction was anticipated for the dicyanoanthracene-capped compound **ℜ-86**. Unfortunately, the reaction between *β*-CD


endo-endo
ℜ-81
exo-exo
ℜ-82
endo-exo
ℜ-83
ℜ-46
hν
i-PrOH
hν
CH3CN / H2O, O2
ℜ-79, X = E
ℜ-80, X = F
pinacol mixture
ℜ-86a, X = C
ℜ-86b, X = D
ε
ℜ-84 + ℜ-85

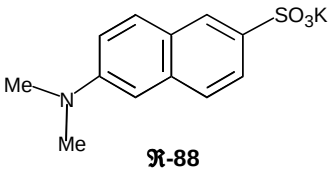
and 9,10-dicyanoanthracene-2,6-di(sulfonicchloride) afforded only a very small amount (1% yield!) of an unseparable mixture of the easily hydrolysed A,D and A,C isomers (76:24 ratio) **ℜ-86**.[68] Their instability is caused by the strongly electron-withdrawing character of the aromatic moiety. A static and dynamic fluorescence quenching study on **ℜ-86** involving different amines as quenchers revealed that binding by the capped host was only more efficient than with native *β*-CD if the guest geometry is suited for more or less complete encapsulation, which is the case for amine **ℜ-87**.[69] Because of better encapsulaion of the somewhat long amines **ℜ-88** and **ℜ-89** in *β*-CD, the binding constants of these guests turned out to be lower with **ℜ-86** than with *β*-CD. It was furthermore observed that the dynamic components represent at least 21% of the Stern-Volmer constants of the tested quenchers, which implies that potential photo-oxidation reactions would take place to some extent outside the cavity.

amine	**ℜ-86**	*β*-CD
ℜ-87	280 ± 10	110 ± 6
ℜ-88	475 ± 3	1270 ± 30
ℜ-89	254 ± 10	358 ± 22

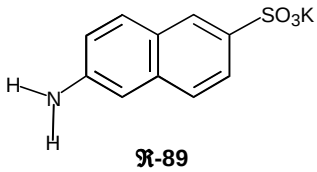
Table 1. Stern-Volmer constants ($dm^3 \cdot mol^{-1}$) for the fluorescence quenching of **ℜ-86** with some amines as well as binding constants with the parent *β*-CD



ℜ-87



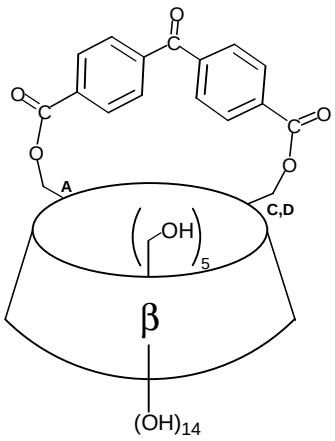
ℜ-88



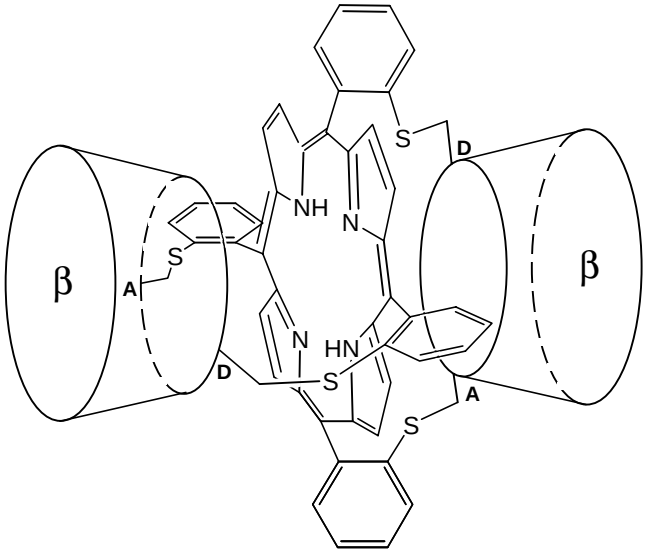
ℜ-89

The first evidence for energy transfer from a CD host to a bound guest was given by Tabushi *et al*. Phosphorescence measurements in aqueous DMF revealed the existence of triplet-triplet energy transfer from benzophenone-4,4'-dicarboxylate capped *β*-CD **ℜ-90** (no regioselectivities were given) to bound bromonaphtalene or bromoethylnaphtalene in 60% and 50% quantum yields, respectively.[70] No significant transfer occurred when simple benzophenone-4,4'-di(methylcarboxylate) was used

instead as a sensitiser, an observation that corroborates the encapsulation of the photoactive guests. Moreover, as expected, no energy transfer was found to take place between the CD host and the very hydrophilic trisodium naphtalene-1,3,6-trisulfonate.

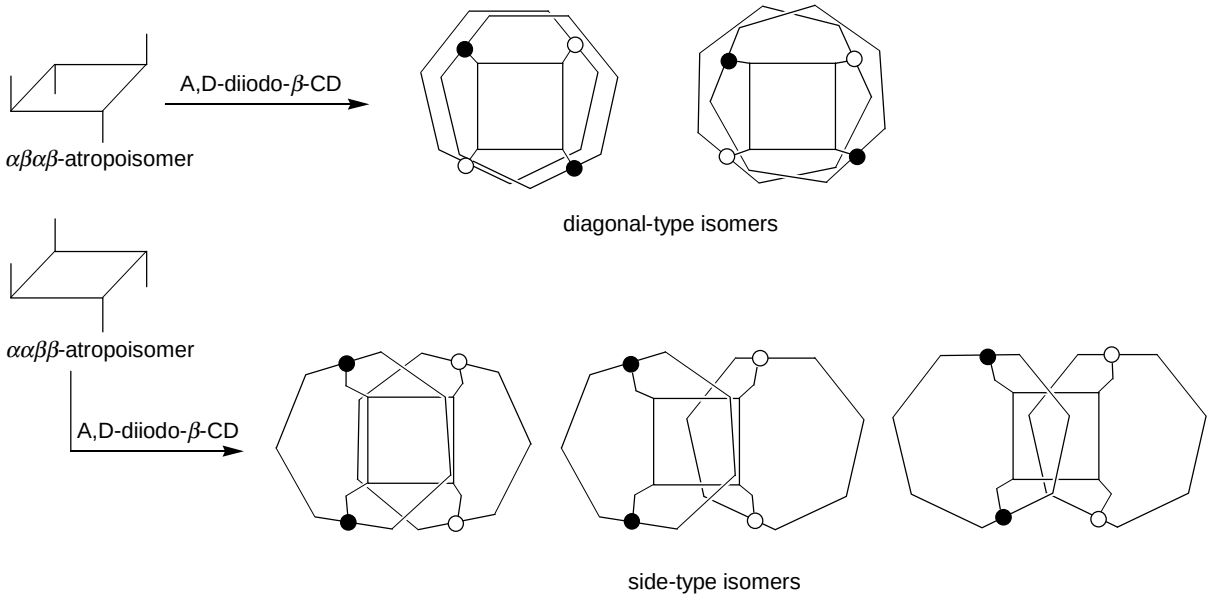


ℜ-90



ℜ-91

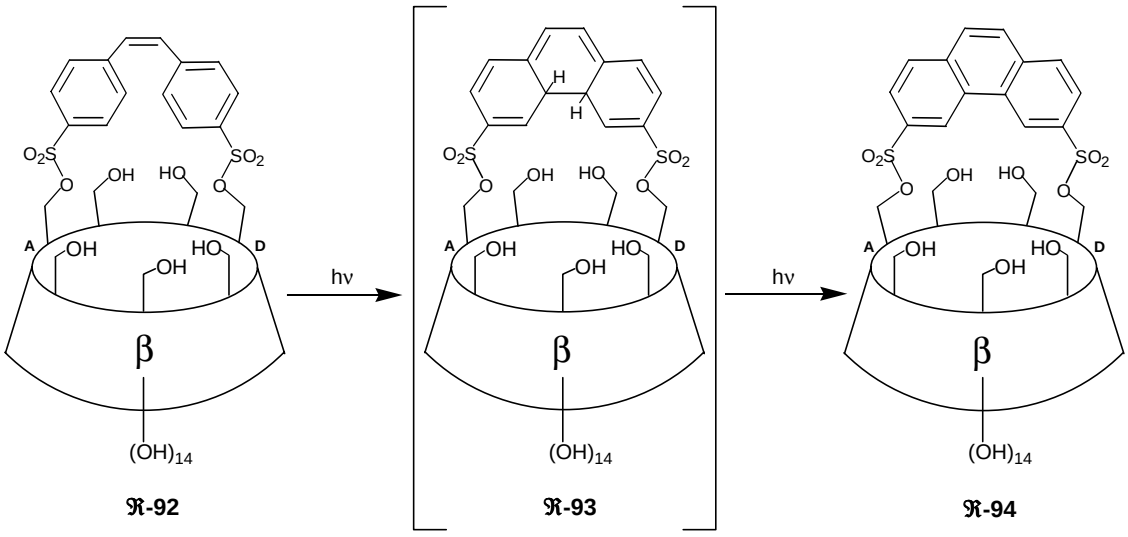
Kuroda *et al*. reported on controlled electron transfer from a *β*-CD-sandwiched porphyrin, **ℜ-91**, onto a bound guest.[71] Its synthesis resulted from a coupling reaction



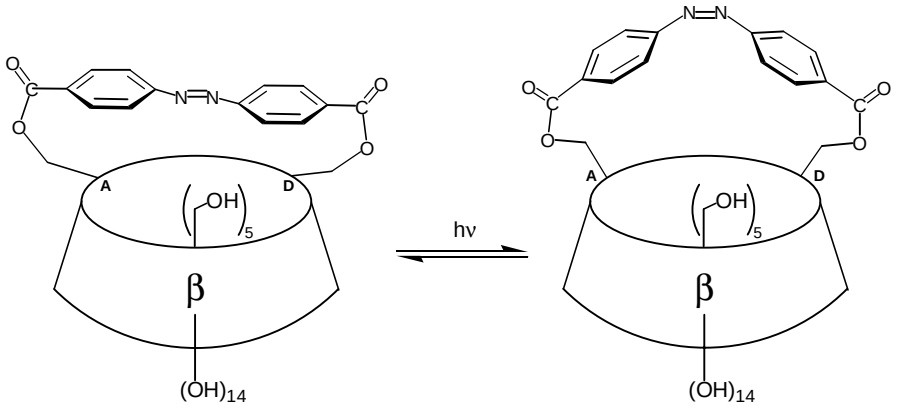
Scheme 6. Schematic representation of the possible dimeric isomers formed, by reacting porphyrin-atropoisomers and A,D-diiodo-*β*-CD

between a thiolato-substituted porphyrin and two equivalents of A,D-diiodo-β-CD. This reaction gave a mixture of five different isomers (Scheme 6),[72] three of which are so-called side-type isomers and originate from the $\alpha\alpha\beta\beta$ porphyrin atropisomer, whereas the two remaining diagonal-type ones comprise an $\alpha\beta\alpha\beta$ porphyrin atropisomer unit (a procedure for the exclusive synthesis of the side-type isomers has also been reported[73]). The fluorescence of **ℜ-91** (which in fact is an equimolar mixture of two possible diagonal-type isomers) was readily quenched in the presence of either anthroquinone-2-sulfonate or naphtoquinone as shown by the non-linear dependency between substrate concentration and fluorescence strength. Benzoquinone on the other hand gave only weak quenching, commensurate with its weak binding to the host, as opposed to the other quinones.

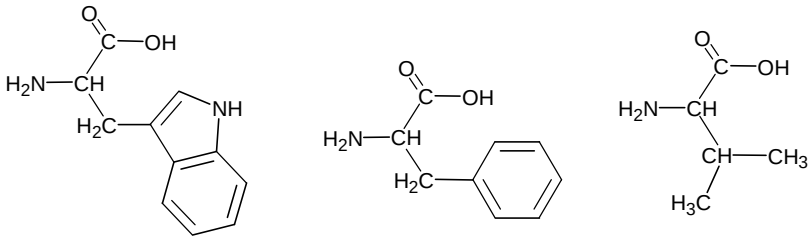
Complete *cis* photoisomerisation of the A,D-*trans*-4,4'-stilbene-disulfonate capped β-CD **ℜ-47** was achieved without reaching a photostationary state,[74] which is usually observed for non-cyclic stilbene derivatives. Upon further irradiation the *cis* isomer **ℜ-92** underwent a rarely encountered cyclisation reaction, leading to the phenantrene-capped species **ℜ-94** (probably via intermediate **ℜ-93**).



Cis / *trans* photoisomeriztion leading to modified binding abilities of the CD cavity have been reported by Ueno *et al*. Reaction of β-CD with 4,4'-bis(chlorocarbonyl)-*trans*-azobenzene afforded capped **ℜ-95** in 20% yield[75] (exclusive A,D-functionalisation was demonstrated later[76]). Upon irradiation **ℜ-95** was converted into the *cis* isomer **ℜ-96**, which displays a much larger cavity space. All aromatic and



ℜ-95 **ℜ-96**



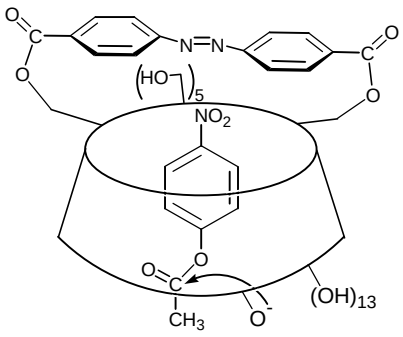
Trp Phe Val

ℜ-97 **ℜ-98** **ℜ-99**

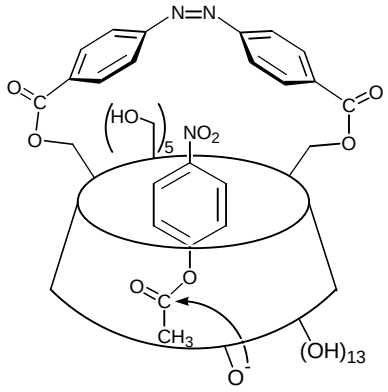
olefinic guest substances tested with **ℜ-96** led to higher binding constants than with *β*-CD. Conversely, smaller association constants than with *β*-CD were found for **ℜ-95** and the same guests, except for toluene which was included more tightly into **ℜ-95**. This feature confirms Breslow's earlier results showing that the cavity size may be significantly changed upon capping.[21] The most striking feature of **ℜ-96** is its ability to bind 4,4'-bipyridine, whereas **ℜ-95** did not at all. For each of the other substrates being tested the cavity of **ℜ-96** provided enough space to include even a second guest. This behaviour was in particular observed for amino acids **ℜ-97**-**ℜ-99**,[77] the size of which decreases in the order L-Trp > L-Phe > L-Val. The second binding constants decrease in the same order, which is consistent with the assumption that the guest which fills up the cavity space best is bound the tightest. On the other hand **ℜ-95** forms no inclusion complex at all with neither L-Trp (too large) nor L-Val (too small), whereas two L-Phe can be included. Although all aforementioned guest inclusion reactions followed a stoechiometrical behaviour (they form either host⊂guest or host⊂guest$_2$ complexes), as evidenced by circular dichroism experiments, non-stoechiometrical changes were sometimes observed between host **ℜ-95** and certain guests. This effect was related to non-covalent interactions between the substrate and the CD cavity outer wall rather than

the inside. Intramolecular hydrogen bond disruption within the CD was also considered to be a possible cause for this phenomenon. Substances likely to give rise to non-stoechiometrical behaviour during titration included those bearing amino and / or carboxylic acid functions[78] as well as some organic solvents.[79]

p-Nitrophenylacetate was found to be more favourably hydrolysed by **ℜ-96** than by **ℜ-95**[80], as could be deduced from the 5-fold increase in the apparent overall hydrolysis rate (k_c/K_m; these constants were evaluated from a Lineweaver-Burk plot[81]). This observation reflects in fact the tighter binding produced by **ℜ-96**, even if the maximum rate constant (k_c) obtained with **ℜ-96** is smaller than with **ℜ-95**. It seems that the substrate undergoes deeper inclusion in **ℜ-96**, which brings the ester group in a less favourable position to a secondary hydroxyl group than in **ℜ-95**. Note that neither **ℜ-95** nor **ℜ-96** displays any catalytic activity in the hydrolysis of *m*-nitrophenylacetate, while *β*-CD promotes the hydrolysis of the *meta* isomer (see above, "*meta* selectivity"[25]). This inversion is triggered by the larger cavity space provided by **ℜ-96**, which allows binding of the *p*-isomer in **ℜ-96**.

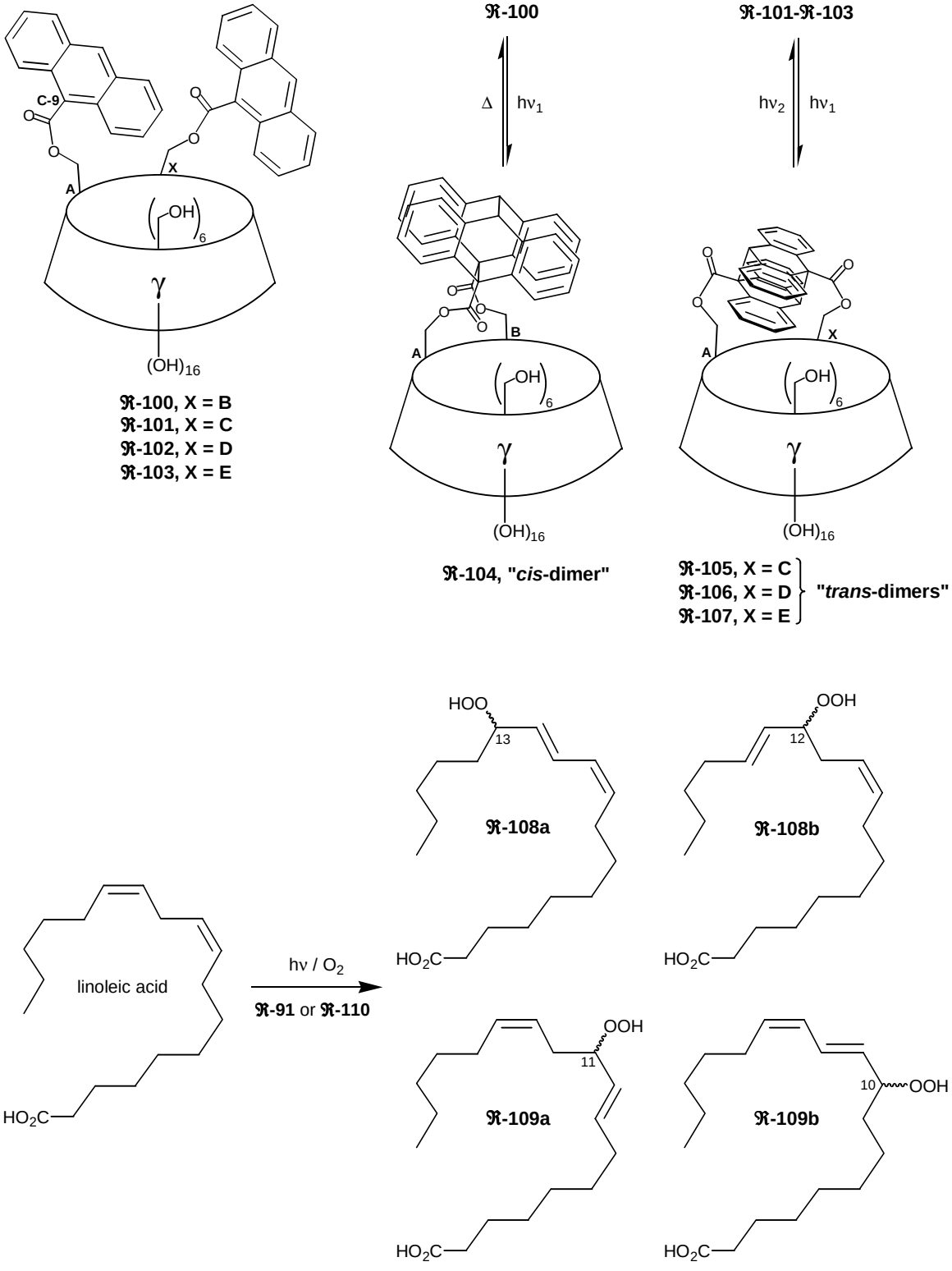


ℜ-95 •*p*-nitrophenylacetate



ℜ-96 •*p*-nitrophenylacetate

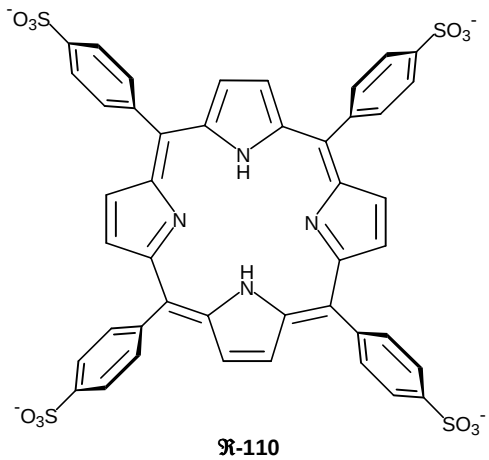
The possibility of linking two pre-functionalised glucose units using photochemical cyclisation has also been reported. The anthracene moieties of *γ*-CDs **ℜ-100**-**ℜ-103** underwent (reversible) dimerisation upon irradiation, thus affording capped compounds **ℜ-104**-**ℜ-107**.[82] Although the "*trans*-dimer" is usually the favoured configuration in C-9-substituted, photo-induced anthracene dimers, **ℜ-104** displays a *cis* geometry, in fact the sole configuration that may be obtained from the A,B-substituted CD **ℜ-100**. Capped **ℜ-104** turned out to be the least stable of the four synthesised compounds, owing to the strain within the short bridge.



Scheme 7. Photo-induced oxidation of linoleic acid

The first stereospecific photo-induced olefin oxidation triggered by a CD was achieved by Kuroda *et al.*[83] Equimolar amounts of the sandwiched porphyrin **ℜ-91**

(diagonal-type isomers) and linoleic acid (octadeca-9,12-dienoic acid) in the presence of singlet oxygen afforded a 82:18 mixture of the hydroperoxidated products **ℜ-108a,b** / **ℜ-109a,b**, respectively (Scheme 7). No regioselectivities were observed when a particular porphyrin derivative bearing no receptor sites (**ℜ-110**) was used. Clearly the CD catalyst favours hydroperoxidation of the C12-C13 double bond. Moreover, significant ees of 20 and 12% for **ℜ-108a** and **ℜ-108b**, respectively, were measured.



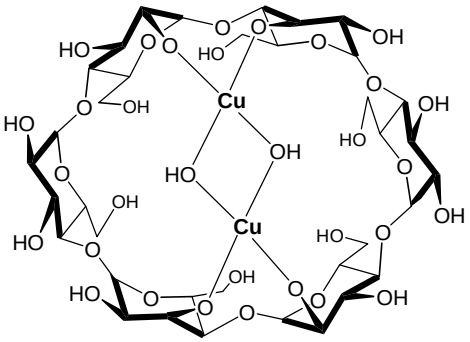
ℜ-110

I.3. Caps bearing metal Centres

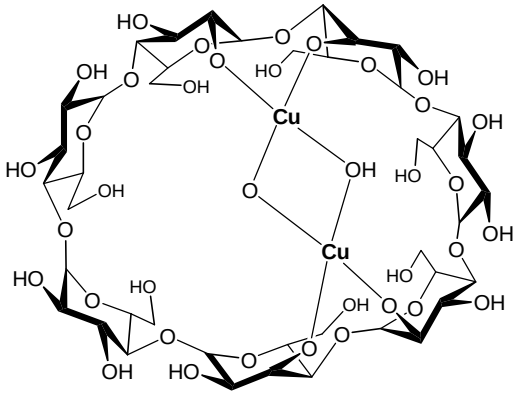
I.3.1. Bridging the secondary rim

The binuclear nature of copper(II) complexes resulting from the reaction in $NaOH/H_2O$ solutions of copper(II) salts with either α- or β-CD has been investigated by Matsui *et al.*[84] Potentiometric and conductometric titrations as well as molecular models have led to the identification of structures **ℜ-111** and **ℜ-112**, where the 3^A and 2^B as well as 3^D and 2^E positions have been bridged by a Cu^{II} ion through covalent bonding.[85] Both metal ions are themselves linked to each other either through two μ-OH (**ℜ-111**) or one μ-OH and one μ-O (**ℜ-112**) bridges. Interestingly, both CDs, initially dextrorotatory, have become levorotatory upon complexation. This effect is likely to arise from the important distortion of the CD macrocycles upon bridging. A later study by Polavarapu *et al*. provided spectroscopic evidence for covalent linking of the Cu^{II} ions to the CD torus.[86] Major changes in the vibrational circular dichroism

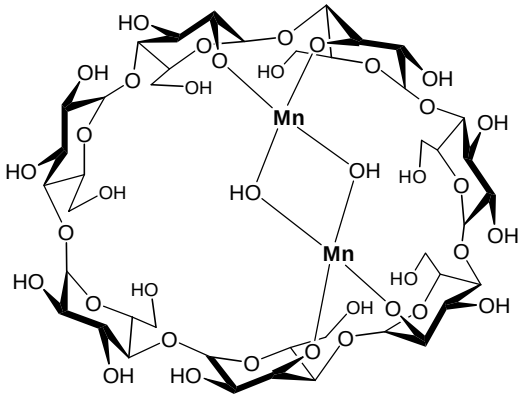
spectrum of α- and β-CD upon copper complexation in the exocyclic C–O–H bending vibrations region as well as an important decrease of the exocyclic C–O stretching bands demonstrate the involvement of secondary hydroxyl groups in copper bonding.



ℜ-111



ℜ-112

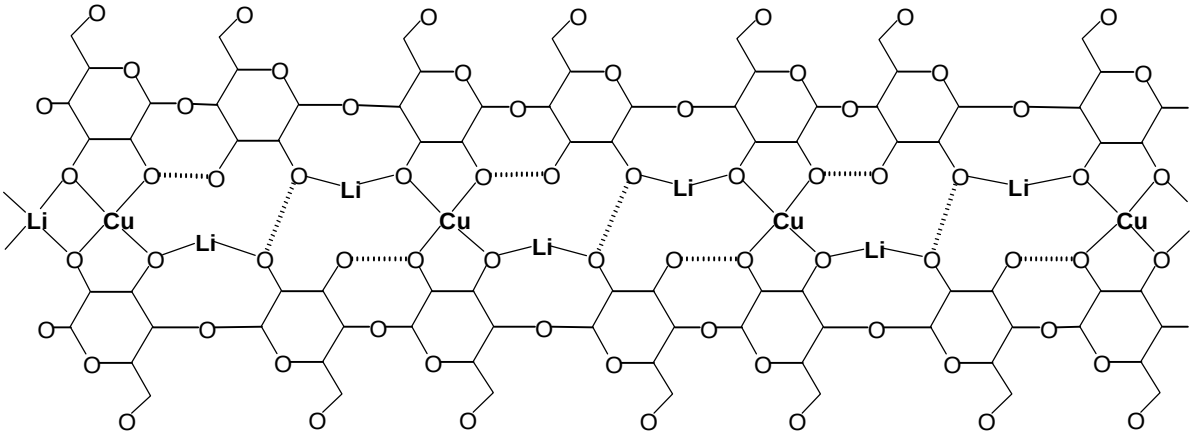


ℜ-113

Dismukes *et al*. have synthesised an analogous binuclear β-CD-manganese(III) complex, **ℜ-113**, in order to provide a model for Mn^{III} and Mn^{IV} cluster-containing enzymes.[87] A reversible two-electron oxidation was observed by cyclic-voltammetry, whereas reduction to the usually more stable Mn^{II} states was not possible.

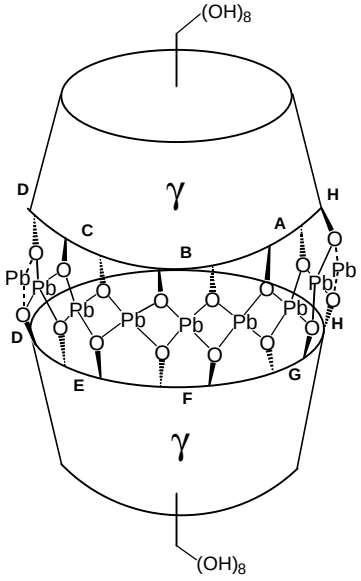
A quite different outcome was observed by Klüfers *et al*. when reacting β-CD with Cu^{II} in the presence of LiOH instead of NaOH. In this case the sandwich-type $Cu^{II}_4Li_7$-complex **ℜ-114** precipitated.[88] An X-ray diffraction study revealed that both cavities are linked via metal centres coordinated to the partially deprotonated secondary face. Each of the four Cu^{II} ions acts as a double linker between two glucose units facing each other and seven tri-coordinated Li^{I} ions are involved in bridging adjacent glucose

units. The partial hydroxyl deprotonation was explained by the existence of an interglycosidic hydrogen bond network which prevents full deprotonation.



ℜ-114 (the position of the remaining O*H* protons is not shown)

Complete deprotonation of the secondary hydroxyls together with a uniform metal coordination pattern linking two γ-CDs was achieved using lead(II) as the metal in the presence of NaOH.[89] In **ℜ-115** each secondary alkoxide anion is coordinated to two bridging Pb^{II} ions. The highly symmetrical CD dimer, which comprises sixteen Pb^{II} ions altogether, is believed to be formed via a cooperative mechanism. Each Pb^{II} ion adopts a square pyramidal configuration.



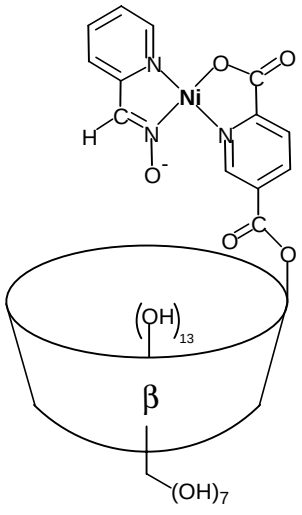
ℜ-115

As will be seen in the next section, the introduction of a metal centre into an organic cap provides the host with an additional recognition site, to which a bound guest

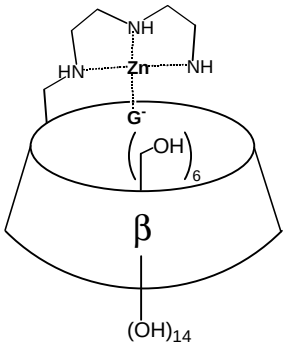
bearing appropriate functionalities can coordinate and thus enhance the binding strength of the host and possibly accelerate a catalytic reaction.

I.3.2. Metals as supplementary recognition sites

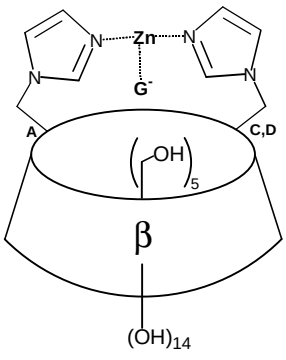
The first metalloenzyme model compound (**ℜ-116**) was developed by Breslow *et al*.[90] The nickel atom of this compound actually does not act as a second recognition site. It was rather meant to connect the active pyridine-carboxaldoxime group to the CD cavity. *p*-Nitrophenylacetate hydrolysis proceeded four times faster than the uncatalysed reaction. A competitive inhibition experiment with cyclohexanol firmly established the substrate binding by the cavity prior to reaction. Tabushi *et al*. demonstrated the utility of a metal centre covalently bound to the CD as a second recognition site for coordinating the anionic functionalities of encapsulated hydrophobic substrates, thus conferring it cooperative binding abilities.[91] For example, **ℜ-117** binds 1-anilino-8-naphtalenesulfonate 4 times stronger than without a zinc centre. Metal-capped **ℜ-118** (A,C and A,D regioisomer mixture), for which the presence of a chelate was verified by electronic spectroscopy,[92] exhibited 6.6 times tighter binding of cyclohexyl-1,4-dicarboxylate than the metal-free derivative.[93] Interestingly, certain anionic guests (G^-), such as cyclohexylcarboxylate, produced slightly stronger hydrophobic interactions with **ℜ-117** than with **ℜ-118**, while coordinated to the metal centre. This effect was attributed to the more flexible nature of the cap in **ℜ-117**, which allows the coordinated guest to optimally fit the cavity.



ℜ-116

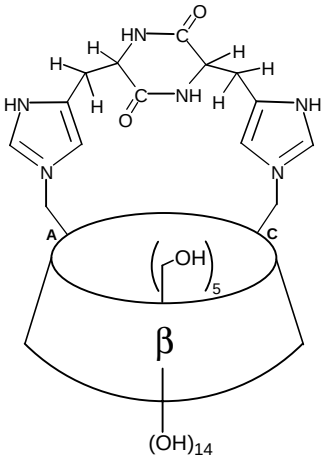


ℜ-117

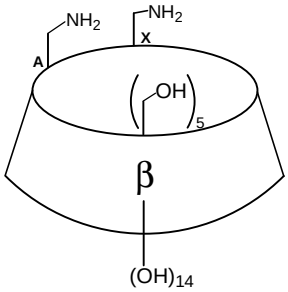


ℜ-118

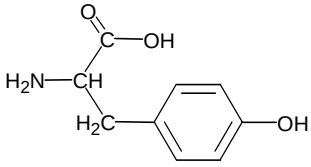
Rizzarelli *et al.* successfully tethered a L-hystidyl-L-hystidyl entity to the positions A and C of a *β*-CD derivative.[94] The resulting diimidazolyl ligand **ℜ-119** was reported to display chelating behaviour towards Cu^{II}, thus making it a potential receptor for anionic organic guests.



ℜ-119



ℜ-120, X = B
ℜ-121, X = C
ℜ-122, X = D

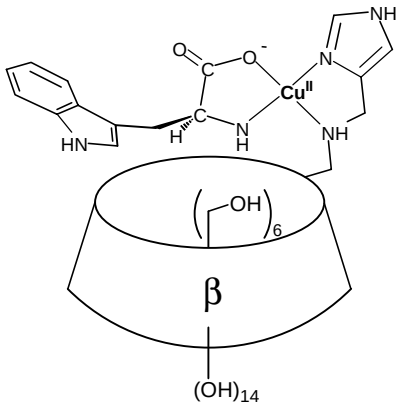


p-Tyr

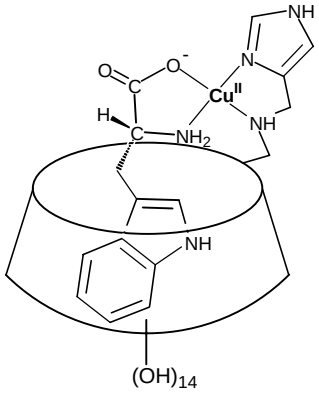
ℜ-123

The molecular recognition of amino acids by Cu^{II} chelate complexes obtained from **ℜ-120**-**ℜ-122** has been investigated by means of ligand exhange chromatography (LEC-HPLC).[95] Enantiomer separation of racemic mixtures of Phe (**ℜ-98**) or *p*-Tyr (**ℜ-123**) could only be achieved with the A,B regioisomer **ℜ-120**. The circular dichroism spectrum of a ternary complex of **ℜ-120** displays specific shapes and intensities depending on the absolute configuration of the included amino acid. Such differences between L- and D-amino acids were neither observed with A,C-capped **ℜ-121** nor with A,D-capped **ℜ-122**, suggesting no significant interactions between the interior of the cavity and the guest. Support for this observation was provided by competition experiments with the non-coordinating adamant-1-ol. Progressive addition of this alcohol to a ternary complex of **ℜ-120** led to a decrease of the absolute value of the molecular ellipticity $|\Delta\varepsilon|$ in circular dichroism for both D- and L-amino acids owing to the competition reaction. For **ℜ-121** and **ℜ-122** the spectra of the corresponding binary complexes remained unchanged, which is in keeping with a coordination of the amino acid outside the CD cavity. It was suggested that in the cases of **ℜ-121** and **ℜ-122** the metal caps partially closed the primary cavity entrance, thus preventing simultaneous coordination of the guest and intra-cavity interaction. The discrimination observed with **ℜ-120** is quite different from the one believed to take place in mono-

histamino-functionalised β-CD cavities, such as **ℜ-124**.[96-98] In the latter case, discrimination was assigned to the formation of an unsymmetrical *cis*-CuN_2 unit. Assuming that the imidazole-N atom favours *trans*-binding of the incoming amino group (and not of the carboxylate), it becomes obvious that only D-Trp can be trapped inside the cavity.

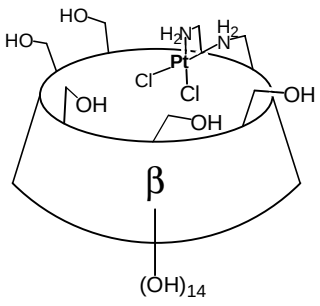


ℜ-124•Cu^{II}•(L-Trp)

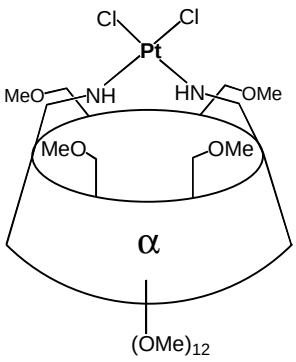


ℜ-124•Cu^{II}•(D-Trp)

The $PtCl_2$-complex **ℜ-125** of the aforementioned A,B-diamino-β-CD led to the third crystal structure determination of a metal-capped CD.[99] It is noteworthy that apart from the slight inward tilting of the substituted glucose units, the macrocyclic torus is not subjected to important distortion upon complexation. All glucose units have kept their initial $^4C_1$ chair conformation. Bearing in mind that the intramolecular HO-2–HO-3 hydrogen bond network is still intact, any dramatic shape modifications of the cavity resulting from the bridging of two glucose units appears unfavourable as long as this rigidifying property remains. One way to induce shape modification, while still retaining hydrosolubilty, consists in using CDs where all non-substituted hydroxy groups have been methylated.[100]



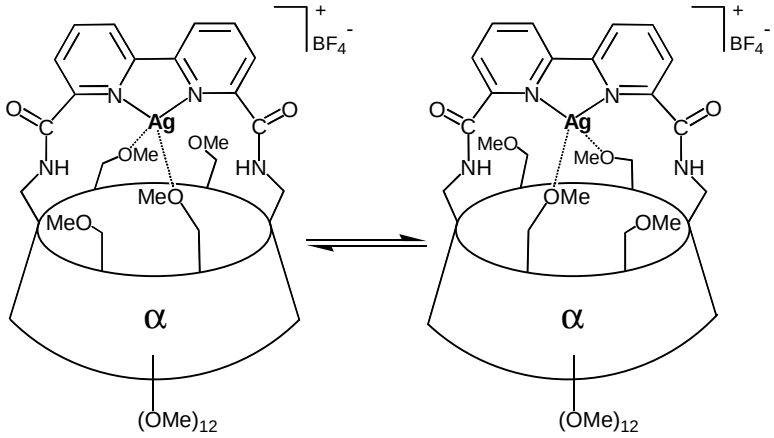
ℜ-125



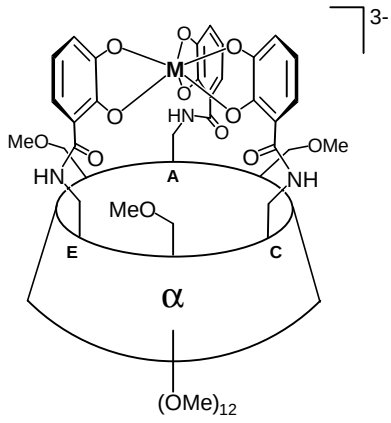
ℜ-126

Evidence for the impressive flexibility acquired by a CD torus that has no hydroxy groups is given by the crystal structure of the $PtCl_2$-capped A,D-diamino-α-CD **ℜ-126**.[101] Here the cavity has undergone an unprecedented narrowing upon transannular bridging with a very short connector. The B an F units have furthermore adopted a $^0S_2$ skew-boat conformation, which was probably induced by hydrogen bonding to a single included (adventitious) water molecule. It can be easily anticipated that such important spatial modifications of the host cavity may lead to unexpected guest selectivities.

In another example the potential multitopic coordinating character of the primary rim methoxy groups (see chapter III) could be illustrated.[102] A VT NMR study established the fluxional behaviour of the four primary face ether groups of the bipyridyl-silver complex **ℜ-127**, which compete for metal-coordination.



ℜ-127



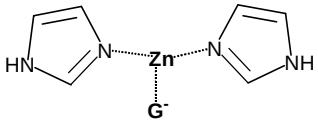
ℜ-128; M = Fe^{III}
ℜ-129; M = Al^{III}

Aiming at the development of novel synthetic analogues of natural siderophiles (molecules produced by micro-organisms under iron-deficient conditions to bind and solubilise iron), Boger *et al.* described the first examples of C_3-symmetrical metal capped CDs (**ℜ-128** and **ℜ-129**).[103] These were obtained after regioselective functionalisation of the A,C and E positions of an α-CD and subsequent methylation of the remaining hydroxyl groups. Introduction of three 2,3-dihydroxybenzoylamino groups afforded a hexadentate ligand able to bind to a single metal centre. Indeed, formation of complex **ℜ-128** was shown to take place in aquous medium at pH values higher than 4, by UV-vis spectroscopy. Moreover, at basic pH, coordination of an Al^{III}

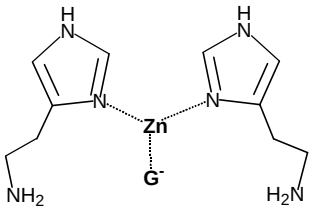
ion, leading to **ℜ-129**, could be evidenced in the ^{1}H NMR spectrum by the upfield shifts of the aromatic protons and of the B,D,F-methyl signals upon complexation. Moreover, the downfield shifts of certain proton signals of *p*-nitrophenolate upon addition of the latter to a solution containing **ℜ-129**, demonstrated the ability of the CD-receptor to bind this anion.

I.3.3. Metals as catalytic centres

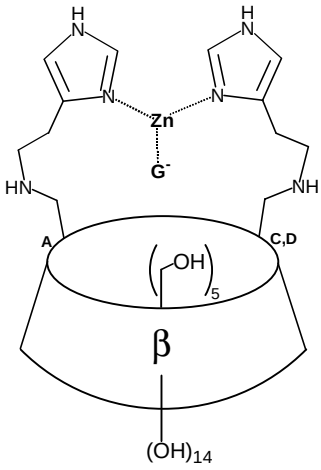
An 8-fold reaction rate increase was found for the carbon dioxide hydration in the presence of the bisimidazole regioisomeric mixture **ℜ-118**[23] when compared to the reaction carried out with complex **ℜ-130**,[104] which lacks a cavity. In keeping with the base-dependant nature of the catalysis, two extra amino groups, as in the bis(*N*-histamino) derivative **ℜ-131** were introduced to improve the catalytic process. Indeed hydration proceeded ten times faster than with **ℜ-118**, but only three times as fast as with the corresponding "cavity-free" complex **ℜ-132**. When the catalytic reactions were carried out in imidazole buffer in the presence of **ℜ-131**, an extra imidazole molecule was reported to coordinate the metal centre.[92]



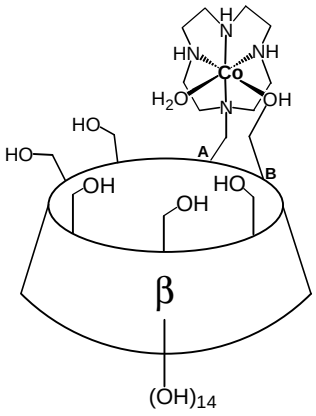
ℜ-130



ℜ-132



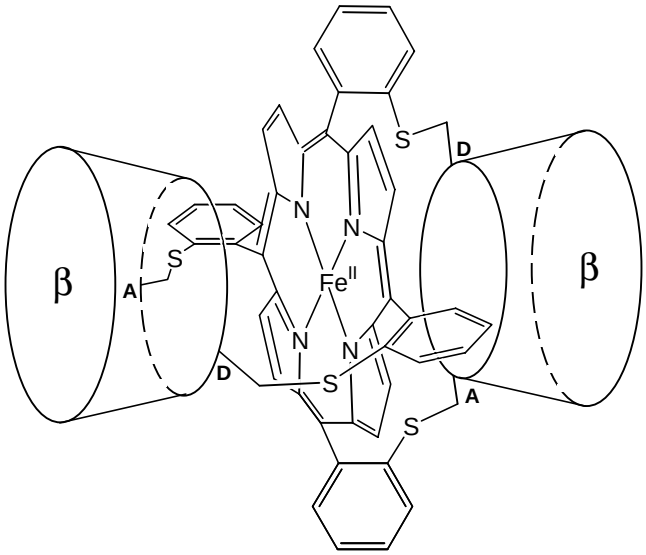
ℜ-131



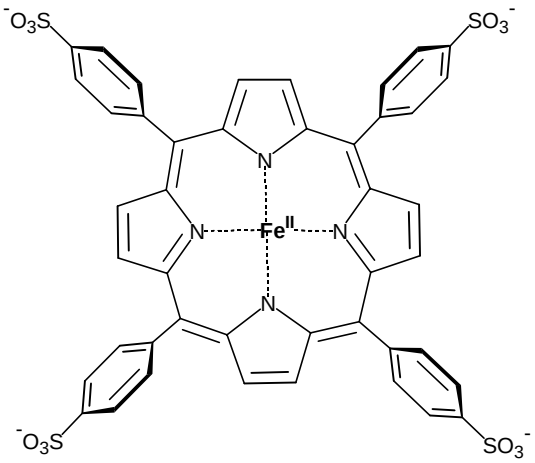
ℜ-133

Czarnik *et al*. reported on a catalytic system (**ℜ-133**) in which a Co^{III}-cyclen moiety is grafted onto the primary rim of a *β*-CD. Noticeably, the metal centre bridges an adjacent glucose unit via coordination of its hydroxyl group.[105] An 900-fold rate acceleration of *p*-nitrophenylacetate hydrolysis compared to the non-catalyzed reaction was achieved.[106] As for Breslow's Ni^{II}-CD catalyst **ℜ-116**[90], intra-cavity binding of the substrate was verified by performing the cyclohexanol inhibition experiment.

Well-improved epoxidation rates of cyclohexene in aqueous media were achieved in the presence of **ℜ-134** (diagonal-type isomers) and iodosobenzene with respect to **ℜ-135**, which bears no hydrophobic binding sites.[107] The enhanced reactivity of an otherwise almost unreactive olefin was attributed to the favourable binding of



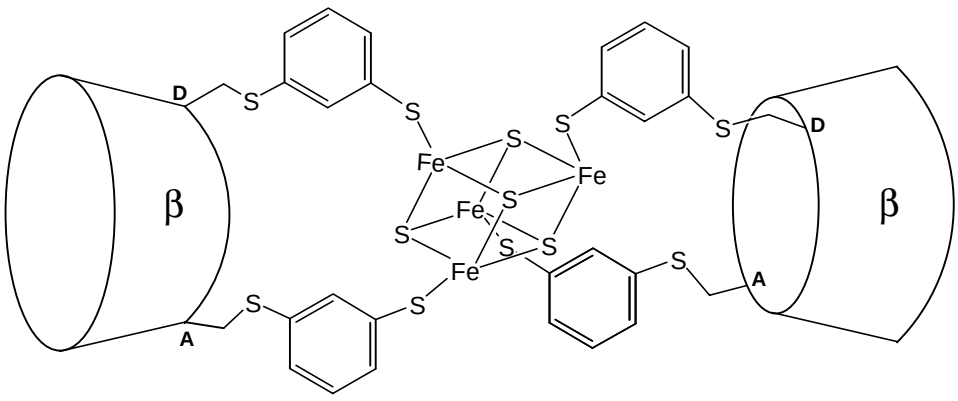
ℜ-134



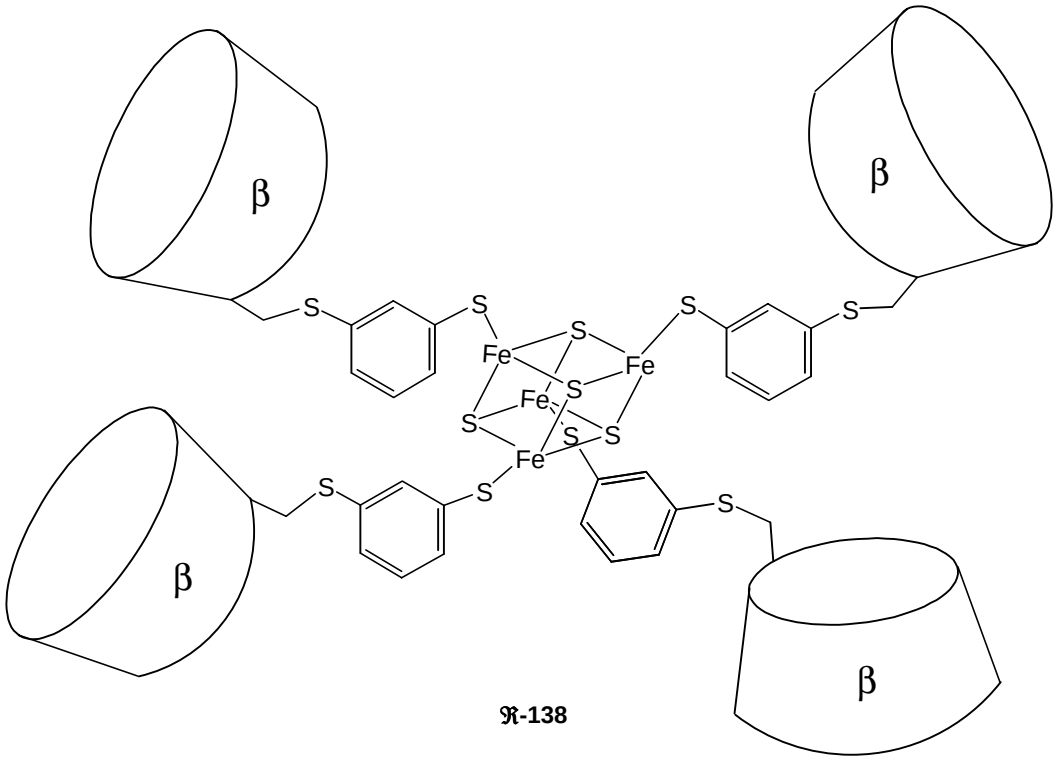
ℜ-135

cyclohexene by the cavity. Conversely, an effective contact between the highly reactive oxene (Fe^{+}=O) species and the olefin in heterogeneous media is very difficult in the case of **ℜ-135**. A possible better stabilisation of the oxene in the presence of a hydrophobic environment has also been considered.

The stabilisation of the naturally occurring Fe_4S_4 cluster in aqueous solution was achieved by grafting two A,D-dimercaptan-functionalised *β*-CDs onto the cluster, in a sandwich-type fashion, affording **ℜ-136**.[108] Clusters like **ℜ-136** are used as

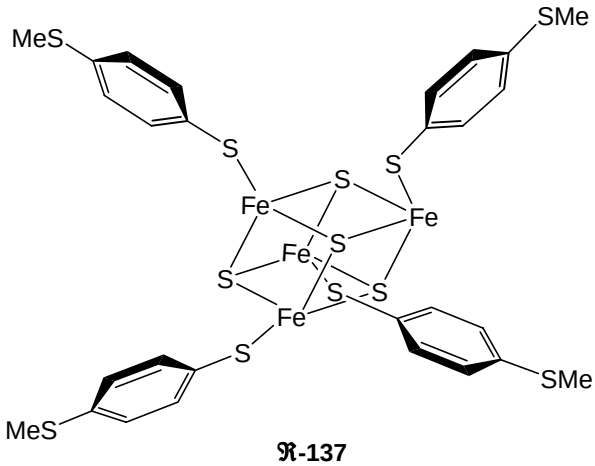


ℜ-136

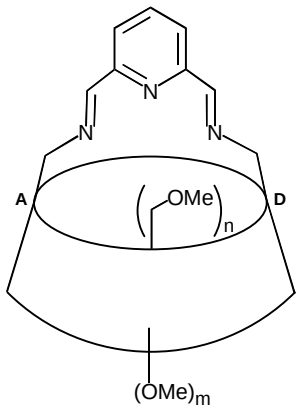


ℜ-138

model compounds for mimicking the active site core of ferredoxin. Indeed **ℜ-136** possesses a 21 times larger stability in water than the reference arylthiolate cluster **ℜ-137** in 5% DMF-H_2O media. Interestingly, the stability increase was only 13-fold for the *flexibly*-capped species **ℜ-138**.



ℜ-137



ℜ-139; n = 4, m = 12
ℜ-140; n = 5, m = 14

An alternative to the recently described 2,6-bis(iminoaryl)pyridine-$FeCl_2$ olefin polymerisation catalysts has been found by Armspach and Matt. Replacement of the classical chain size-controlling iminoaryl residues with permethylated α- and β-CD derivatives afforded tridentate ligands **ℜ-139** and **ℜ-140**, respectively.[109] The MAO-

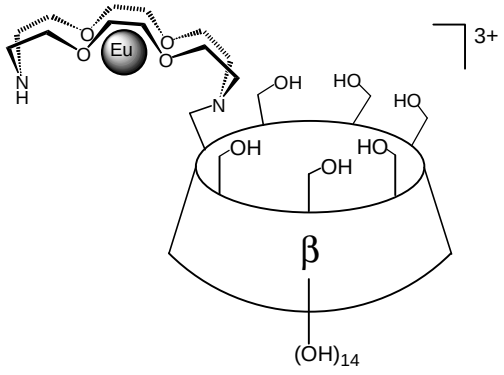
activated (methylaluminoxane) complex **ℜ-140**-$FeCl_2$ displays a similar behaviour in the polymerisation of ethylene as the known 2,6-bis[imino(2,6-dimethylphenyl)]pyridine-based Fe^{II}-complex, in terms of molecular weight and cristallinity of the polymer, although the latter is more active. The significantly lower activity of the α-CD derivative **ℜ-139** is thought to be the result of the smaller cavity size of the latter as well as difficulties in catalyst activation by MAO, partly arising from unfavourable interactions between the Lewis acid and the CD-ether oxygen atoms.

I.3.4. Photochemical interactions between included guests and a rigidly positioned metal centre

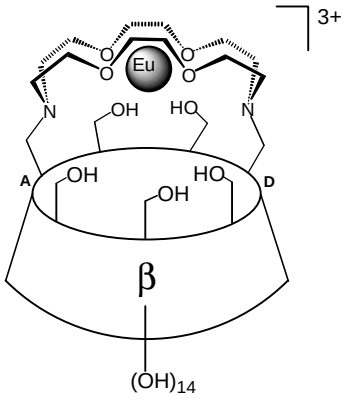
Attempts to develop chemosensors bearing photoactive centres able to emit light upon recognition of a guest by an adjacent binding site led Nocera *et al*. to the design of the β-CD derivative **ℜ-141**, which is flexibly-capped with a diaza crown-ether unit prone to coordinate a lanthanide centre.[110] In a benzene-containing D_2O solution, the Eu^{III} luminescence, which is weak, was found to depend on the benzene concentration. This phenomenon was attributed to an absorption – energy transfer – emission (AETE) process; note, luminescence was not observed with a related $Eu^{III}\subset$aza complex that does not contain an appended CD. However emission was easily quenched by H_2O (study carried out in D_2O), indicating that the metal-containing cap is not maintained in close proximity to the guest and therefore must be pointing away from the cavity. The rigidly A,D-capped version of the previous host, **ℜ-142**,[111] was expected to remedy the lack of energy transfer efficiency, because of the shorter distance separating the cap from the cavity. Unfortunately, owing to the location of the highly positive metal charge close to the cavity, a drastic decrease of the binding strength of **ℜ-142** towards benzene was observed.[112] Therefore no emission resulting from energy transfer from bound benzene could be brought to a fore. This problem was solved by introducing a cap bearing three carboxylate functions (**ℜ-143**), which neutralise the lanthanide ion charge.[113] Due to the interference of ligand-to-metal charge transfer from the carboxylate groups to Eu^{III} with the AETE process, Tb^{III} was chosen as emission centre instead. Thus, encapsulated mono- or bicyclic aromatic compounds were able to trigger highly sensitive luminescence responses. Recently, the fact that this property was found

to be preserved in microfluidic media led to the design of a novel supramolecular microfluidic optical chemosensor, after incorporation of **ℜ-143** into a sol-gel film.[114]

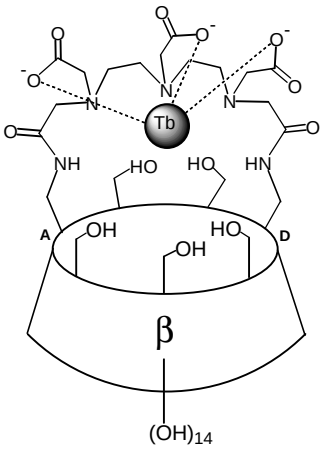
The first example of electron transfer through a CD cavity from a ruthenium(II) centre to a bound guest molecule has been reported by Armspach and Matt. Benzoquinone was shown to form a 1:1 inclusion complex with the tris(bipyridyl)Ru^{II}-capped, permethylated α-CD derivative **ℜ-144**.[115] Upon irradiation of the *exo*-oriented metal centre, the fluorescence quenching by benzoquinone at variable guest concentrations was studied. Static and diffusional quenching processes through electron transfer were found to take place along with intra-cavity electron transfer, which accounts for *ca*. 10% of the overall quenching process.



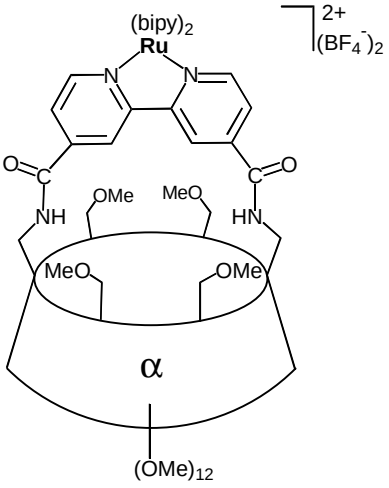
ℜ-141



ℜ-142



ℜ-143



ℜ-144

I.4. Conclusion

As has become apparent from the studies discussed in this review, the regioselective capping of a CD entrance constitutes an efficient means to achieve di- or trifunctionalisation of one of the cavity rims. Moreover, the bridging of two glucose units with an appropriate organic moiety allows tuning of the receptor binding properties in aqueous media. Depending on the shape and the size of the cap, substrate preferences can be dramatically altered with respect to those observed for native or flexibly functionalised CDs. This may result in inverted selectivities during catalytic reactions.

As outlined in the last section of this review, the interactions between bound guests and a metal centre integrated in a cap are most favourable when the latter is rigidly fixed above the cavity entrance. An interesting challenge is to extend the application of such systems to catalytic reactions of industrial importance (*i.e.* transition metal-catalysed reactions), which has been realised for the first time in our group. The studies aiming at the development of P(III)-containing CD catalysts active for this type of reactions will be presented in the following chapters.

I.5. References

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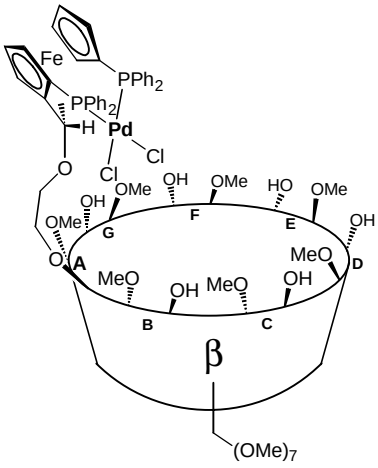
Chapter II. Synthesis of large chelate rings with diphosphites built on a cyclodextrin scaffold

II. Synthesis of large chelate rings with diphosphites built on a cyclodextrin scaffold

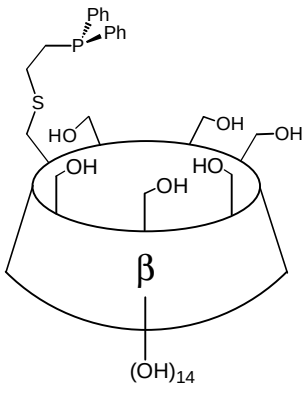
II.1. Introduction

II.1.1. P(III)-containing mono- and difunctionalised CDs

The first CDs bearing appended P(III) ligands were reported independently by the groups of Ito and Reetz in 1993. These ligands were obtained from easily available monofunctionalised CDs. The group of Ito managed to attach a chiral ferrocenyldiphosphine onto an O-3 position of a 2,6-permethylated *β*-CD.[1] Although the resulting ligand is almost insoluble in water, the corresponding $PdCl_2$ complex **ℜ-145** displays high solubility in this medium. It was shown by means of conductivity measurements that **ℜ-145** assembled in micelle-like aggregates above a given concentration. So far, however, no catalytic results involving this ligand have been reported.



ℜ-145



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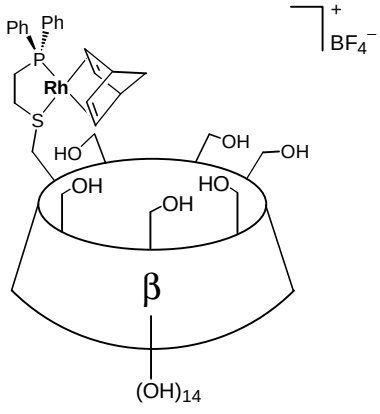
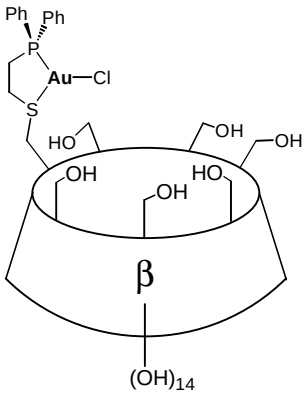
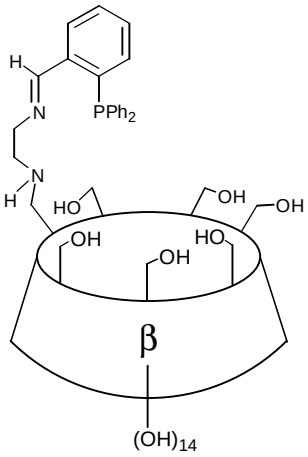


ℜ-147

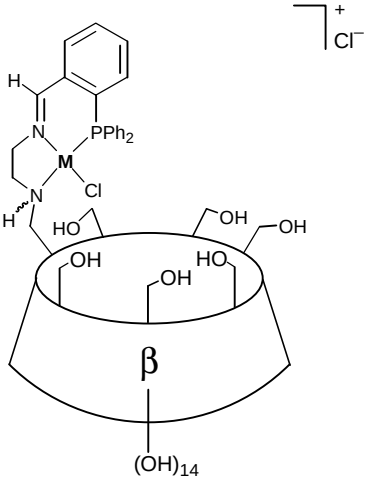
Reetz *et al.* reported the monophosphine **ℜ-146** which was used for the synthesis of the rhodium complex **ℜ-147**.[2] Surprisingly, unlike the related $[Rh(Ph_2PCH_2CH_2SMe)(NBD)]^+$ complex, **ℜ-147** turned out to be rather ineffective as a hydrogenation catalyst.[3] No explanation was given for this behaviour. A recent X-ray study showed that the cavity of **ℜ-146** is able to recognise specifically one of the two P-phenyl groups, by forming a self-inclusion complex in the solid state. There is no evidence for such a discriminating behaviour in solution. Formation of the gold(I) complex **ℜ-148**, which is expected to display antiarthritic and antitumor properties, has also been described.[4]



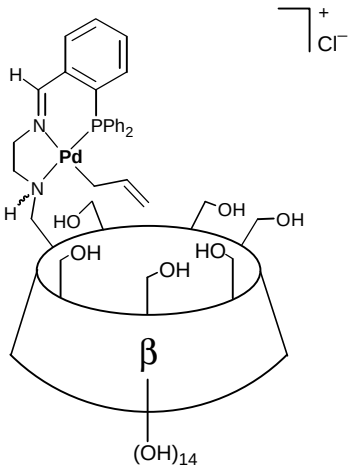
ℜ-148



ℜ-149



ℜ-150, **M** = **Pd**
ℜ-151, **M** = **Pt**

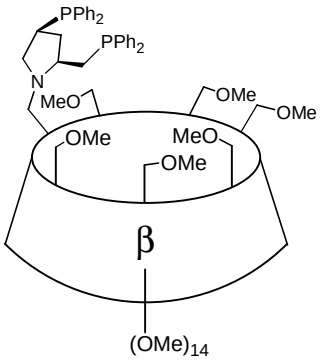


ℜ-152

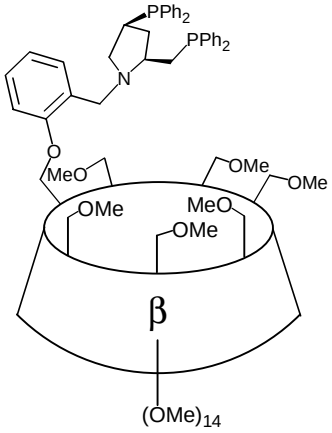
Jia *et al.* recently reported the synthesis of the *β*-CD derivative **ℜ-149**, containing a potential *PNN* tridentate ligand. This ligand was used for the preparation of the

palladium(II) and platinum(II) complexes **ℜ-150**-**ℜ-152**.[5] In both cases the NH nitrogen became stereogenic upon complexation, which resulted in the formation of two diastereoisomeric species, as revealed by the presence of two singlets in the corresponding ^{31}P NMR spectrum.

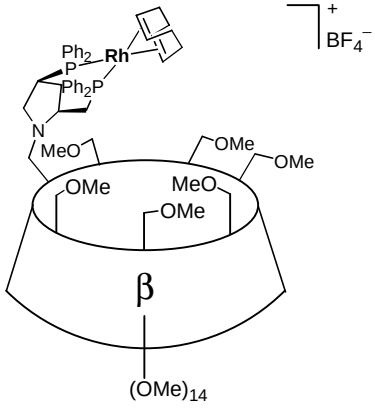
The chiral (2*S*,4*S*)-(−)-4-(diphenylphosphino)-2-(diphenylphosphinomethyl) pyrrolidine fragment could be successfully attached to a *β*-CD derivative, leading to diphosphines where the pyrrolidine is either directly connected to the C-6 carbon (**ℜ-153**) or separated from the CD by an *o*-xylyl spacer (**ℜ-154**). The two phosphines were used for the preparation of complexes **ℜ-155**/**ℜ-156** and **ℜ-157**/**ℜ-158**, respectively[6]. Note that the trigonal bipyramid structure proposed for the rhodium atom of **ℜ-157** could not be unequivocally confirmed spectroscopically.



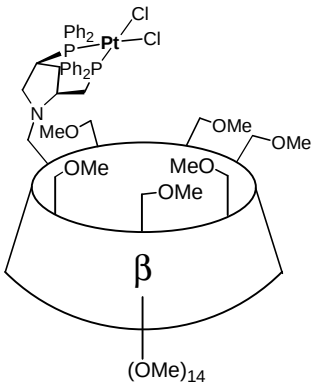
ℜ-153



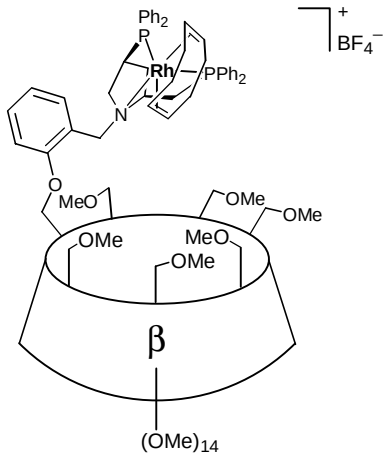
ℜ-154



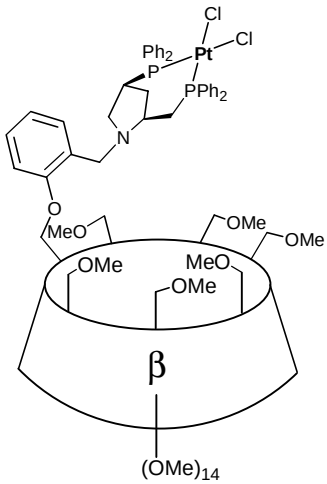
ℜ-155



ℜ-156

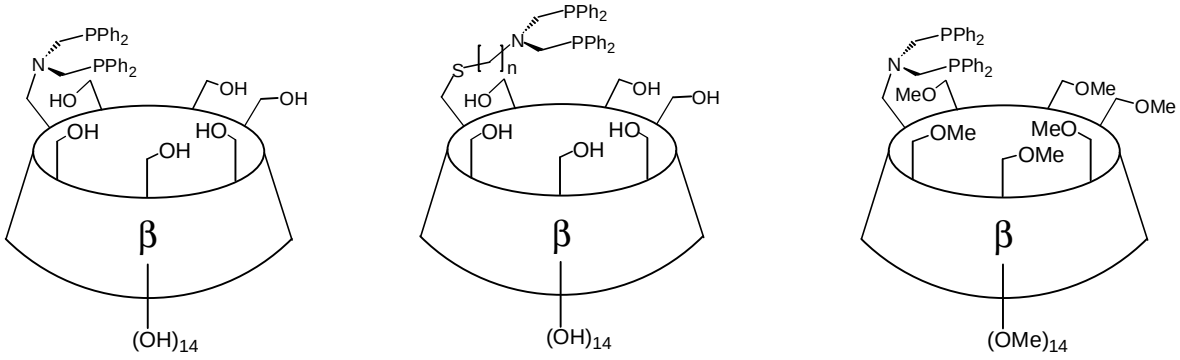


ℜ-157



ℜ-158

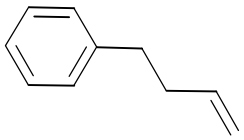
The first system which was shown to be able to combine the properties of a hydrophobic receptor with those of a catalytic centre was devised by Reetz *et al.* using diphosphines **ℜ-159**-**ℜ-163**.[7] Competitive hydrogenation experiments, carried out in 30% DMF-water with an *in situ* prepared Rh(I)- **ℜ-163** catalyst showed that olefin **ℜ-164** is converted 6.7 times faster than **ℜ-165**. Preferential substrate binding by the cavity, as demonstrated by a drop in selectivity upon addition of *p*-xylene to the reaction mixture, is undoubtedly responsible for this remarkable product distribution. Carrying out the same reaction with a related CD-free catalyst led to no substrate preference. The highest n/iso ratio in the hydroformylation of oct-1-ene (solvent: 30% DMF-H_2O) was observed with **ℜ-160** (n/iso = 3.2 *vs*. 2.6 for Rh/PPh_3-based systems), but the observed selectivity increase with respect to Rh/PPh_3-based systems remains weak. It is likely that the flexible nature of the coordinating fragment does not allow the catalytic centre to be held in a sufficiently rigid manner above the cavity entrance, thus preventing the cavity to behave as a second coordination sphere for the substrate.



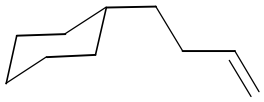
ℜ-159

ℜ-160, **n = 2**
ℜ-161, n = 3
ℜ-162, n = 4

ℜ-163



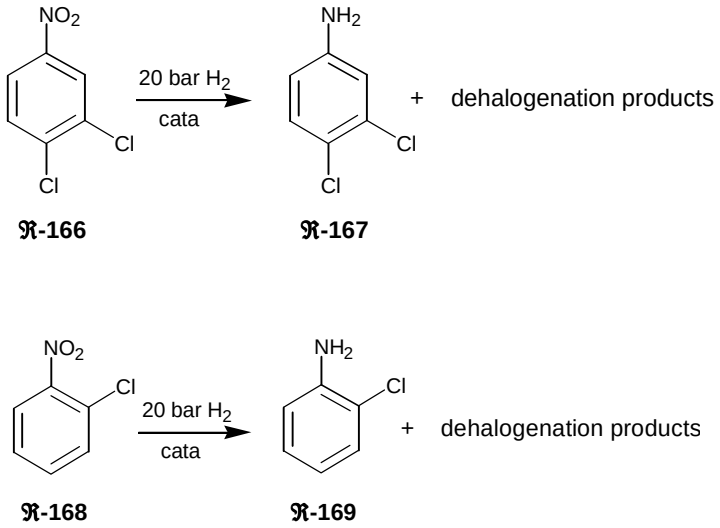
ℜ-164



ℜ-165

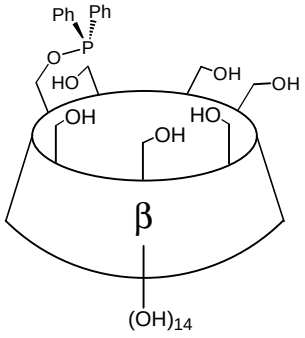
Interesting results came from the use of diphosphine **ℜ-159** as ligand in the rhodium(I)- and platinum(II)-catalysed chemoselective reduction of halo-nitro aromatic compounds under biphasic conditions (no additional organic solvent is needed).[8] Using a catalytic system obtained by mixing **ℜ-159** with $PtCl_2$(COD) allowed clean reduction of **ℜ-166** into **ℜ-167** (selectivity 99.5%), only trace amounts of dehalogenation products

being produced. Similarly, the **ℜ-159**/[Rh(COD)$_2$]BF$_4$ system afforded **ℜ-169** in 97.3% selectivity upon reduction of **ℜ-168**. The overall improved chemoselectivities provided by these systems over classic heterogeneous catalysts like Raney nickel are again believed to be the result of substrate inclusion in the CD cavity. Regardless of whether this is true or not, the above systems constitute a promising alternative to classical systems in terms of chemoselectivity and catalyst separation.

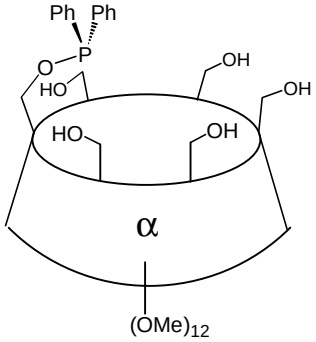


Hydroformylation with other CD-derived phosphines have been reported by Ichikawa *et al*.[9] In a one-phase medium (solvent: DMF), an *in situ* prepared rhodium(I) complex derived from the *β*-CD-derived monophosphinite **ℜ-170** displayed moderate activity in the hydroformylation of dec-1-ene, 4-phenyl-but-1-ene (**ℜ-164**) and oct-1-ene. The observed regioselectivities fall again in the range of those observed for conventional systems (l/b = 2.38; 1.80 and 2.88, respectively). Competition reactions carried out with dec-1-ene and **ℜ-164** in the presence of the *β*-CD-based catalytic system **ℜ-170**/[RhCl$_2$(COD)]$_2$ showed that the latter displays a marked substrate selectivity in favour of **ℜ-164** (61:39 at 60% conversion). For comparison, the substrate selectivity found for the classical Rh/PPh$_3$ catalyst is only 55:45. The analogous *α*-CD-based catalytic system **ℜ-171**/[RhCl$_2$(COD)]$_2$ showed no selectivity change with respect to the control experiment. Although the authors claim that the observed selectivity enhancement obtained with **ℜ-170** stems from substrate binding inside the cavity, it is likely that the catalytic process does not involve the receptor, not only because the

reaction is carried out in an organic solvent (DMF, which occupies the cavity interior), but also because the loosely anchored catalytic centre is located away from the cavities.

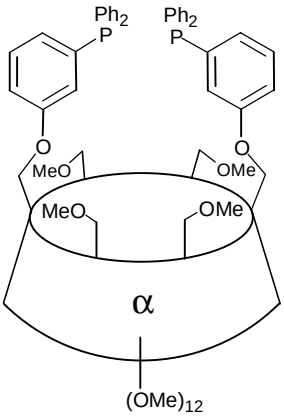


ℜ-170

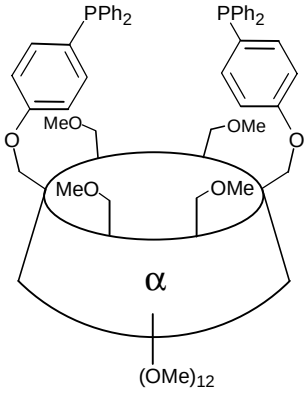


ℜ-171

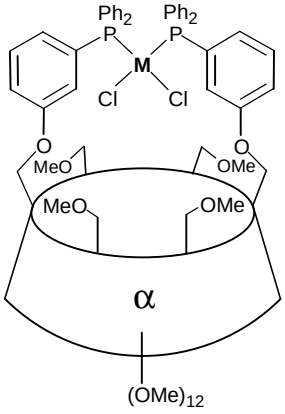
As already mentioned in chapter I, a way to reduce the flexible character of the metal centre in CD-based catalysts consists in using CDs equipped with two independent binding sites so as to form a chelate complex that positions the metal centre above the cavity entrance. The first diphosphine ligands meeting this requirement have been synthesised in our group. The chelating C_2-symmetrical bidentates **ℜ-172** and **ℜ-173** were obtained from α-CD using a regioselective difunctionalisation procedure[10] which allows the convenient tethering of two phosphine fragments onto two diametrically opposed (A and D) glucose units. Although the formation of *cis* chelate complexes has been observed, both ligands clearly favour *trans* chelation, as exemplified by complexes **ℜ-177**-**ℜ-182**.[11] Note that **ℜ-175** and **ℜ-180** as well as **ℜ-176** and **ℜ-181** are rapidly interconverting so that isolation of the individual isomers was not possible. Furthermore, **ℜ-182** efficiently catalysed the hydroformylation of oct-1-ene in a MeOH/H_2O mixture. However, in this particular solvent mixture (the complex is not soluble in pure water), the formation of an inclusion complex between the olefin and the cavity is rather unlikely. This is reflected by the observed linear / branched aldehyde selectivity (l/b = 2.3), which corresponds to standard values. Clearly, to access the concept formulated above, water-soluble catalysts of the type described in this paragraph need to be synthesised.



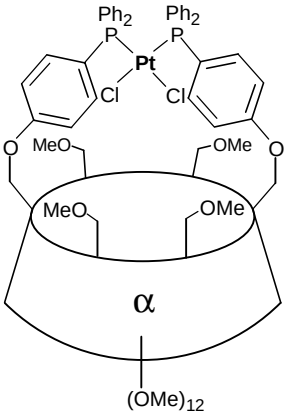
ℜ-172



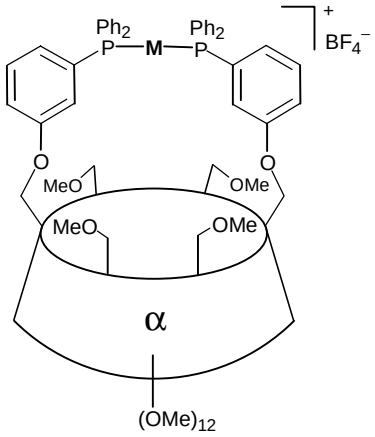
ℜ-173



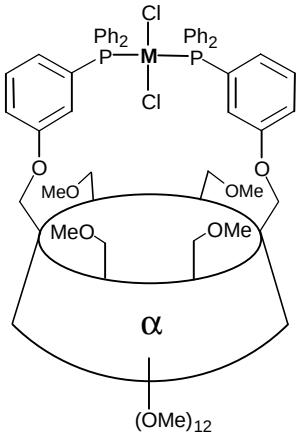
ℜ-174, **M** = **Pt**
ℜ-175, **M** = **Pd**



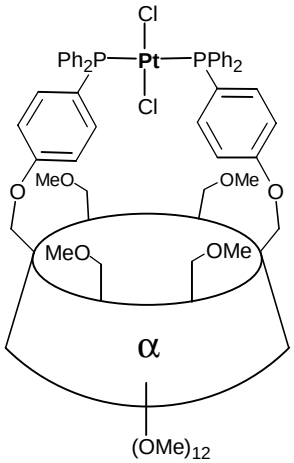
ℜ-176



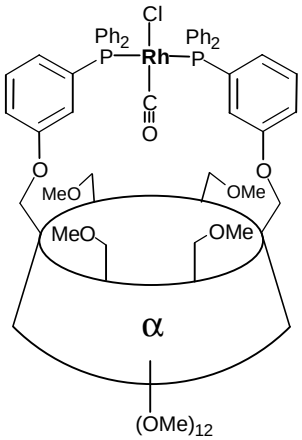
ℜ-177, **M** = **Ag**
ℜ-178, **M** = **Au**



ℜ-179, **M** = **Pt**
ℜ-180, **M** = **Pd**



ℜ-181

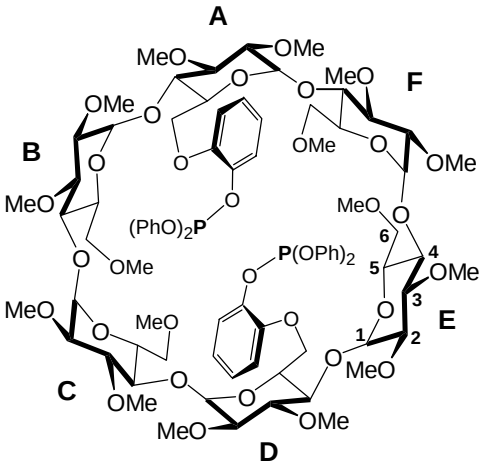


ℜ-182

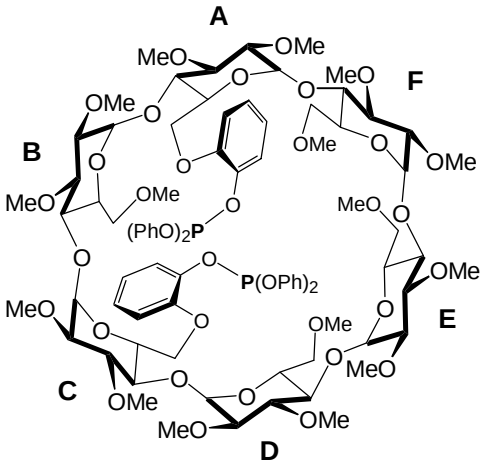
II.1.2. Large chelate rings derived from P(III)-modified CDs

Chelate complexes obtained from diphosphanes where the phosphorus centres are separated by more than twenty bonds remain relatively uncommon.[11-13] Reaction of such large bidentate ligands with transition metal complexes often produces oligomeric material rather than chelate structures.[14,15] As already noted by Ogino, the chemical literature contains many examples of chelate complexes, the ring structure of which has not been firmly established.[16] This is in particular the case for ligands, which contain more than three or four bonds between the coordination centres. A rational way to favor chelating over bridging behaviour consists in performing the complexation reaction at high dilution, but this requires the coordination steps to proceed quickly. Alternatively, preorganisation of the complexing units brought about by increasing the ligand backbone rigidity may result in better metal chelation. We have recently studied the coordinative behaviour of a series of large bidentate ligands built on bucket-shaped units, notably cyclodextrin and calixarene backbones.[17] All these ligands consisted of two podands tethered at the same rim of a cone-shaped cavity. We found that such long chain diphosphines *systematically* lead to chelate complexes when opposed to cationic species bearing *labile* ligands, *e.g.* $[Rh(COD)(solvent)_2]^+$, $[PdMe(solvent)_2(COD)]^+$, $Ru(p\text{-cymene})(solvent)_3]^{2+}$, $[Au(solvent)_2]^+$, etc. whilst their reaction with neutral starting complexes containing poorer leaving groups (*e.g.* MeCN) usually affords oligomeric compounds.[18,19]

Although a number of studies have been carried out on P(III)-derivatized CDs, none deals with phosphite ligands.[2,5-9,11,20-22] As part of our studies on cavity-derived bidentates, we report here on the synthesis of diphosphites **L1** and **L2**, both built on a α-cyclodextrin platform, and their ability to form catalytically active large chelate complexes with transition metals. In the following, the letters "**a**" and "**b**" refer to AD- and AC-disubstituted CDs, respectively. A unique example of α-CD capped with a short bridging fragment is also reported.



L1

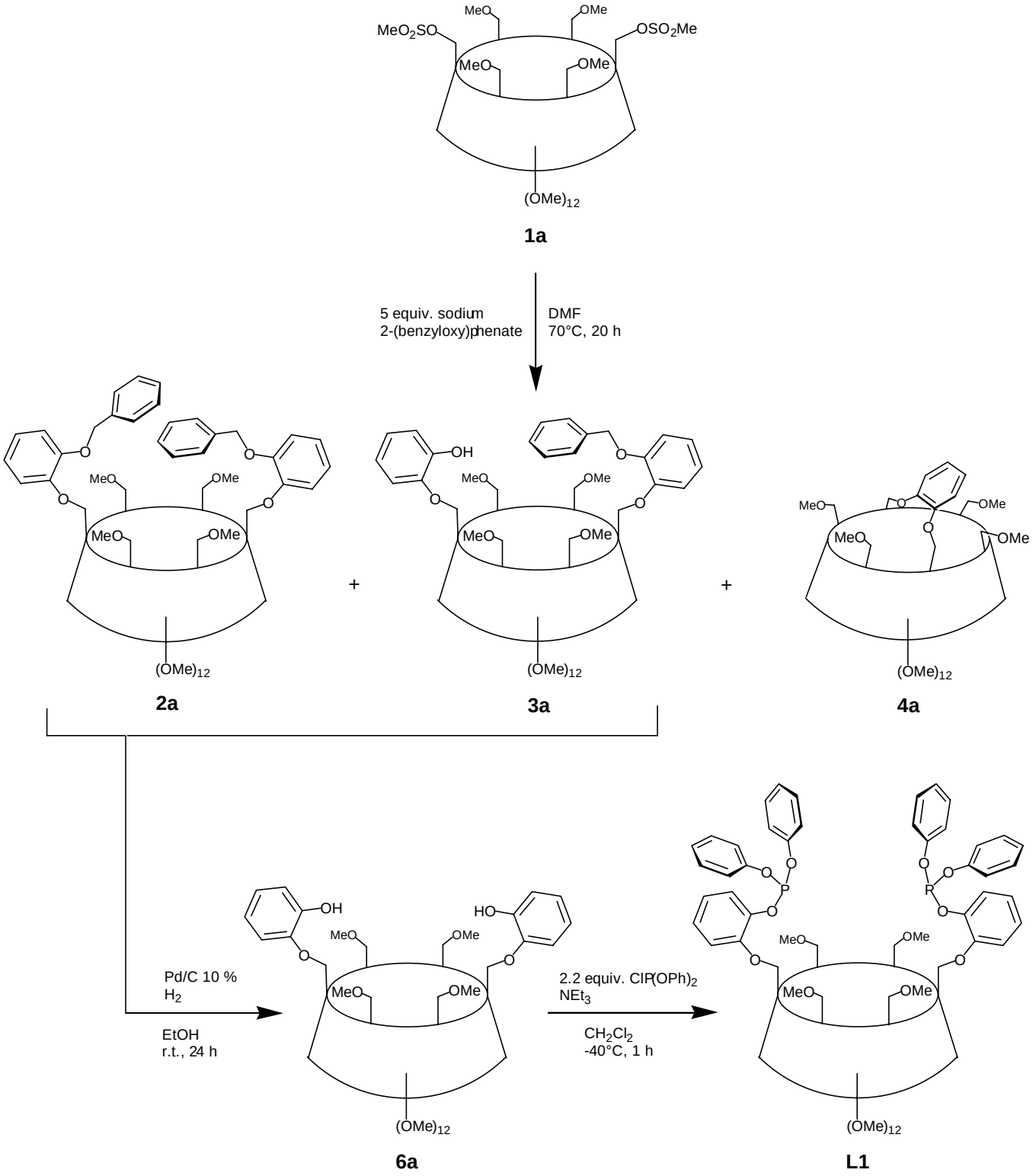


L2

II.2. Results and Discussion

II.2.1. Syntheses of ligands and complexes

The C_2-symmetrical ligand **L1** was synthesised in three steps from the known dimesylate **1a** (Scheme 1).[20] Thus, reaction of 5 equivalents of sodium 2-(benzyloxy)phenolate with **1** in DMF at 70°C afforded a mixture of three products among which we isolated the desired compound **2a** in 65% yield. The presence of three doublets for the H-1 protons (see experimental part) as well as 8 singlets for the methyl groups in the ^{1}H NMR spectrum is consistent with a molecule having C_2 symmetry, thus confirming substitution of both available mesylate groups. Partial loss of one benzyl group under these reaction conditions led to the formation of **3a** (7%). Its ^{1}H NMR spectrum reveals the absence of symmetry and indicates clearly the presence of a phenolic proton. The ^{1}H NMR spectrum of the third species **4a** (17 %) is also indicative of C_2 symmetry. However, compared to **2a**, the H-1 signals of **4a** are much more spread out ($\Delta\delta$ = 0.30 ppm *vs.* 0.11 ppm for **2a**), indicating the presence of a distorted CD matrix (Figure 1, top). As confirmed by a single crystal X-ray diffraction study (*vide infra*), the latter results from the capping of the CD platform with a short 1,2-phenylene unit characterized by a pseudo AA'BB' system in the aromatic region of the ^{1}H NMR spectrum. Only benzyl cleavage of the monosubstituted intermediate **5a** and subsequent



Scheme 1. Synthesis of a C_2-symmetrical chiral diphosphite

intramolecular substitution of the remaining mesylate group can explain the formation of such a capped derivative. In the solid state (Figure 2[23]), the C(11) and C(21) glucose

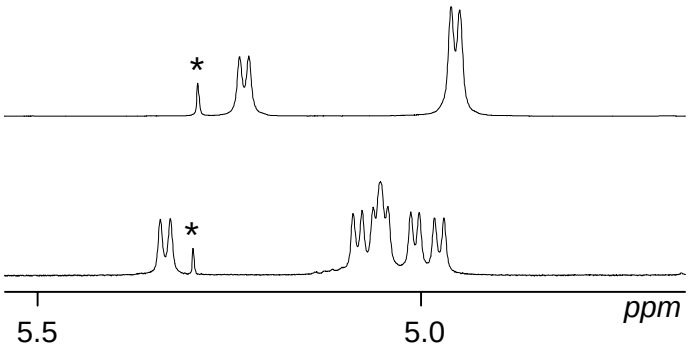
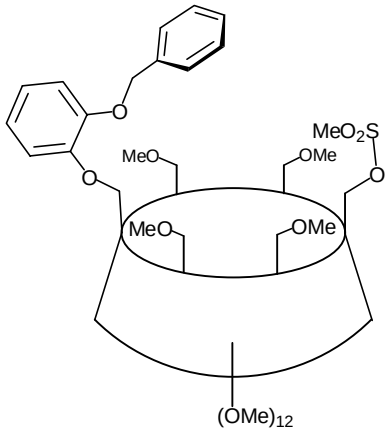
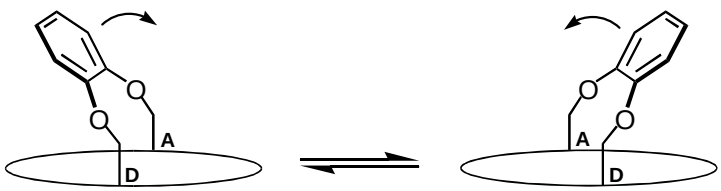


Figure 1. Anomeric regions of the ^{1}H NMR spectra of **4a** (top) and **4b** (bottom) (300 MHz, $CDCl_3$). The asterisk denoted residual CH_2Cl_2.



5a

units and their symmetrical counterparts are strongly tilted with respect to the plane constituted by the six O-4 atoms (tilt angles[20]: 35.0(3)° (C(11)) and 31.8(3)° (C(21)), *vs.* 14.4(3)° for the C(1) ring) so as to accommodate the capping unit. Remarkably, in spite of the considerable strain imposed on the CD framework,[20] all glucose units display the usual $^{4}C_1$ conformation.[24] The 1,2-phenylene moiety, which adopts two possible orientations (occupancy 1:1), is inclined by ± 39.5° with respect to the CD axis. Note, the 2D NMR ROESY spectrum contains cross-peaks corresponding to through-space interactions between the phenylene and all OMe-6 protons. In keeping with the fact that the molecule has averaged C_2-symmetry, this observation indicates a fan-like



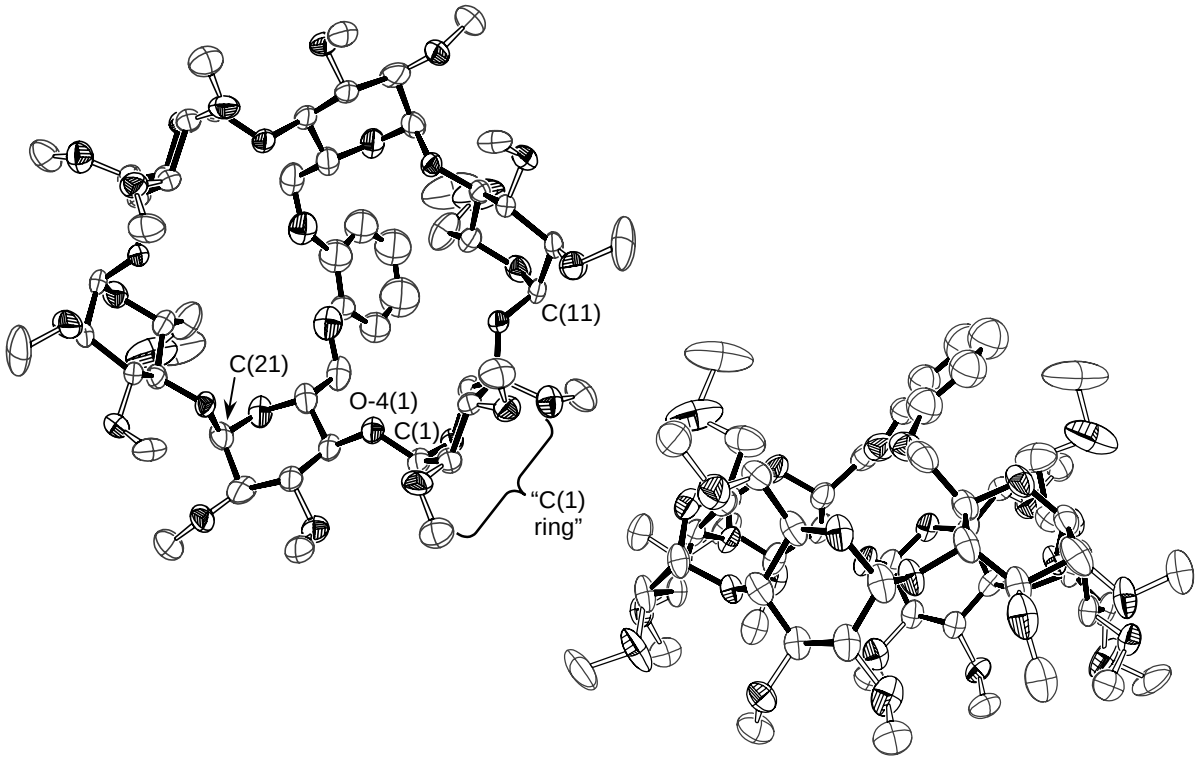


Figure 2. Ortep views of **4a**; bottom (left) and side view along the phenylene plane (right). Ellipsoids are drawn at the 30% probability level, the included heptane molecule has been omitted for clarity

motion of the phenylene ring above the CD cavity in solution.

The same capped species was obtained in moderate yield (*ca.* 30%) when the dimesylate was reacted with disodium catecholate. However, in this case, some oligomeric material was formed. Treatment of **2a** and **3a** with H_2 in the presence of Pd/C afforded the diphenol **6a** quantitatively. The latter reacted smoothly with two equivalents of chlorodiphenylphosphite $ClP(OPh)_2$ in the presence of NEt_3 at -40°C to give ligand **L1**, whose ^{31}P NMR spectrum consists of a singlet at 127.5 ppm commensurate with the expected C_2 symmetry. As expected, the ^{1}H NMR spectrum of **L1** (Figure 3) displays three anomeric signals and 8 methyl peaks. In **L1**, 26 bonds separate the two phosphorus atoms.

The bis(triaryl)phosphite regioisomer **L2** was synthesised from the known tris(4-*tert*-butylphenyl)methyl AC-disubstituted CD derivative **7b**. Thus, removal of the protecting groups was achieved with aqueous HBF_4 in MeCN to give diol **8b** which was then converted to dimesylate **1b** using MsCl in pyridine in the presence of 4-

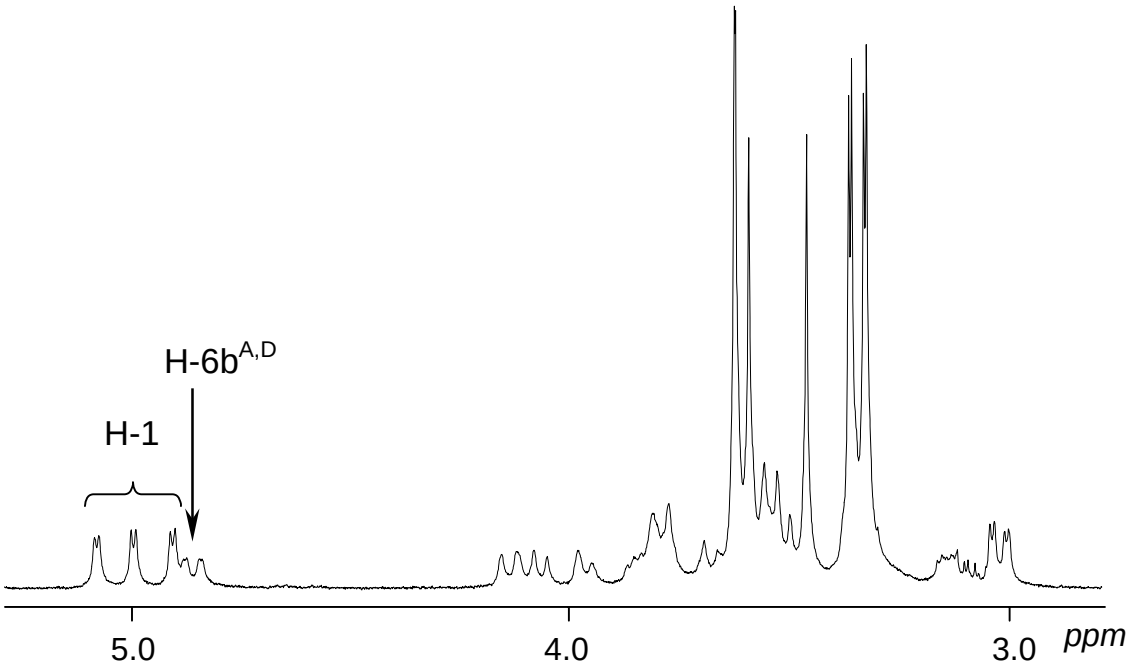
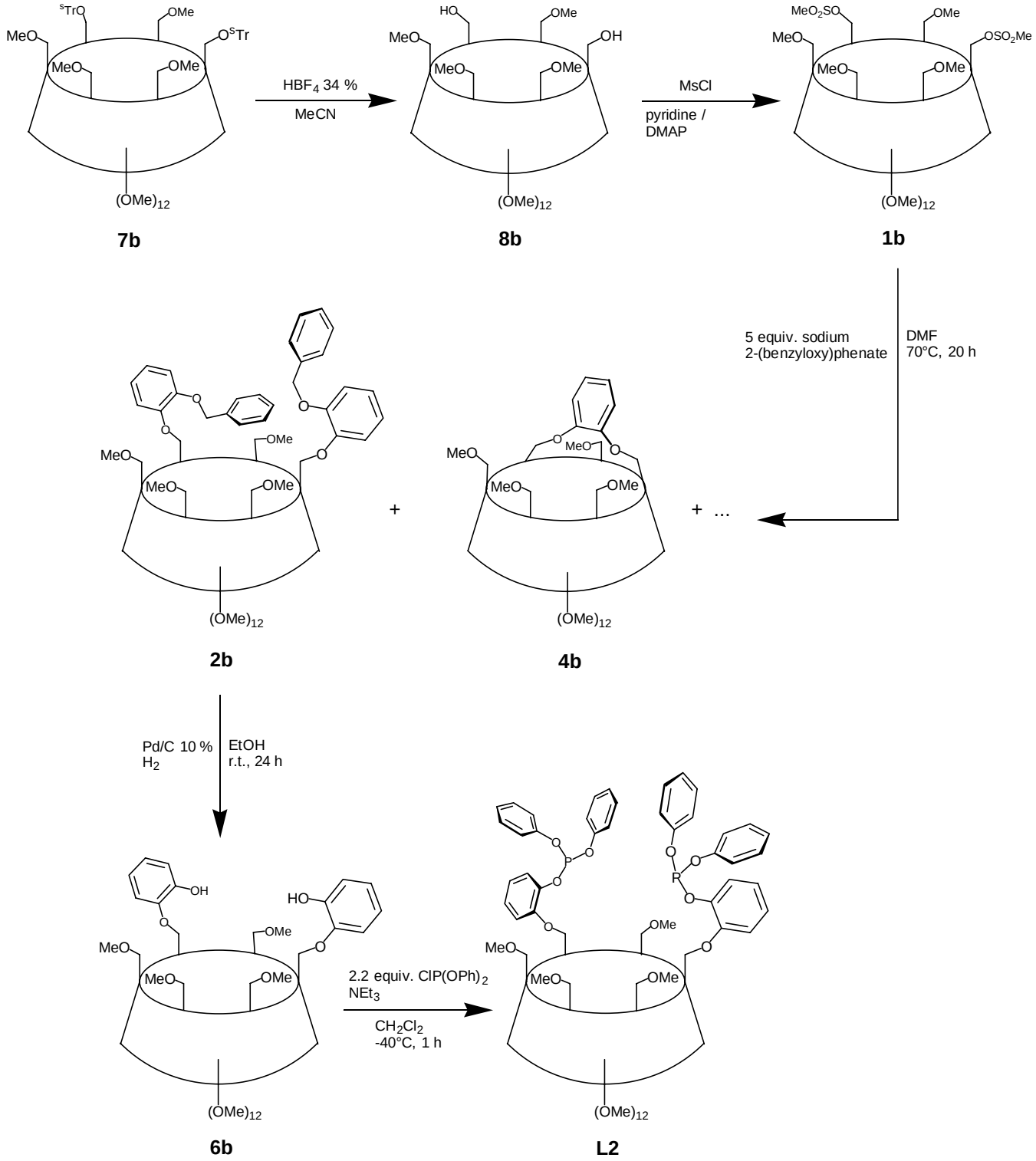


Figure 3. ^{1}H NMR spectrum of **L1** recorded at 300 MHz in $CDCl_3$

(dimethylamino)pyridine (DMAP) (Scheme 2). As for **1a**, treatment of **1b** with 5 equivalents of sodium 2-(benzyloxy)phenolate produced a mixture of four products amongst which the desired disubstituted product **2b** was isolated in 57% yield. Again, bridging of two primary positions with a catechol unit was found to take place and the capped species **4b** was isolated in 18% yield. As for **4a**, the large dispersion of the H-1 signals ($\Delta\delta$ = 0.37 ppm *vs.* 0.11 ppm for **2b**) in the ^{1}H NMR spectrum indicate the presence a distorted CD torus (Figure 4, bottom). However, as revealed by 2D ROESY experiments, the phenylene protons are in close proximity to only three of the four OMe-6 protons, suggesting that the phenylene plane is tilted towards the cavity centre and does not swing in this case about the O-6^{A}–O-6^{C} axis. Beside **2b** and **4b**, two further, inseparable, species whose ^{1}H NMR spectra are consistent (see experimental part) with products resulting from cleavage of one benzyl group from **2b** were obtained in very low yield. Catalytic hydrogenation of **2b** afforded diphenol **6b** quantitatively, the ^{1}H and ^{13}C NMR spectra of which show remarkable asymmetry. The latter may result from the presence of hydrogen bonding between the two hydroxy groups and the CD matrix, which helps rigidifying the overall structure. Compound **6b** reacted smoothly with 2 equivalents of $ClP(OPh)_2$ to give ligand **L2**. Surprisingly,



Scheme 2. Synthesis of a C_1-symmetrical chiral diphosphite

both phosphorus atoms appear as magnetically equivalent (δ = 127.5 ppm) in the ^{31}P NMR spectrum. In keeping with a C_1-symmetrical compound, the ^{1}H NMR spectrum (Figure 4) shows six H-1 signals.

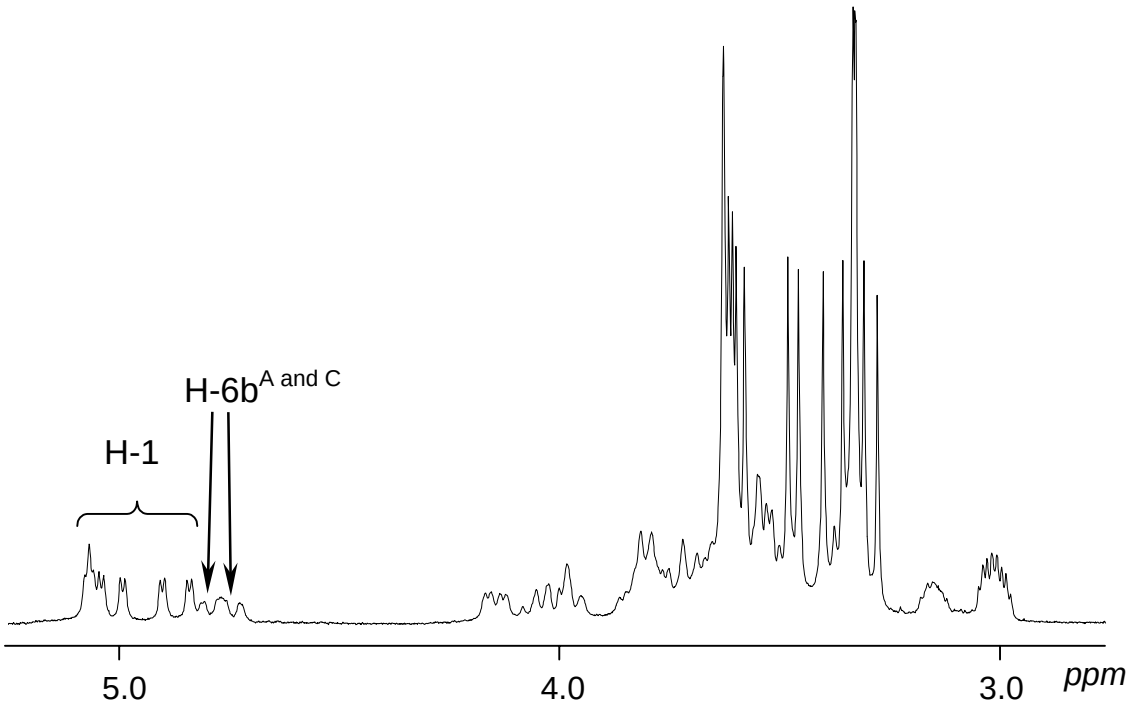
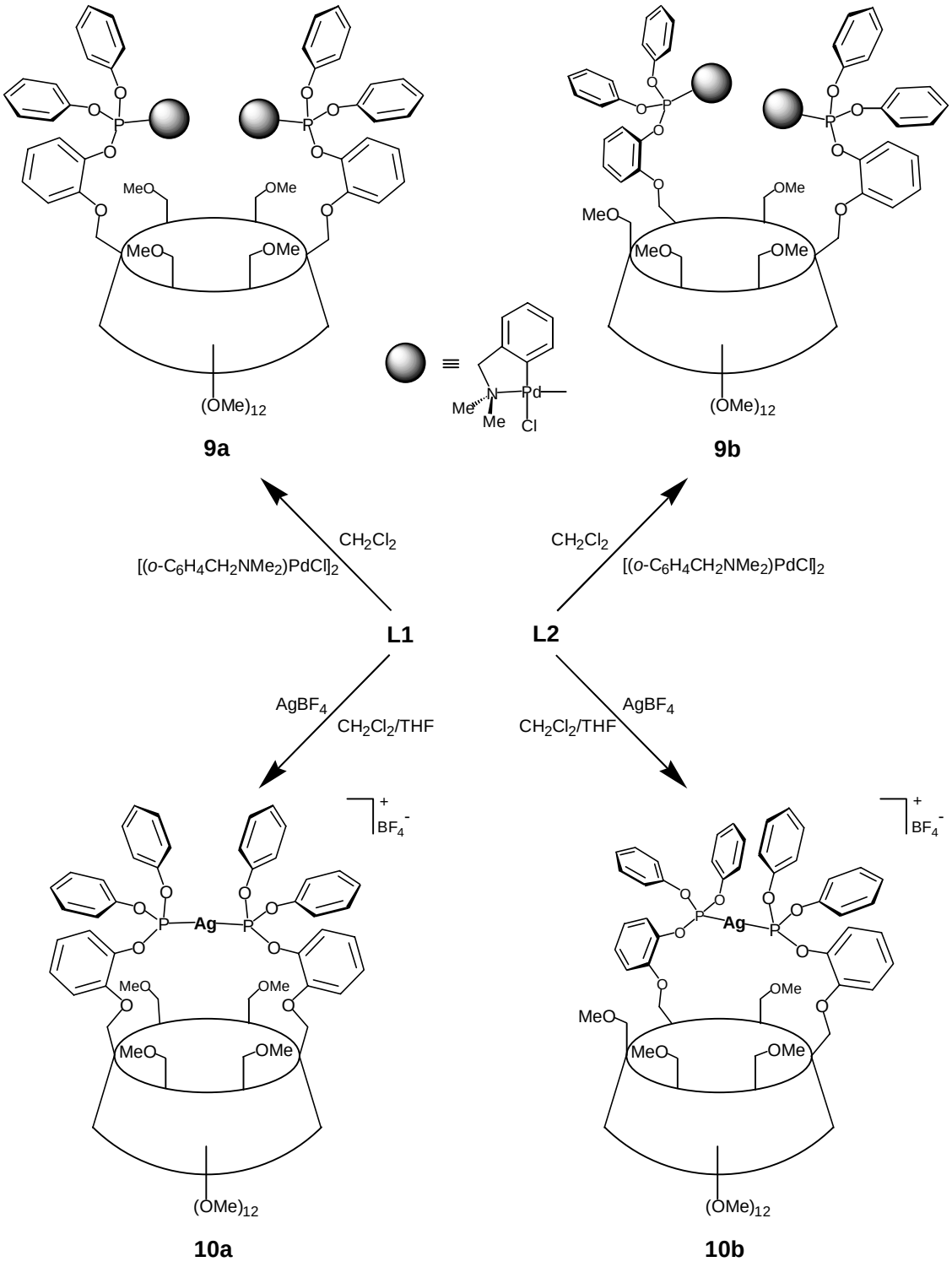


Figure 4. ^{1}H NMR spectrum of **L2** recorded at 300 MHz in $CDCl_3$

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

When either **L1** or **L2** was treated with one equivalent of $AgBF_4$, the exclusive formation of the chelates **10a/10b** was observed. The capping of the CD cavity with an Ag^+ cation was confirmed by FAB-MS spectrometry. Both complexes produce an intense peak at 1921.3 corresponding to the molecular ion $[M\text{-}BF_4]^+$. As expected, in the ^{31}P NMR spectrum of C_2-symmetrical **10a**, the phosphorus atoms give rise to two doublets centred at 116.7 ppm ($J(^{107}AgP)$ = 1083 Hz, $J(^{109}AgP)$ = 1231 Hz) whereas they resonate as two ABX systems (X = ^{107}Ag and ^{109}Ag, δ_A = 108.3 and δ_B = 114.5



ppm, ^{2}J(PP') = 256 Hz, J(^{107}AgP') = 977 Hz, J(^{109}AgP') = 1088 Hz) in **10b** (Figure 5). The J(AgP) values are rather large when compared to those of *phosphine* silver complexes, but this has also been observed recently for the J(PtP) coupling constants of tris(aryl)phosphite platinum(II) complexes.[25] Unlike that of **10a**, the ^{1}H NMR spectrum of **10b** is rather broad which suggests fluxional behaviour, possibly resulting

from exchanging methoxy groups that compete for coordination to the silver cation. Similar dynamics have been observed recently in other silver-capped CDs (see chapter III).[21]

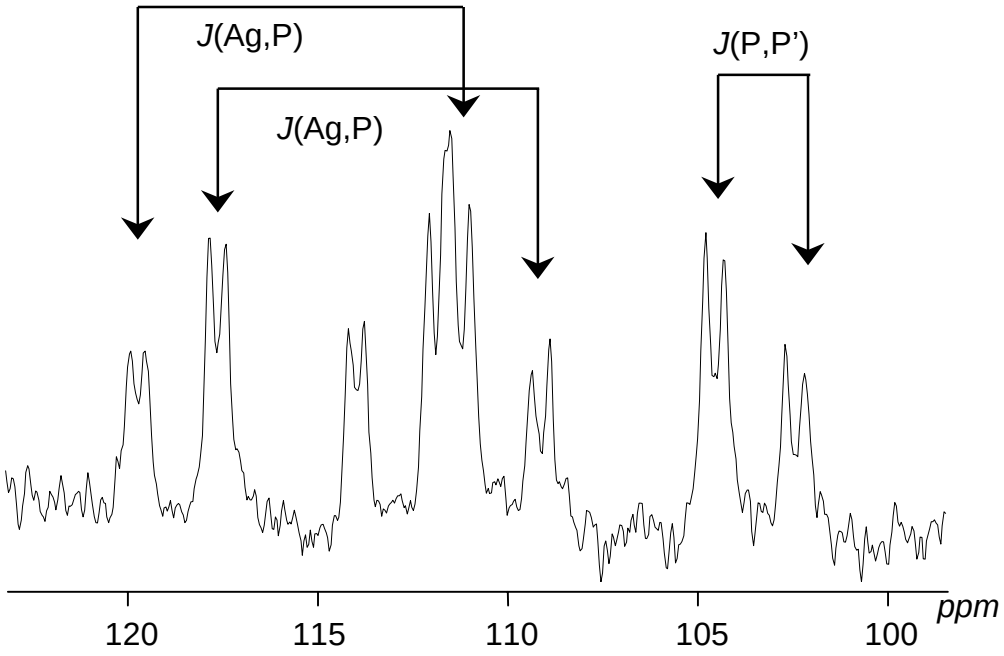


Figure 5. ^{13}P NMR spectrum of **10b** showing the ABX system (121.5 MHz in $CDCl_3$)

Likewise, chelate complexes **11a**/**11b** were obtained in high yields when the *in situ* formed cationic precursors $[Rh(NBD)(THF)_2]PF_6$ and $[Rh(NBD)(THF)_2]BF_4$ were reacted with one equivalent of **L1** and **L2**, respectively. Once again, the FAB-MS spectra of **11a**/**11b** left no doubt on the monomeric nature of the complexes, showing intense peaks at 2007.7 and 2008.4 for the $[M\text{-}PF_6]^+$ (**11a**) and $[M\text{-}BF_4]^+$ (**11b**) cations, respectively. Both ^{31}P NMR spectra display a single doublet centred at 110.5 ppm (J(RhP) = 264 Hz (**11a)**, 259 Hz (**11b**)). It is interesting to point out that again, the phosphorus atoms of **11b** give rise to an A_2X pattern (X = Rh) despite the complex' lack of symmetry. This unexpected feature arises probably from the fact that the distance separating the phosphorus atoms from the chiral cavity is quite large in the absence of MeO-6 ether coordination. Furthermore, at room temperature, the ^1H NMR spectra of **11a** and **11b** are both broad suggesting that these molecules are dynamic in solution. Recording the ^1H NMR spectrum of **11a** at 60 °C caused all signals to sharpen but did not reduce their number (Figure 6). These findings suggest that the metal plane is tilted with respect to the CD axis and that the metal-containing handle is subject to

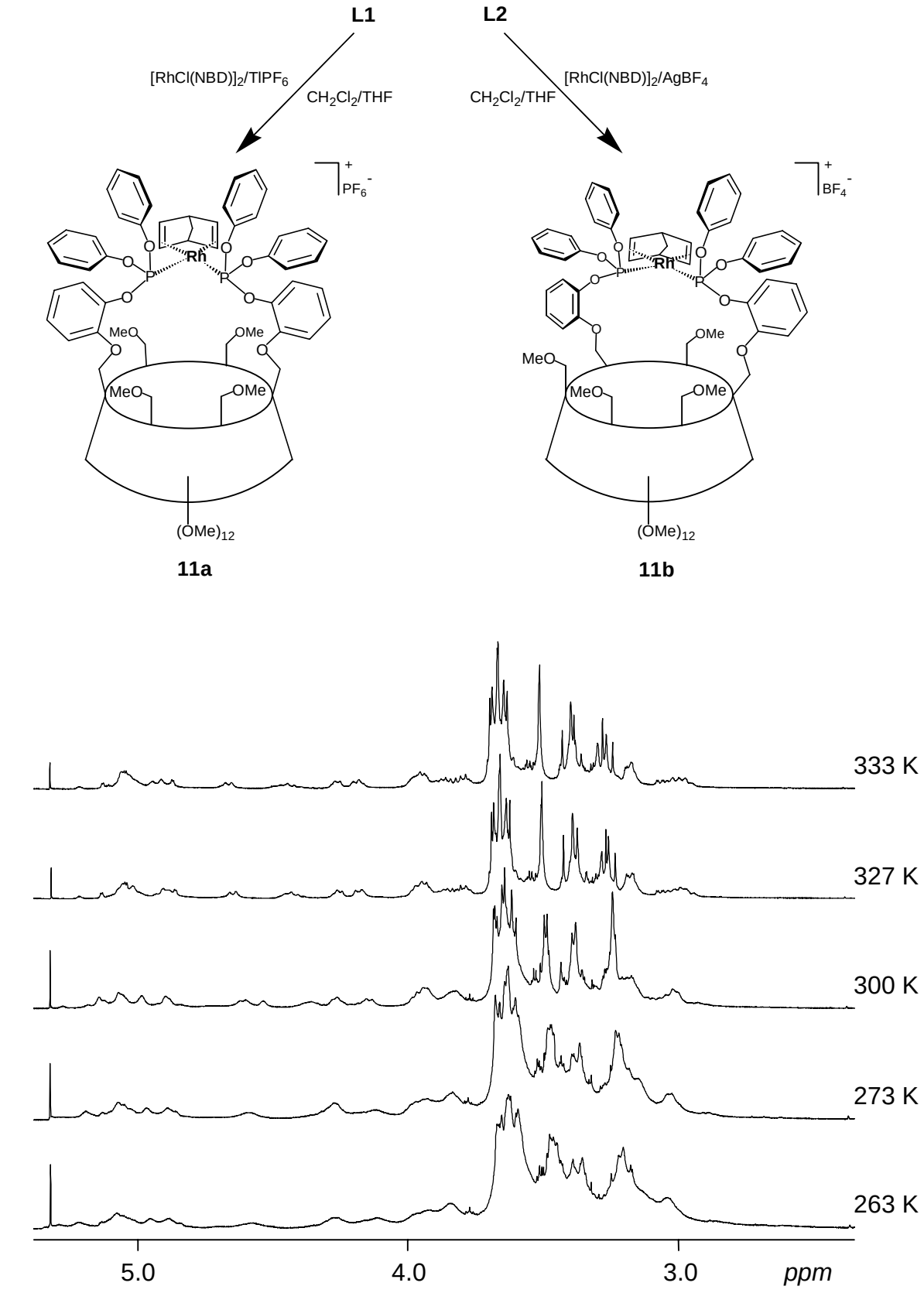


Figure 6. VT ^{1}H NMR study of **11a** (500 MHz in $CDCl_3$)

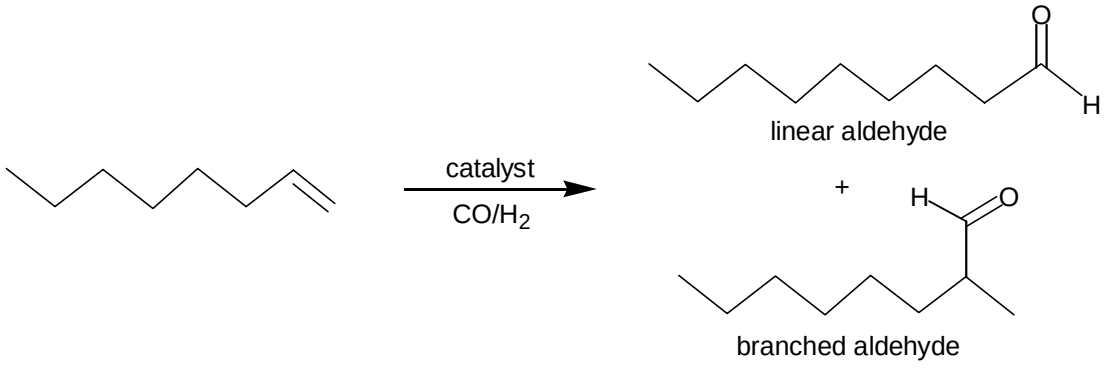
conformational changes. No indication for a metal plane describing a pendulum motion about the P,P axis could be inferred from our observations.

Finally, we observed that reaction of **L1** and **L2** with $[Rh(COD)_2]BF_4$, which contains poorer leaving groups, produces a mixture of monomeric and oligomeric species. Undoubtedly, the selective formation of chelate complexes using $[Rh(NBD)(THF)_2]^+$ originates from a combination of the following features: firstly, the use of starting cationic complexes bearing highly labile ligands promotes a fast coordination of both phosphorus centres. Secondly, the rigid CD core orientates the two phosphite substituents in the same direction and therefore maintains the two phosphorus centres in close proximity.

II.2.2. Catalytic properties of L1 and L2

Our catalytic attempts focused on the hydroformylation of oct-1-ene (Scheme 3) and the hydrogenation of prochiral dimethyl itaconate (Scheme 4), two commonly used reactions for testing P(III) ligands.[26] For the hydroformylation studies the complexes were formed in situ according to standard literature procedures using $[Rh(acac)(CO)_2]$ as starting complex. Thus formation of complexes other than chelate ones cannot be excluded.

II.2.2.1. Hydroformylation of oct-1-ene



Scheme 3. Hydroformylation of oct-1-ene

The catalytic performance of **L1** and **L2** are summarised in Table 1. The catalytic runs were carried out in the presence of 5 equivalents of diphosphine. Both rates and regioselectivities are comparable to those observed with the flexible and medium bulky diphosphite **12** (l/b = 2.2, TOF = 1550, isomerisation 20%) but the percentage of isomerisation does not exceed 5% in our case.[27] Consistent with van Leeuwen's observations made for other diphosphites, the flexible nature of our chelating complexes probably accounts for the observed poor linear aldehyde selectivity. Interestingly, activity is doubled on going from **L1** to **L2** (entries 3 and 4), probably reflecting a larger steric hindrance about the metal centre in the **L2**/rhodium system. This feature is likely to reduce the number of coordinated phosphorus atoms during the catalytic cycle which in turn leads to less stable hence more reactive intermediate species. Raising the octene / rhodium ratio from 600 to 1200 produced a two-fold increase of the reaction rate. Such a substrate concentration dependency has also been observed by van Leeuwen when operating in low olefin concentration.[26,27] No evidence was found for a supramolecular interaction between the CD cavity and the olefinic substrate under the used reaction conditions (solvent : toluene).

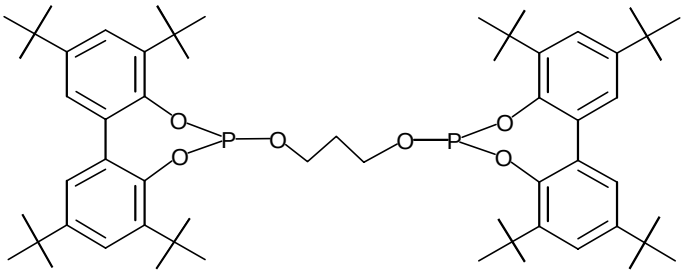
Table 1. Hydroformylation of oct-1-ene

entry	ligand	L/Rh ratio	S/Rh ratio	% conv.[a] (1h)	l/b ratio	TOF[b]
1	**L1**	5	600	69	1.8	300
2	**L1**	5	1200	56	1.9	550
3	**L2**	5	600	98	1.9	600
4	**L2**	5	1200	98	2.0	1200

Conditions: T = 80°C; $6.62 \cdot 10^{-3}$ mmol (1.7 mg) of $[Rh(acac)(CO)_2]$ in toluene (15 mL); $P_{H2} = P_{CO}$ = 10 bar

[a] The conversion was determined after 1 hour reaction time.

[b] mol aldehyde · mol^{-1} Rh · h^{-1}



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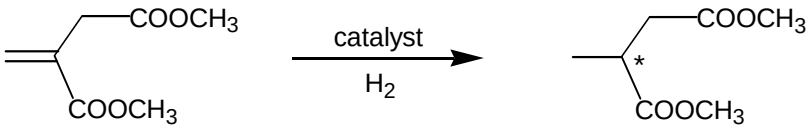
II.2.2.2. Hydrogenation of dimethylitaconate



Scheme 4. Hydrogenation of dimethyl itaconate

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

Table 2. Hydrogenation of dimethylitaconate

entry	catalyst	S/Rh ratio	% conv. (24h)[a]	% ee	TOF[b]
1	$[Rh(COD)_2]BF_4$ /**L1**[c]	500	58	10	13
2	$[Rh(COD)_2]BF_4$ /**L2**[c]	500	47	17	10
3	**11a**[d]	500	1	n.d.[e]	0.2
4	**11b**[d]	500	17	83.4 (*R*)	3.5

Conditions: T = 25°C; CH_2Cl_2 (15 mL), P_{H2} = 1 bar

[a] The conversion was determined after 24 h reaction time.

[b] mol product · mol^{-1} Rh · h^{-1} after 24 h

[c] diphosphite/Rh = 1; $2.76 \cdot 10^{-2}$ mmol of $[Rh(COD)_2]BF_4$

[d] $2.42 \cdot 10^{-2}$ mmol of complex

[e] not determined

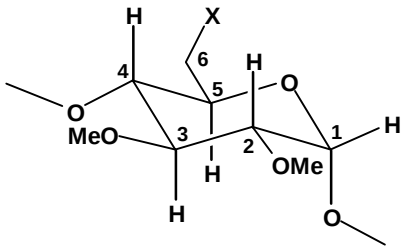
II.3. Conclusion

In this chapter, we have shown that by grafting two phosphite ligands onto a methylated CD platform at either AC or AD positions, diphosphites with chelating properties can be obtained. Metallomacrocycles consisting of up to 29 membered-rings were produced as the sole products when the preorganised diphosphites were reacted with transition metal cations bearing labile ligands. The interesting hydrogenation properties displayed by complex **11b** illustrate the potential of unsymmetrically capped CDs as enantioselective catalysts.

II.4. Experimental section

II.4.1. General procedures

All commercial reagents were used as supplied. All manipulations involving phosphites were performed in Schlenk-type flasks under argon. Solvents were dried by conventional methods and distilled immediately prior to use. Column chromatography was performed on silica gel 60 (particle size 40-63 μm, 230-240 mesh). $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under argon over molecular sieves (4 Å). Routine ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded with FT Bruker AC200 (^1H: 200.1 MHz, ^{13}C: 50.3 MHz) and AC300 (^1H: 300.1 MHz, ^{31}P: 121.5 MHz) instruments at 25°C while 500 MHz-spectra were recorded on an Avance 500 Bruker instrument (^1H: 500.1 MHz). ^1H NMR spectral data were referenced to residual protiated solvents (δ 7.26 for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuterated solvents (δ 77.0 for $CDCl_3$), and the ^{31}P NMR data are given relative to external H_3PO_4. All mass spectra were recorded on a ZAB HF VG Analytical spectrometer using *m*-nitrobenzyl alcohol as matrix. 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. Cyclodextrins **1a**[20] and **7b**,[10] chlorodiphenylphosphite[28,29] and complexes $[(o\text{-}C_6H_4CH_2NMe_2)PdCl]_2$,[30] $[RhCl(NBD)]_2$[31] and $[Rh(COD)_2]BF_4$[9] were synthesised according to literature procedures. DMBA stands for *o*-dimethylbenzylamine. The numbering of the atoms within a glucose unit is as follows:



Hydroformylation studies were performed in a stainless steel autoclave (100 mL) containing a glass beaker and a magnetic stirring bar. The beaker was charged with toluene solutions of both the diphosphite ligand and $[Rh(acac)(CO)_2]$ (total volume 15

mL), followed by the internal standard (decane). The autoclave was flushed several times with CO/H_2 (1:1, v/v), then pressurised to 20 bar, and finally heated to 80 °C for one hour. After depressurising and cooling down to room temperature, the substrate (oct-1-ene) was added, and the mixture was again pressurised and heated to reaction temperature. Samples were taken at different reaction times and analysed by GC.

Hydrogenation experiments were carried out in a Schlenk tube under ambient pressure and room temperature. Experiments using $[Rh(COD)_2]BF_4$: The diphosphite ligand was dissolved in 15 mL of CH_2Cl_2. After addition of $[Rh(COD)_2]BF_4$, the solution was saturated with H_2 for 10 min., whereupon the substrate (dimethyl itaconate) was added. Samples were taken at different reaction times and analysed by GC. Enantiomeric excess was determined by ^1H NMR using using tris[3-heptafluoropropylhydroxymethylene)-(+)-camphorato] europium (III) ((+)-Eu(hfc)$_3$) as an optically active shift reagent. A $CDCl_3$ solution of the organic substrate was prepared in an NMR tube and small amounts of the shift reagent were gradually added until a clean splitting of the peaks was achieved (*ca.* 5 % of shift reagent). Experiments using **11a** or **11b**: the complex was dissolved in 15 mL of CH_2Cl_2, and the solution was saturated with H_2 for 10 min. Then dimethylitaconate was added. The reaction was followed by GC. The enantiomeric excess was detemined by GC using a Cyclodextrin/OV1701 column.

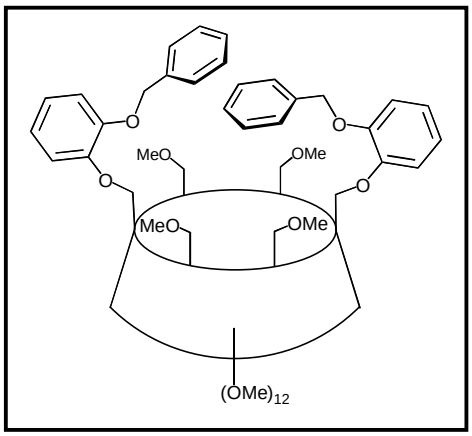
II.4.2. Synthesis of Ligands and Complexes

$6^A,6^D$-Bis-*O*-(2-benzyloxyphenyl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$ hexadeca-*O*-methyl-α-cyclodextrin (2a) and 6^A-*O*-(2-hydroxyphenyl),6^D-*O*-(2-benzyloxyphenyl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$-hexadeca-*O*-methyl-*α*-cyclodextrin (3a) and $6^A,6^D$-*O*-(1,2-phenylene)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$-hexadeca-*O*-methyl-*α*-cyclodextrin (4a)

NaH (60%, 0.170 g, 4.29 mmol) was added to a solution of 2-benzyloxyphenol (0.860 g, 4.29 mmol, 0.98 mL) in DMF (25 mL). After 20 min., **1a** (1.158 g, 0.86 mmol) was added. The solution was stirred overnight whereupon water (50 ml) was added. The mixture was extracted with Et_2O (4 × 100 mL), and the ether phase was

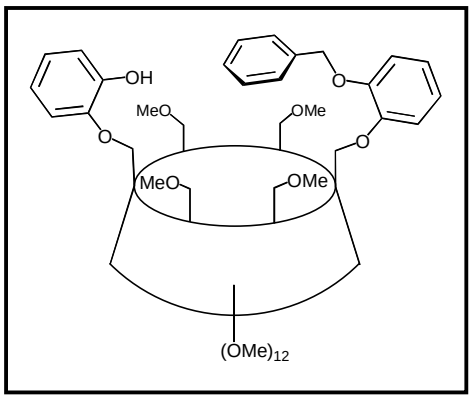
subsequently washed with an aqueous 2M NaOH solution (100 mL), dried over $MgSO_4$ and filtered. Removal of the solvent in *vacuo* gave a colourless residue (1.832 g) which was purified by column chromatography (SiO_2, hexane/ethyl acetate 20 : 80 → 0 : 100, v/v) to afford three fractions:

Fraction1: $6^A,6^D$-Bis-*O*-(2-benzyloxyphenyl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$ hexadeca-*O*-methyl-α-cyclodextrin (**2a**)



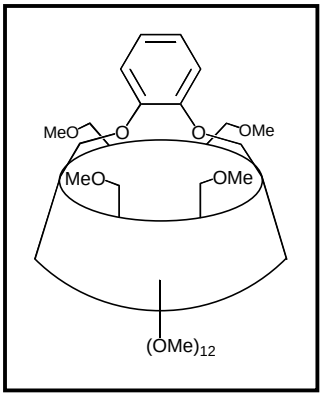
(0.869g, 65%); R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.37; Mp 100-102°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.23 (s, 6H, OCH_3), 3.31 (s, 6H, OCH_3), 3.37 (s, 6H, OCH_3), 3.47 (s, 6H, OCH_3), 3.51 (s, 6H, OCH_3), 3.63 (s, 6H, OCH_3), 3.66 (s, 12H, OCH_3), 2.94-4.23 (32H, H-2, H-3, H-4, H-5, H-$6^{B,C,E,F}$), 4.31 (d, $^2J_{H\text{-}6b,H\text{-}6a}$ $^2J_{H\text{-}6b,H\text{-}6a}$ = 10.1 Hz, 2H, H-$6a^{A,D}$), 4.57 (dd, ^3J= 3.2 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 10.1 Hz, 2H, H-$6b^{A,D}$), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-$1^{A,D}$), 5.08 (t, ^{3}J = 1.7 Hz, 4H, OCH_2Ph), 5.12 (2d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 4H, H-$1^{B,C,E,F}$), 6.84-6.99 (8H, catecholate H), 7.24-7.44 (10H, benzyl arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 57.52, 57.92, 57.95, 58.93 and 59.10 (CH_3O-2, CH_3O-6), 61.79 and 61.85 [×2] (CH_3O-3), 68.64 (OCH_2Ph), 70.90 (C-$6^{A,D}$), 71.13 and 71.39 [×2] (C-5), 71.49 [×2] (C-$6^{B,C,E,F}$), 81.29 [×3], 82.14 [×2], 82.27, 82.50 [×2] and 82.90 (C-2, C-3, C-4), 99.84 (C-$1^{A,D}$), 100.20 and 100.27 (C-$1^{B,C,E,F}$), 114.86, 115.15, 121.41 and 121.58 (catecholate CH), 126.8, 127.67 and 128.50 (benzyl arom. CH), 137.58, 149.04 and 149.41 (C_{ipso}); elemental analysis (%): calcd for $C_{78}H_{112}O_{32}$ (1561,71): C 59.99, H 7.23; found: C 59.94, H 7.19.

Fraction 2: 6^{A}-*O*-(2-hydroxyphenyl),6^{D}-*O*-(2-benzyloxyphenyl)-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F}, 3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (**3a**)



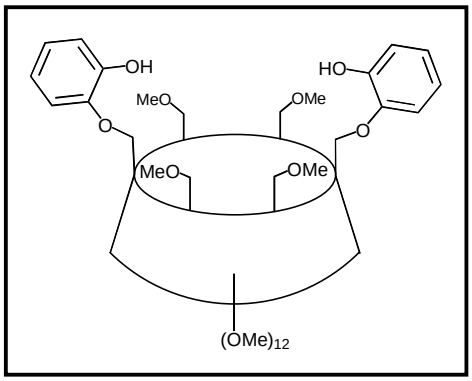
(0.086g, 7%); R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.23; Mp 123-126°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.19 (s, 3H, OCH_3), 3.21 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.48 (s, 6H, OCH_3), 3.50 (s, 6H, OCH_3), 3.52 (s, 3H, OCH_3), 3.66 (s, 18H, OCH_3), 3.10-4.36 (35H, H-2, H-3, H-4, H-5, H-$6^{B,C,E,F}$, H-$6a^{A\ or\ D}$), 4.51 (dd, $^3J_{H\text{-}6b,H\text{-}5}$ = 3.2 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 10.1 Hz, 1H, H-$6b^{A\ or\ D}$), 5.00 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 1H, H-1), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 1H, H-1), 5.08 (t, ^3J = 1.7 Hz, 2H, OCH_2Ph), 5.05-5.11 (4d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 4H, H-1), 6.69 (s, 1H, OH), 6.79-7.02 (8H, catecholate H), 7.21-7.44 (5H, arom. benzyl H); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 57.56, 57.86 [×4], 58.12, 58.74, 58.81, 58.94 and 59.23 (CH_3O-2, CH_3O-6), 61.56 and 61.79 [×5] (CH_3O-3), 68.20 (*O*-CH_2-Ph), 70.80, 70.85 and 70.94 [×3], 71.23[×3], 71.35, 71.46, 71.50 and 71.55 (C-5, C-6), 81.26 [×4], 81.39 [×2], 82.02 [×5], 82.15 [×2], 82.24 [×2], 82.38, 82.70 and 82.97 (C-2, C-3, C-4), 99.59, 99.78 [×2], 99.90, 100.11 and 100.37 (C-1), 114.60, 115.06, 115.25, 115.78, 120.04, 121.32 [×2] and 122.76 (catecholate CH), 126.76, 127.51 and 128.37 (benzyl CH), 137.54, 146.56, 146.95 [×2] and 148.89 (C_{ipso}); elemental analysis (%): calcd for $C_{71}H_{106}O_{32}$ (1471.59): C 57.95, H 7.26; found: C 57.71, H 7.30.

Fraction 3: 6^{A},6^{D}-*O*-(1,2-phenylene)-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{E}, 6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (**4a**)



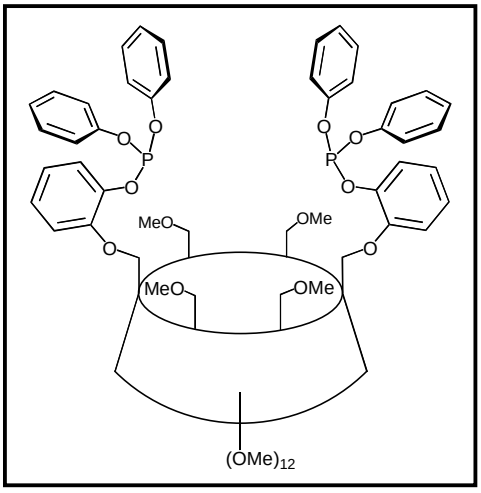
(0.183g, 17%); R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.15; Mp 127-130°C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, assignement by ROESY and COSY): δ 2.90 (d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.4 Hz, 2H, H-$6a^{B,E}$), 3.12 (dd, 2H, $^3J_{H\text{-}2,H\text{-}1}$ = 3.6 Hz, H-$2^{B,E}$), 3.15 (dd, 2H, H-$2^{C,F}$), 3.19 (dd, 2H, H-$2^{A,D}$), 3.20 (s, 6H, OCH_3), 3.30 (t, 2H, H-$4^{A,D}$), 3.30 (s, 6H, OCH_3), 3.46 (s, 6H, OCH_3), 3.47 (s, 6H, OCH_3), 3.51 (t, 2H, H-$3^{C,F}$), 3.55 (s, 6H, OCH_3), 3.56 (t, 2H, H-$3^{A,D}$), 3.60 (dd, 2H, H-$4^{B,E}$), 3.60 (dd, 2H, H-$5^{C,F}$), 3.60 (dd, 2H, H-$5^{B,E}$), 3.60 (s, 6H, OCH_3), 3.62 (dd, 2H, H-$6a^{C,F}$), 3.67 (t, 2H, H-$3^{B,E}$) 3.68 (s, 6H, OCH_3), 3.74 (d, 2H, H-$6b^{C,F}$), 3.75 (s, 6H, OCH_3), 3.78 (t, 2H, H-$4^{C,F}$), 3.89 (dd, 2H, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.4 Hz, $^3J_{H\text{-}6b,H\text{-}5}$ = 2.3 Hz, H-$6b^{B,E}$), 4.20 (d, 2H, H-$6b^{A,D}$), 4.24 (dd, 2H, H-$6a^{A,D}$), 4.33 (dd, 2H, $^3J_{H\text{-}5,H\text{-}6a}$ = 10.4 Hz, $^3J_{H\text{-}5,H\text{-}4}$ = 4.5 Hz, H-$5^{A,D}$), 4.96 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 4H, H-$1^{A,D}$), 4.96 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 4H, H-$1^{C,F}$), 5.23 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, 2H, H-$1^{B,E}$), 6.83-6.94 (AA'BB' system, 4H, arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 57.58 [×2], 58.93 [×2] and 59.67 (CH_3O-2, CH_3O-6), 61.00, 61.68 and 61.94 (CH_3O-3), 69.39, 70.45 and 71.39 (C-6), 71.03, 71.59 and 72.37 (C-5), 79.56, 80.56, 80.92 and 81.47 [×2], 81.68, 82.44 and 82.65 [×2] (C-2, C-3, C-4), 97.16, 98.46 and 99.59 (C-1), 112.87 and 120.35 (arom. CH), 148.59 (C_{ipso}); elemental analysis (%): calcd for $C_{58}H_{94}O_{30}$•C_7H_{16} (1271.35 + 100.20): C 56.92, H 8.08; found: C 56.78, H 7.58.

6^A,6^D-Bis-*O*-(2-hydroxyphenyl)-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (6a)



Pd/C (10%, 0.100 g) was added to a solution of **2a** (0.869 g, 0.556 mmol) in EtOH (100 mL). The mixture was stirred for 48 h under H_2 (1 atm.) before being filtered over Celite. Evaporation of the filtrate *in vacuo* yielded pure **6a** (0.717 g, 94%). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.24; Mp 136-139°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.23 (s, 6H, OCH_3), 3.30 (s, 6H, OCH_3), 3.49 (s, 6H, OCH_3), 3.51 (s, 6H, OCH_3), 3.52 (s, 6H, OCH_3), 3.65 (s, 12H, OCH_3), 3.67 (s, 6H, OCH_3), 3.13-4.45 (36H, H-2, H-3, H-4, H-5, H-6), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1), 5.08 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 2H, H-1), 5.10 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 2H, H-1), 6.60 (s, 2H, OH), 6.73-7.02 (8H, arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 57.92 [×2], 58.26, 58.87 and 59.03 (CH_3O-2, CH_3O-6), 61.77 and 61.90 [×2] (CH_3O-3), 70.93 and 71.40 [×2] (C-6), 71.59 [×3] (C-5), 81.23, 81.33, 81.40, 81.92 [×2], 82.24 [×2], 82.44 and 82.67 (C-2, C-3, C-4), 99.77 [×2] and 100.48 (C-1), 115.53, 115.84, 120.09 and 122.88 (arom. CH), 146.66 and 147.05 (C_{ipso}); elemental analysis (%): calcd for $C_{64}H_{100}O_{32}$ (1381.46): C 55.64, H 7.30; found: C 55.63, H 7.05.

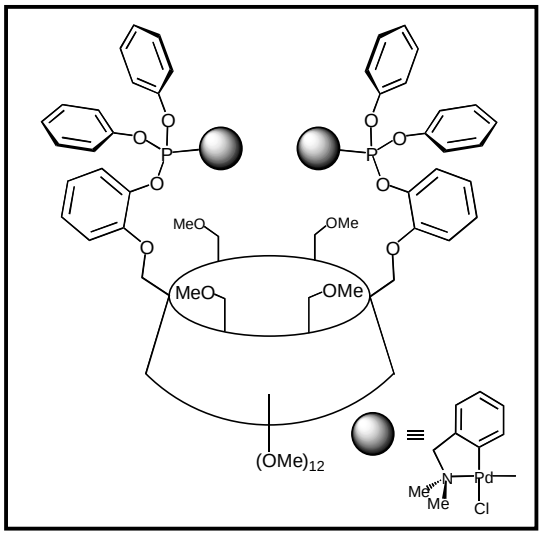
6^{A},6^{D}-Bis-*O*-{2-[(diphenoxyphosphino)oxy]phenyl}-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E}, 3^{F},6^{B},6^{C},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (L2)



Chlorodiphenylphosphite (0.220 g, 0.89 mmol, 0.18 ml) was added to a stirred solution of **6a** (0.500 g, 0.36 mmol) in CH_2Cl_2 (25 mL) at -40°C. The reaction mixture was stirred for 15 min. at -40°C whereupon triethylamine (0.12 mL, 0.89 mmol, 1 equiv.) was added. After 1 h, addition of pentane (200 mL) caused the triethylammonium salt to precipitate. The latter was filtered off and the filtrate was evaporated to dryness under vacuum. The residue was washed with boiling hexane (10 mL). The hot suspension was then cooled down to 0°C and allowed to settle whereupon the hexane phase was discarded. The colourless residue was found to be pure **L1** (0.630 g, 96%). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.31; Mp 83-86°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.34 (s, 6H, OCH_3), 3.35 (s, 6H, OCH_3), 3.38 (s, 6H, OCH_3), 3.39 (s, 6H, OCH_3), 3.48 (s, 6H, OCH_3), 3.62 (s, 6H, OCH_3), 3.65 (s, 12H, OCH_3), 3.01-4.19 (34H, H-2, H-3, H-4, H-5, H-6a, H-$6b^{B,C,E,F}$), 4.90 (d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.6 Hz, 2H, H-$6b^{A,D}$), 4.93 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 2H, H-1), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1), 5.10 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.5 Hz, 2H, H-1), 6.84-7.40 (28H, arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 57.27 and 57.89 [×2] (CH_3O-2), 58.94 and 59.13 (CH_3O-6), 61.72 [×3] (CH_3O-3), 67.95 (C-$6^{A,D}$), 70.84, 71.26 and 71.39 (C-5), 71.62 and 72.15 (C-$6^{B,C,E,F}$), 81.10, 81.23 [×2], 81.65, 81.82, 81.92, 82.28, 82.47 and 82.97 (C-2, C-3, C-4), 99.42 (C-$1^{A,D}$), 100.24 and 100.47 (C-$1^{B,C,E,F}$), 113.98 (s, C_{para}), 120.80 (d, $^3J_{C,P}$ = 6.6 Hz, C_{ortho}), 121.37 [×2] (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 122.45 (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 124.02 [×2] (d, $^4J_{C,P}$ = 4.9 Hz, C_{para}), 124.63 (s, C_{meta}), 129.47 [×2] (d, $^3J_{C,P}$ = 8.2 Hz, C_{ortho}), 141.22 (d, $^2J_{C,P}$ = 3.3 Hz,

C_{ipso}), 150.23 (d, $^{2}J_{C,P}$ = 3.3 Hz, C_{ipso}), 151.48 (s, C_{ipso}), 151.81 (d, $^{2}J_{C,P}$ = 3.3 Hz, C_{ipso}); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 127.5 (s); elemental analysis (%): calcd for $C_{88}H_{118}O_{36}P_2$ (1813.81): C 58.27, H 6.56; found: C 58.32, H 6.36; MS (FAB): *m/z* (%): 1813.6 (50) $[M+H]^+$.

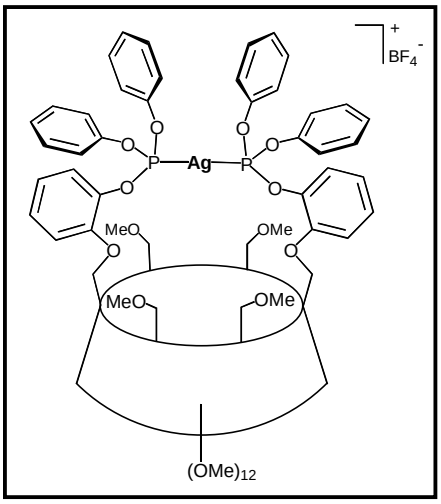
_P,P'_-(6^{A},6^{D}-di-*O*-{2-[(diphenoxyphosphino)oxy]phenyl}-2^{A},2^{B}, 2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C}, 3^{D},3^{E},3^{F},6^{B},6^{C},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin)-bis-[chloro(*o*-dimethylaminobenzyl)palladium(II)] (9a)



[(*o*-$C_6H_4CH_2NMe_2$)PdCl]$_2$ (0.030 g, 0.055 mmol) was added to a solution of **L1** (0.100 g, 0.055 mmol) in CH_2Cl_2 (5 mL). After 20 min., the product was precipitated by addition of pentane (250 mL) and then collected on celite. The precipitate was dissolved in CH_2Cl_2 (15 mL), and upon filtration, the organic solution was evaporated to dryness *in vacuo* to afford pure **9a** as a yellow powder (0.073 g, 56%). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.40; Mp 123-125°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.61 (d, 6 H, $^{4}J_{H,P}$ = 3.9 Hz, NCH_3), 2.63 (d, 6H, $^{4}J_{H,P}$ = 4.2 Hz, NCH_3), 3.30 (s, 6H, OCH_3), 3.33 (s, 12H, OCH_3), 3.35 (s, 6H, OCH_3), 3.47 (s, 6H, OCH_3), 3.60 (s, 6H, OCH_3), 3.63 (s, 12H, OCH_3), 2.84-4.15 (38H, H-2, H-3, H-4, H-5, H-6a, H-6b^{B,C,E,F}, C*H*$_2$Ph), 4.86 (d, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 9.3 Hz, 2H, H-6b^{A,D}), 5.01 (2d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 4H, H-1^{B,C,E,F}), 5.13 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1^{A,D}), 6.83-7.72 (36H, arom. H); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 50.00 (d, $^{3}J_{C,P}$ = 3.3 Hz, NCH_3), 50.15 (d, $^{3}J_{C,P}$ = 3.3 Hz, NCH_3), 57.40 and 57.86 [×2] (CH_3O-2), 58.91 and 59.17 (CH_3O-6), 61.53, 61.66 and 61.72 (CH_3O-3), 67.69 (C-

$6^{A,D}$), 70.90, 71.17, 71.39 (C-5), 71.59 and 72.21 (C-$6^{B,C,E,F}$), 72.68 (CH_2Ph), 81.23 [×3], 81.65, 81.75, 81.79, 82.21, 82.28 and 82.93 (C-2, C-3, C-4), 99.39 (C-$1^{A,D}$), 100.14 and 100.44 (C-$1^{B,C,E,F}$), 114.04 (s, C_{para}), 120.67 (s, DMBA), 121.21 (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 121.95 (d, $^4J_{C,P}$ = 6.6 Hz, DMBA), 122.41 (s C_{ortho}), 124.57 (s, C_{meta}), 124.80 (s, C_{para}), 125.23 (s, C_{meta}), 125.92 (d, $^4J_{C,P}$ = 6.6 Hz, DMBA), 129.29 (d, $^3J_{C,P}$ = 3.3 Hz, C_{ortho}), 136.92 (d, $^3J_{C,P}$ = 11.5 Hz, DMBA), 140.81 (d, $^2J_{C,P}$ = 4.9 Hz, C_{ipso}), 147.62 (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 149.83 [×2] (d, $^2J_{C,P}$ = 4.9 Hz, C_{ipso}), 151.06 (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 151.22 (s, C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 104.5 (s); elemental analysis (%): calcd for $C_{106}H_{142}Cl_2N_2O_{36}P_2Pd_2$ (2365.96): C 53.81, H 6.05; found: C 54.07, H 6.07.

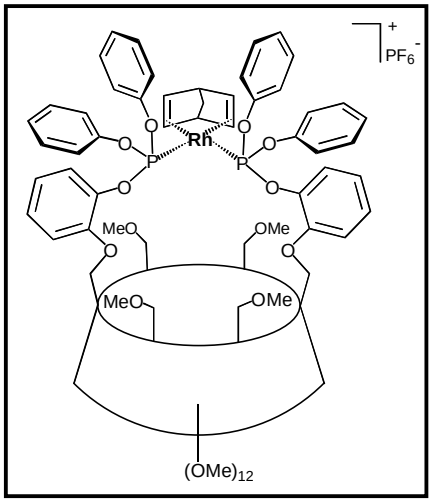
_P,P'_-(6^A,6^D-bis-_O_-{2-[(diphenoxyphosphino)oxy]phenyl}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C, 3^D,3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-_O_-methyl-α-cyclodextrin) silver(I) tetrafluoroborate (10a)



A solution of $AgBF_4$ (0.011 g, 0.055 mmol) in THF (20 mL) was added to a solution of **L1** (0.100 g, 0.055 mmol) in CH_2Cl_2 (200 mL) under vigorous stirring. After 20 min., the reaction mixture was concentrated to 5 mL and pentane (250 mL) was added to precipitate the product, which was collected on celite. The precipitate was dissolved in CH_2Cl_2 (15 mL), and upon filtration, the organic solution was evaporated to dryness *in vacuo* to afford pure **10a** as a colourless powder (0.060 g, 55%). ^1H NMR (200 MHz, $CDCl_3$): δ = 3.16 (s, 6H, OCH_3), 3.37 (s, 6H, OCH_3), 3.41 (s, 6H, OCH_3),

3.42 (s, 6H, OCH_3), 3.44 (s, 6H, OCH_3), 3.59 (s, 6H, OCH_3), 3.61 (s, 12H, OCH_3), 2.86-4.67 (36H, H-2, H-3, H-4, H-5, H-6), 4.92 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 2H, H-1), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 2H, H-1), 5.07 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1), 6.90-7.46 (28H, arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 57.59, 57.79 and 57.99 (CH_3O-2), 60.28 [×2] (CH_3O-6), 61.53, 61.63 and 61.65 (CH_3O-3), 68.71 (C-$6^{A,D}$), 69.69, 70.67 and 71.26 (C-5), 71.59 and 71.85 (C-$6^{B,C,E,F}$), 80.77, 81.29 [×3] and 82.02 [×5] (C-2, C-3, C-4), 99.95 [×2] (C-$1^{B,C,E,F}$), 101.09 (C-$1^{A,D}$), 115.58 (s, C_{para}), 121.06 (d, $^3J_{C,P}$ = 6.6 Hz, C_{ortho}), 121.26 [×2] (d, $^4J_{C,P}$ = 6.6 Hz, C_{meta}), 122.60 (d, $^4J_{C,P}$ = 3.3 Hz, C_{meta}), 126.17 [×2] (s, C_{para}), 127.32 (s, C_{meta}) , 130.40 [×2] (d, $^4J_{C,P}$ = 6.6 Hz, C_{ortho}), 138.40 (s, C_{ipso}), 149.74 [×2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 150.04 (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 116.7 [2d, $^{107}J_{Ag,P}$ = 1083 Hz, $^{109}J_{Ag,P}$ = 1231 Hz]; elemental analysis (%): calcd for $C_{88}H_{118}AgBF_4O_{36}P_2 \bullet 1.5\ CHCl_3$ (2008.48 + 179.07): C 49.14, H 5.51; found: C 49.05, H 5.38; MS (FAB): *m/z* (%): 1937.3 (20) $[M\text{-}BF_4\text{+O}]^+$, 1921.3 (100) $[M\text{-}BF_4]^+$.

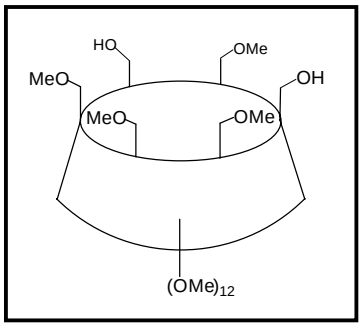
***cis*-*P*,*P*'-(6^A,6^D-Bis-*O*-{2-[(diphenoxyphosphino)oxy]pheny}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin)-[(norbornadiene)rhodium(I)] hexafluorophosphate (11a)**



Powdered $TlPF_6$ (0.022 g, 0.063 mmol) was added to a solution of $[RhCl(NBD)]_2$ (0.013 g, 0.028 mmol) in THF/CH_2Cl_2 (50:50, v/v, 50 mL). After stirring the suspension vigorously for 15 min., the precipitate was collected on Celite and the

filtrate was directly added to a solution of **L1** (0.106 g, 0.058 mmol) in CH_2Cl_2 (200 mL) under vigorous stirring. The reaction mixture was then stirred at room temperature for 20 min. before being concentrated to 5 ml. Addition of pentane (250 mL) caused the product to precipitate. The solid was then filtered over Celite before being dissolved in CH_2Cl_2 (15 mL). Upon filtration, the organic solution was evaporated to dryness *in vacuo* to afford pure **11a** as an orange powder (0.110 g, 90%). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.10; Mp 118°C dec; ^{1}H NMR (500 MHz, $CDCl_3$, 54°C): δ = 3.21 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3), 3.25 (s, 3H, O-CH_3), 3.26 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.37 (s, 6H, OCH_3), 3.40 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 3.64 (s, 6H, OCH_3), 3.66 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 2.95-5.04 (50 H, H-1, H-2, H-3, H-4, H-5, H-6, HC=CH and CH of NBD), 6.75-7.50 (28H, arom. H); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = (all signals are broad) 47.24 (CH_2 of NBD), 57.66 (CH_3O-2), 58.71 and 59.10 (CH_3O-6), 61.72 (CH_3O-3), 69.82 (CH of NBD), 71.13 (C-5, C-6), 81.29 (HC=CH of NBD), 82.27 (C-2, C-3, C-4), 100.18 (C-1), 115.32, 119.29, 120.53, 126.10, 127.25, 129.68 and 130.30 (arom. CH), 138.63, 150.53 (C_{ipso}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = -145 (hept. PF_6), 110.5 (d, $J_{Rh,P}$ = 264 Hz); elemental analysis (%): calcd for $C_{95}H_{126}F_6O_{36}P_3Rh$•$CHCl_3$ (2153.86 + 119.38): C 50.72, H 5.63; found: C 50.72, H 5.73; MS (FAB): *m/z* (%): 2023.6 (37) [*M*-PF_6+O], 2007.7 (49) [*M*-PF_6]$^+$, 1915.5 (58) [*M*-PF_6-NBD]$^+$.

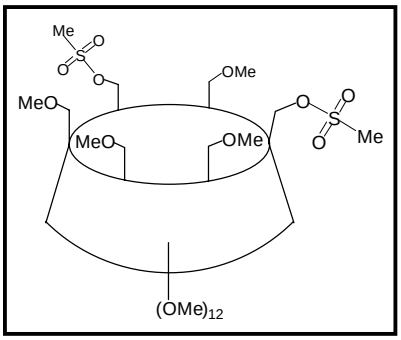
2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (8b)



Tetrafluoroboric acid (34%, 24.1 mL) was added to a solution of **7b** (12.000 g, 5.95 mmol) in MeCN (50 mL). The solution was stirred for 20 min. at room

temperature whereupon Et_3N (45 mL) was added. Addition of water (1000 mL) caused ^{s}TrOH to precipitate. The latter was filtered and the filtrate extracted with CH_2Cl_2 (4 x 300 mL). The organic extract was washed with saturated aqueous $NaHCO_3$ (2 x 300 mL) before being dried ($MgSO_4$), and evaporated to dryness. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 88:12,v/v) to afford **8b** as a colourless solid (6.04 g, 85 %). R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.32; Mp 162-164°C; ^{1}H NMR (200 MHz, C_6D_6): δ = 3.29 (s, 6H, OCH_3), 3.30 (s, 6H, OCH_3), 3.32 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 3.41 (s, 6H, OCH_3), 3.74 (s, 3H, OCH_3), 3.75 (s, 12H, OCH_3), 3.76 (s, 3H, OCH_3), 3.09-4.35 (36H, H-2, H-3, H-4, H-5, H-6), 5.01 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.5 Hz, 1H, H-1), 5.04-5.08 (3d, 3H, H-1), 5.11-5.12 (2d, 2H, H-1); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 57.76, 57.82 [×2], 57.92, 58.81, 58.87 and 58.97 [×4] (CH_3O-2, CH_3O-6), 61.50 [×2] and 61.63 [×4] (CH_3O-3), 62.15, 62.20, 71.30, 71.39, 71.46 and 71.62 (C-6), 71.10 [×2], 71.17 [×2], 72.33 and 72.54 (C-5), 81.23 [×6], 81.72, 81.95 [×5], 82.11 [×5] and 82.24 (C-2, C-3, C-4), 99.32, 99.52 and 99.75 [×4] (C-1); elemental analysis (%): calcd for $C_{52}H_{92}O_{30}$•0.5 CH_2Cl_2 (1197.27 + 42.47): C 50.86, H 7.56; found: C 50.63, H 7.93.

6^{A},6^{C}-Di-*O*-methylsulfonyl-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (1b)



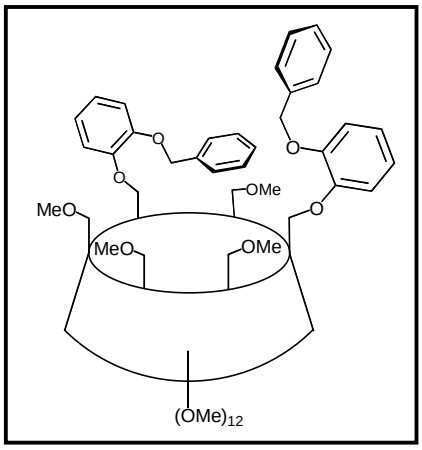
Methylsulfonyl chloride (1.180 g, 10.29 mmol) was added to a solution of **8b** (5.600 g, 4.68 mmol) and DMAP (0.930 g, 7.58 mmol) in anhydrous pyridine (80 mL). The reaction mixture was stirred overnight at room temperature whereupon brine (150 mL) was added. The solution was then extracted with EtOAc (4 x 200 mL), and the organic phase washed respectively with HCl 2M (2 x 200 mL), NaOH 2M (200 mL), before being dried ($MgSO_4$) and filtered. Removal of the solvent *in vacuo* afforded pure

1b as a colorless solid. R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.44; Mp 113-115°C; ^{1}H NMR (200 MHz, C_6D_6): δ = 2.82 (s, 3H, OSO_2CH_3), 2.84 (s, 3H, OSO_2CH_3), 3.26 (s, 3H, OCH_3), 3.28 (s, 9H, OCH_3), 3.31 (s, 6H, OCH_3), 3.38 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.69 (s, 6H, OCH_3), 3.71 (s, 6H, OCH_3), 3.76 (s, 3H, OCH_3), 3.06-4.45 (34H, H-2, H-3, H-4, H-5, H-6), 4.76 (dd, $^3J_{H\text{-}5,H\text{-}6a}$ = 4.5 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.3 Hz, 1H, H-6), 4.92 (dd, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.3 Hz, 1H, H-6), 4.96 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.7 Hz, 1H, H-1), 5.00 (2d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.7 Hz, 2H, H-1), 5.02 (d, 1H, H-1), 5.15 (2d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 2H, H-1); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 37.26 and 37.48 (OSO_2CH_3), 57.56, 57.63, 57.69, 58.02, 58.38, 58.81 [×2] and 59.00 [×3] (CH_3O-2, CH_3O-6), 61.43, 61.59 [×3], 61.69 and 61.76 (CH_3O-3), 69.53, 70.94, 71.00 [×2], 71.20 and 71.33 (C-5), 69.92 [×3], 70.08, 71.53 and 71.85 (C-6), 80.84 [×2], 80.95 [×2], 81.03, 81.16, 81.33, 81.49, 81.75, 81.88 [×2], 81.98, 82.11 [×2], 82.24 [×2], 82.31 and 83.13 (C-2, C-3, C-4), 98.60, 98.90, 99.98, 100.21 [×2] and 100.40 (C-1); elemental analysis (%): calcd for $C_{54}H_{96}O_{34}S_2$•0.5 $CHCl_3$ (1353.45 + 59.69): C 46.32, H 6.88; found: C 46.28, H 7.08.

6^A,6^C-Bis-*O*-(2-benzyloxyphenyl)-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (2b) and 6^A,6^C-*O*-(1,2-phenylene)-2^A,2^B,2^C,2^D, 2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D, 6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (4b)

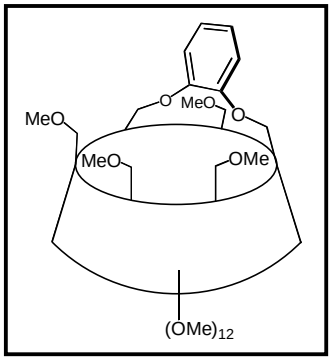
NaH (60%, 0.148 g, 3.69 mmol) was added to a solution of 2-benzyloxyphenol (0.740 g, 3.69 mmol, 0.85 mL) in DMF (25 mL). After 20 min., **1b** (1.000 g, 0.739 mmol) was added. The solution was stirred overnight whereupon water (50 ml) was added. The mixture was extracted with Et_2O (4 × 100 mL), and the ether phase was subsequently washed with an aqueous 2M NaOH solution (100 mL), dried over $MgSO_4$ and filtered. Removal of the solvent in *vacuo* gave a colourless residue (1.410 g) which was purified by column chromatography (SiO_2, hexane/ethyl acetate 20 : 80 → 0 : 100, v/v) to afford two major compounds as well as small amounts of debenzylation products, which were not separated:

Fraction 1: 6^{A},6^{C}-Bis-*O*-(2-benzyloxyphenyl)-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (**2b**)



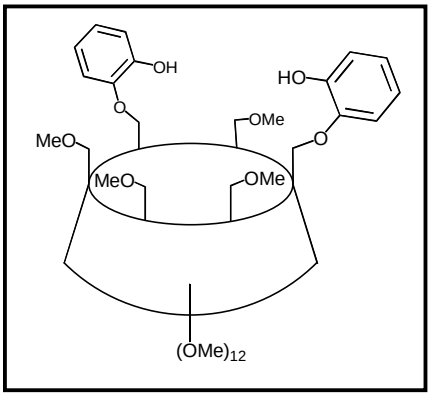
(0.650g, 57%); R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.36; Mp 111-113°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.15 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.37 (s, 9H, OCH_3), 3.47 (s, 3H, OCH_3), 3.49 (s, 6H, OCH_3), 3.51 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.64 (s, 6H, OCH_3), 3.66 (s, 9H, OCH_3), 3.08-4.54 (36H, H-2, H-3, H-4, H-5, H-6), 5.01-5.10 (10H, H-1, OCH_2Ph), 6.82-6.96 (8H, catecholate H), 7.26-7.44 (10H, arom. benzyl H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 57.40 [×2], 57.76 [×2], 57.82 [×2], 58.81 [×2] and 58.94 [×2] (CH_3O-2, CH_3O-6), 61.59 [×2] and 61.66 [×4] (CH_3O-3), 68.41 [×2] (OCH_2Ph), 70.67 [×2] (C-$6^{A,C}$), 70.84 [×2] ,71.13 [×4] (C-5), 71.20 [×2] and 71.33 [×2] (C-$6^{B,D,E,F}$), 81.16 [×4], 81.95 [×2], 82.08 [×4], 82.24 [×4], 82.34 [×2] and 82.42 [×2] (C-2, C-3, C-4), 99.75 [×2] (C-$1^{A,C}$), 100.08 [×4] (C-$1^{B,D,E,F}$), 114.60 [×2], 114.96 [×2], 121.22 [×2] and 121.35 [×2] (catecholate CH), 126.73 [×2], 127.48 [×2] and 128.33 [×2] (benzyl CH), 137.41 [×2], 148.83 [×2] and 149.25 [×2] (C_{ipso}) (The ^{13}C NMR spectrum shows an apparent C_2 symmetry); elemental analysis (%): calcd for $C_{78}H_{112}O_{32}$ (1561.71): C 59.99, H 7.23; found: C 59.79, H 7.28.

Fraction 2: $6^{A},6^{C}$-*O*-(1,2-phenylene)-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{E},6^{F}$-hexadeca-*O*-methyl-$\alpha$-cyclodextrin (**4b**)



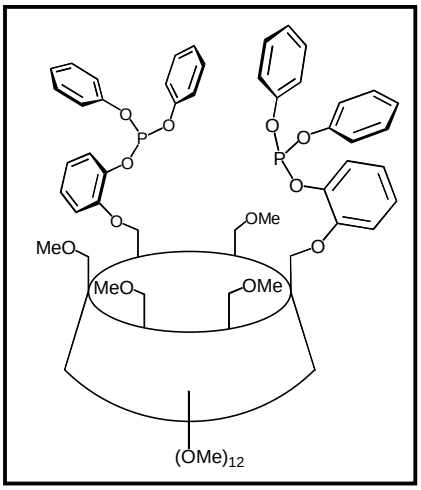
(0.183g, 18%); R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.25; Mp 124-126°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.03 (s, 3H, OCH_3), 3.20 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.48 (s, 6H, OCH_3), 3.49 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.60 (s, 6H, OCH_3), 3.64 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.11-4.41 (36H, H-2, H-3, H-4, H-5, H-6), 4.97 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 1H, H-1), 5.00 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H, H-1), 5.05 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.7 Hz, 2H, H-1), 5.06 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.5 Hz, 1H, H-1), 5.08 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, 1H, H-1) 5.33 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 1H, H-1), 6.81-7.00 (4H, arom. H); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 57.39, 57.45, 57.62, 58.29, 58.46 [×2], 58.58, 58.83 [×2] and 59.54 (CH_3O-2, CH_3O-6) 60.75, 61.24, 61.39 [×2], 61.63 and 61.78 (CH_3O-3), 68.01, 68.81, 71.24, 71.62 and 73.09 [×2] (C-6), 70.68 [×3], 70.82 and 70.99 [×2] (C-5), 79.03, 79.89, 80.37, 80.82, 81.05 [×3], 81.36 [×3], 81.62, 81.75, 81.87, 82.03, 82.25 [×2], 82.51 and 82.75 (C-2, C-3, C-4), 94.71, 97.58, 98.82, 98.87, 99.52 and 99.99 (C-1), 112.83, 118.98, 120.46 and 123.03 (arom. CH), 148.00 and 151.13 (C_{ipso}); elemental analysis (%): calcd for $C_{58}H_{94}O_{30}$ (1271.35): C 54.80, H 7.45; found: C 55.01, H 7.55.

6^A,6^C-Bis-*O*-(2-hydroxyphenyl)-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (6b)



Pd/C (10%, 0.065 g) was added to a solution of **2b** (0.650 g, 0,416 mmol) in EtOH (65 mL). The mixture was stirred for 48 h under H_2 (1 atm.) before being filtered over Celite. Evaporation of the filtrate *in vacuo* yielded pure **6b** (0.540 g, 94%). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.28; Mp 102-104°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.14 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.48 (s, 6H, OCH_3), 3.50 (s, 6H, OCH_3), 3.52 (s, 3H, OCH_3), 3.63 (s, 6H, OCH_3), 3.64 (s, 6H, OCH_3), 3.66 (s, 6H, OCH_3), 3.19-4.46 (36H, H-2, H-3, H-4, H-5, H-6), 5.01 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, 1H, H-1), 5.02 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, 1H, H-1), 5.04 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H, H-1), 5.08 (3d, 3H, H-1), 6.61 (br s, 1H, OH), 6.67 (br s, 1H, OH), 6.74-7.02 (8H, arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 57.75 [×3], 57.84, 58.01 [×2], 58.75, 58.87 [×2] and 59.03 (CH_3O-2, CH_3O-6), 61.65 [×5] and 61.83 (CH_3O-3), 70.56, 70.83 [×4], 71.30 (C-6), 71.07, 71.35 [×4] and 71.73 (C-5), 81.20 [×4], 81.32, 81.49, 81.75, 81.89, 82.05 [×2], 82.11 [×3], 82.22, 82.49 [×2], 82.66 and 83.10 (C-2, C-3, C-4), 99.38, 99.72, 99.82 [×2] and 100.21 [×2] (C-1), 115.16, 115.62 [×2], 115.89, 119.85, 120.02, 122.57 and 122.80 (arom. CH), 146.47, 146.61 and 146.86 [×2] (C_{ipso}); elemental analysis (%): calcd for $C_{64}H_{100}O_{32}$ (1381.46): C 55.64, H 7.30; found: C 55.41, H 7.24.

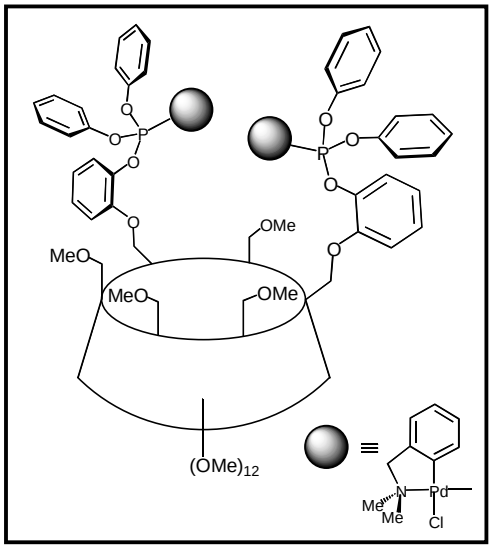
6^{A},6^{C}-Bis-*O*-{2-[(diphenoxyphosphino)oxy]phenyl}-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E}, 3^{F},6^{B},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (L2)



Chlorodiphenylphosphite (0.247 g, 0.98 mmol, 0.20 mL) was added to a stirred solution of **6b** (0.540 g, 0.39 mmol) in CH_2Cl_2 (25 mL) at -40°C. The reaction mixture was stirred for 15 min. at -40°C whereupon triethylamine (0.14 mL, 0.98 mmol, 1 equiv.) was added. After 1 h, addition of pentane (200 mL) caused the triethylammonium salt to precipitate. The latter was filtered off and the filtrate was evaporated to dryness under vacuum. The residue was washed with boiling hexane (10 mL). The hot suspension was then cooled down to 0°C and allowed to settle whereupon the hexane phase was discarded. The colourless residue was found to be pure **L2** (0.700 g, 99%). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.38; Mp 61-63°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.29 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 3.34 (s, 6H, OCH_3) 3.36 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.64 (s, 6H, OCH_3), 2.98-4.18 (34H, H-2, H-3, H-4, H-5, H-6a, H-$6b^{B,D,E,F}$), 4.75 (dd, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 10.5 Hz, 2H, H-$6b^{A\ or\ C}$), 4.80 (dd, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 10.7 Hz, 2H, H-$6b^{C\ or\ A}$), 4.85 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, 1H, H-1), 4.91 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H, H-1), 5.01 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H, H-1), 5.05 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, 1H, H-1), 5.07 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.8 Hz, 1H, H-1), 5.08 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H, H-1), 6.84-7.35 (28H, arom. H); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 57.27 [×2] and 57.82 [×4] (CH_3O-2), 58.81, 58.91 and 59.00 [×2] (CH_3O-6), 61.66 [×6] (CH_3O-3), 67.85 [×2] (C-$6^{A,C}$), 70.51 [×2], 70.67 [×2], 71.30 [×2] (C-5), 71.50 [×2] and 71.92 [×2] (C-$6^{B,D,E,F}$), 81.16

[×8], 81.62 [×2], 81.85 [×2], 82.18 [×2], 82.34, 82.57 [×2] and 82.83 (C-2, C-3, C-4), 99.42 (C-$1^{A,C}$), 100.11 [×2] and 100.27 [×2] (C-$1^{B,C,E,F}$), 113.81 [×2] (s, C_{para}), 120.74 [×2] (d, $^3J_{C,P}$ = 8.2 Hz, C_{ortho}), 121.26 [×4] (d, $^4J_{C,P}$ = 6.6 Hz, C_{meta}), 122.38 [×2] (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 123.98 [×4] (d, $^4J_{C,P}$ = 3.3 Hz, C_{para}), 124.56 [×2] (s, C_{meta}), 129.42 [×4] (d, $^3J_{C,P}$ = 9.9 Hz, C_{ortho}), 141.19 [×2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 150.13 [×2] (s, C_{ipso}), 151.44 [×2] (s, C_{ipso}), 151.74 [×2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 127.5 [×2] (s); elemental analysis (%): calcd for $C_{88}H_{118}O_{36}P_2$ (1813.81): C 58.27, H 6.56; found: C 58.32, H 6.36.

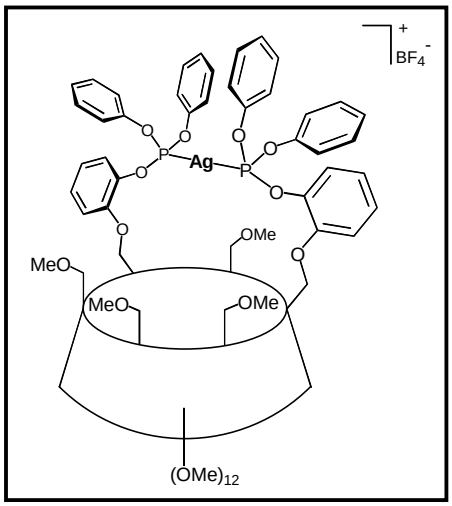
_P,P'_-(6^A,6^C-Di-_O_-{2-[(diphenoxyphosphino)oxy]phenyl}-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-_O_-methyl-α-cyclodextrin)-bis-[chloro(o-dimethylaminobenzylpalladium(II)] (9b)



[(_o_-$C_6H_4CH_2NMe_2$)PdCl]$_2$ (0.031 g, 0.057 mmol) was added to a solution of **L2** (0.103 g, 0.057 mmol) in CH_2Cl_2 (5 mL). After 20 min., the product was precipitated by addition of pentane (250 mL) and then collected on Celite. The precipitate was dissolved in CH_2Cl_2 (15 mL), and upon filtration, the organic solution was evaporated to dryness *in vacuo* to afford pure **9b** as a yellow powder (0.100 g, 75%). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.30; Mp 97-99°C; ^1H NMR (500 MHz, $CDCl_3$, 25°C): δ = 2.60 (d, 6 H, $^4J_{H,P}$ = 3.9 Hz, NCH_3), 2.62 (d, 6H, $^4J_{H,P}$ = 3.7 Hz, NCH_3), 3.21 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3), 3.31 (s, 6H, OCH_3), 3.32 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 3.49 (s, 3H,

OCH_3), 3.59 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 3.62 (s, 6H, OCH_3), 3.64 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 2.94-4.17 (38H, H-2, H-3, H-4, H-5, H-6a, H-6b^{B,D,E,F}, CH_2Ph), 4.73 (dd, $^2J_{\text{H-6a,H-6b}}$ = 10.6 Hz, $^3J_{\text{H-6a,H-5}}$ = 3.0 Hz, 1H, H-6b$^{A\text{ or }C}$), 4.79 (dd, $^2J_{\text{H-6a,H-6b}}$ = 10.6 Hz, $^3J_{\text{H-6a,H-5}}$ = 2.8 Hz, 1H, H-6b$^{C\text{ or }A}$), 4.94 (d, $^3J_{\text{H-1,H-2}}$ = 3.4 Hz, 1H, H-1), 4.99 (2d, $^3J_{\text{H-1,H-2}}$ = 2.6 Hz, 1H, H-1), 5.00 (2d, $^3J_{\text{H-1,H-2}}$ = 2.9 Hz, 1H, H-1), 5.05 (d, $^3J_{\text{H-1,H-2}}$ = 3.4 Hz, 1H, H-1), 5.11 (2d, $^3J_{\text{H-1,H-2}}$ = 3.1 Hz, 2H, H-1), 6.85-6.91 (8H, arom. H), 6.98-7.10 (8H, arom. H), 7.20-7.33 (18H, arom. H), 7.63-7.72 (2H, arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 49.98 (d, $^3J_{C,P}$ = 3.3 Hz, *N*CH_3) , 50.14 (d, $^3J_{C,P}$ = 4.9 Hz, *N*CH_3), 57.40 [×2] and 57.79 [×4] (CH_3O-2), 58.81, 58.94, 59.00 and 59.07 (CH_3O-6), 61.50 [×2], 61.65, 61.69 [×2] and 61.76 (CH_3O-3), 67.59 (C-6^{A,C}), 70.61, 70.71 and 71.26 (C-5), 71.39 and 71.98 (C-6^{B,D,E,F}), 72.64 and 72.74 (*C*H_2Ph), 81.20 [×2], 81.69 [×2], 81.85, 82.18, 82.28, 82.51 and 82.93 (C-2, C-3, C-4), 99.45 (C-1^{A,C}), 100.08 and 100.31 (C-1^{B,D,E,F}), 113.88 [×2] (s, C_{para}), 120.63 [×2] (s, DMBA), 121.17 [×4] (d, $^4J_{C,P}$ = 4.9 Hz, C_{meta}), 122.03 [×2] (d, $^4J_{C,P}$ = 8.2 Hz, DMBA), 122.37 [×2] (s C_{ortho}), 124.50 [×2] (s, C_{meta}), 124.80 [×4] (d, $^5J_{C,P}$ = 3.3 Hz, C_{para}), 125.19 [×2] (s, C_{meta}), 125.86 [×2] (d, $^4J_{C,P}$ = 8.2 Hz, DMBA), 129.22 [×4] (d, $^3J_{C,P}$ = 3.3 Hz, C_{ortho}), 136.88 [×2] (d, $^3J_{C,P}$ = 11.5 Hz, DMBA), 140.77 [×2] (d, $^2J_{C,P}$ = 4.9 Hz, C_{ipso}), 147.55 [×2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 149.72 [×4] (d, $^2J_{C,P}$ = 4.9 Hz, C_{ipso}), 151.02 [×2] (d, $^2J_{C,P}$ = 3.3 Hz, C_{ipso}), 151.18 [×2] (s, C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 104.6 [×2] (s); elemental analysis (%): calcd for $C_{106}H_{142}Cl_2N_2O_{36}P_2Pd_2$ (2365.96): C 53.81, H 6.05; found: C 53.78, H 6.16.

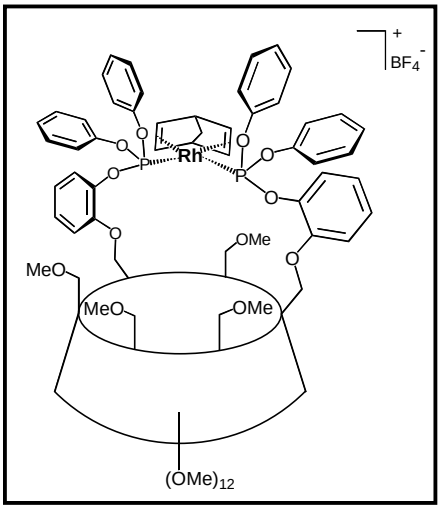
{6^{A},6^{C}-Bis-*O*-[2-(diphenylphosphito)phenyl)]-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F}, 6^{B},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin}silver(I) tetrafluoroborate (10b)



A solution of $AgBF_4$ (0.011 g, 0.056 mmol) in THF (20 mL) was added to a solution of **L2** (0.110 g, 0.056 mmol) in CH_2Cl_2 (200 mL) under vigorous stirring. After 20 min., the reaction mixture was concentrated to 5 mL and pentane (250 mL) was added to precipitate the product, which was collected on Celite. The precipitate was dissolved in CH_2Cl_2 (15 mL), and upon filtration, the organic solution was evaporated to dryness *in vacuo* to afford pure **10b** as a white powder (0.090 g, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.40 (s, 6H, OCH_3), 3.43 (s, 6H, OCH_3), 3.47 (s, 6H, OCH_3), 3.56 (s, 6H, OCH_3), 3.60 (s, 6H, OCH_3), 3.62 (s, 6H, OCH_3), 3.63 (s, 6H, OCH_3), 3.64 (s, 6H, OCH_3), 2.86-4.25 (36H, H-2, H-3, H-4, H-5, H-6), 4.96 (br d, 1H, H-1), 4.99 (2d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H, H-1), 5.04 (br d, 1H, H-1), 5.11 (br d, 1H, H-1), 5.20 (br d, 1H, H-1), 6.60-7.60 (28H, arom. H); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 57.43 [×2], 57.53 [×2] and 57.76 [×2] (CH_3O-2), 58.91 [×2] and 59.04 [×2] (CH_3O-6), 61.66 [×2], 61.72 [×2] and 61.79 [×2] (CH_3O-3), 70.21 [×2], 70.90 [×4], 71.17 [×2] and 71.50 [×2] (C-5, C-6), 80.97 [×2], 81.23 [×6], 82.02 [×2], 82.10 [×2] and 82.28 [×6] (C-2, C-3, C-4), 100.11 [×6] (C-1), 115.35-129.94 (arom. CH), 140.00-150.26 (C_{ipso}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 108.3 and 114.5 (ABX, $^{107}J_{Ag,P}$ = 1095 Hz, $^{109}J_{Ag,P}$ = 1203 Hz and $^{107}J_{Ag,P'}$ = 977 Hz, $^{109}J_{Ag,P'}$ = 1088 Hz, $^{2}J_{P,P'}$ = 256 Hz, P and P'); elemental analysis (%): calcd for $C_{88}H_{118}AgBF_4O_{36}P_2$•0.75 $(CH_3)_2CO$ (2008.48 + 43.56): C 52.83, H 6.02;

found: C 53.10, H 6.09; MS (FAB): *m/z* (%): 1937.3 (20) $[M\text{-}BF_4\text{+O}]^+$, 1921.3 (100) $[M\text{-}BF_4]^+$.

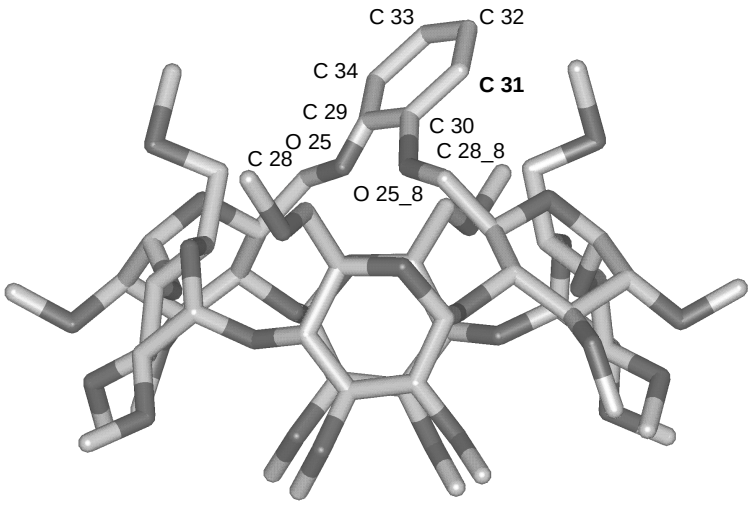
***cis*-*P,P'*-(6^{A},6^{C}-Bis-*O*-{2-[(diphenoxyphosphino)oxy]pheny}-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B}, 3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin)-[(norbornadiene)rhodium(I)] tetrafluoroborate (11b)**



$AgBF_4$ (0.013 g, 0.067 mmol) was added to a solution of $[RhCl(NBD)]_2$ (0.016 g, 0.035 mmol) in THF/CH_2Cl_2 (50:50, v/v, 50 mL). After stirring the suspension vigorously for 15 min., the precipitate was collected on Celite and the filtrate was directly added to a solution of **L2** (0.125 g, 0.069 mmol) in CH_2Cl_2 (200 mL) under vigorous stirring. The reaction mixture was then stirred at room temperature for 20 min. before being concentrated to 5 ml. Addition of pentane (250 mL) caused the product to precipitate. The solid was then filtered over Celite before being dissolved in CH_2Cl_2 (15 mL). Upon filtration, the organic solution was evaporated to dryness *in vacuo* to afford pure **11b** (0.120 g, 83%) as an orange powder. R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.30; Mp 155° dec. All ^{1}H signals are broad. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): all signals are broad, δ = 57.46 (CH_3O-2), 58.81 (CH_3O-6), 61.63 (CH_3O-3), 70.71 (C-5, C-6), 81.36 and 82.31 (C-2, C-3, C-4), 100.18 (C-1), 115.35, 120.47, 126.07, 129.28, 129.55 and 130.27 (arom. CH), 138.50 and 150.43 (C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 110.5 (d, $J_{Rh,P}$ = 259 Hz). elemental analysis (%): calcd for $C_{95}H_{126}BF_4O_{36}Rh$ (2096.64): C 54.42, H 6.06; found: C 54.21, H 6.10; MS (FAB): *m/z* (%): 2024.4 (10) $[M\text{-}BF_4\text{+O}]^+$, 2008.4 (18) $[M\text{-}BF_4]^+$, 1915.3 (40) $[M\text{-}BF_4\text{-NBD}]^+$.

II.4.3. X-ray crystallographic data

II.4.3.1. X-ray crystallography data of 4a•C_7H_{16}



The included heptane molecule has been omitted for clarity

Crystals of compound **4a** suitable for diffraction study were obtained by slow diffusion of heptane into an EtOAc solution of the compound. Data were collected on Nonius KappaCCD (graphite-monochromated MoKα radiation 0.71073Å). The structure was solved with SHELLXD,[32] which revealed the non-hydrogen atoms of the structure. After anisotropic refinement of the cyclodextrin moiety, the bridging aromating ring appeared as having two well-defined orientations each of 50 % occupancy. The presence of a disordered *n*-heptane chain in the cavity was also detected. The whole structure was refined with SHELLXL by the full-matrix least-squares techniques (use of F^2; x, y, z, β_{ij} for the cyclodextrine O and C atoms, x, y, z, B_{iso} for the other non-H atoms and x, y, z in riding mode for H atoms; 391 variables, 4864 observations with $I>2.0\sigma(I)$, w = $1/[\sigma^2(Fo^2) + (0.2P)^2]$ where P = $(Fo^2 + 2Fc^2)/3$). A summary of the crystallographic data is given in Table 3.

Table 3. Crystallographic data for compound **4a**•C_7H_{16}

Crystal Data	
Empirical formula	$C_{32.50}H_{55}O_{15}$
M_r	685.76
Crystal system	Hexagonal
Space group	$P6_222$
Temperature	293(2) K
Unit cell dimensions	
a	31.2588(2) Å
b	31.2588(2) Å
c	15.03730(10) Å
α	90°
β	90°
γ	120°
V	12724.62(14) Å^3
Z	12
D (calculated)	1.072 g/cm^3
F(000)	4428
μ	0.084 mm^{-1}
Data Processing and Reduction	
θ range for data collection	1.99 to 26.37°
Index ranges	$0 \leq h \leq 39$, $-33 \leq k \leq 0$, $0 \leq l \leq 18$
Reflections collected	8690
Reflections [$I>2\sigma(I)$]	4864
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8690 / 0 / 391
Goodness-of-fit on F^2	1.359
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.1300$, $wR2 = 0.3394$
R indices (all data)	$R1 = 0.1885$, $wR2 = 0.3827$
Largest diff. peak and hole	0.891 and –0.392 e.Å^{-3}

Table 4. Atomic coordinates and equivalent isotropic displacement parameters for **4a**

	x	y	z	U(eq)
O(1)	0.87061(15)	0.28773(15)	0.7795(2)	0.1081(15)
O(2)	0.86158(15)	0.25298(15)	0.9206(2)	0.1036(13)
O(3)	0.84159(16)	0.3548(2)	0.8473(4)	0.1305(18)
O(4)	0.91633(15)	0.39954(15)	0.9776(3)	0.1024(12)
O(5)	0.9036(2)	0.2501(2)	1.0873(4)	0.1375(18)
O(11))	0.98430(12)	0.36149(13)	0.9678(2)	0.0803(9)
O(12)	1.02932(17)	0.32415(19)	1.0067(3)	0.1135(15)
O(13)	1.04637(19)	0.4425(3)	1.0666(4)	0.167(3)
O(14)	1.13746(16)	0.46553(18)	0.9768(3)	0.1102(14)
O(15)	1.0925(4)	0.2881(4)	0.9413(10)	0.260(7)
O(21)	1.12124(14)	0.39836(16)	0.8371(2)	0.0892(11)
O(22)	1.1340(2)	0.3464(2)	0.7417(3)	0.1233(17)
O(23)	1.22448(17)	0.4714(2)	0.8249(3)	0.1296(19)
O(24)	1.22226(18)	0.4844(3)	0.6362(3)	0.142(2)
O(25)	1.0450(3)	0.2802(3)	0.6370(4)	0.145(2)
C(1)	0.8463(2)	0.2790(3)	0.8616(4)	0.111(2)
C(2)	0.8572(2)	0.3266(3)	0.9034(4)	0.106(2)
C(3)	0.91166(19)	0.3588(2)	0.9261(4)	0.0920(16)
C(4)	0.9312(2)	0.3314(2)	0.9751(4)	0.0963(18)
C(5)	0.9134(2)	0.2783(2)	0.9405(4)	0.1007(19)
C(6)	0.8034(3)	0.3599(3)	0.8815(7)	0.138(3)
C(7)	0.9505(3)	0.4433(3)	0.9492(7)	0.140(3)
C(8)	0.9190(2)	0.2450(2)	1.0024(4)	0.0969(17)
C(9)	0.9072(4)	0.2176(3)	1.1516(7)	0.162(4)
C(11)	1.0143(2)	0.3582(3)	1.0317(3)	0.0981(19)
C(12)	1.0602(2)	0.4084(3)	1.0437(4)	0.111(2)
C(13)	1.0917(2)	0.4238(2)	0.9583(3)	0.0902(16)
C(14)	1.1000(2)	0.3826(3)	0.9233(3)	0.0888(15)
C(15)	1.0527(2)	0.3339(3)	0.9202(4)	0.0958(16)
C(16)	1.0713(7)	0.4715(4)	1.1373(6)	0.225(8)
C(17)	1.1501(2)	0.5056(3)	0.9181(6)	0.123(2)
C(18)	1.0546(6)	0.2871(5)	0.8845(8)	0.180(5)
C(19)	1.0911(8)	0.2406(6)	0.903(2)	0.347(18)
C(21)	1.1557(3)	0.3842(3)	0.8053(5)	0.107(2)
C(22)	1.2006(3)	0.4315(4)	0.7628(6)	0.138(3)
C(23)	1.1811(2)	0.4451(3)	0.6830(4)	0.115(2)
C(24)	0.8462(2)	0.2501(2)	0.7128(4)	0.107(2)
C(25)	1.1138(3)	0.3562(3)	0.6665(4)	0.111(2)
C(26)	1.2570(4)	0.4668(5)	0.8779(7)	0.167(4)
C(27)	1.2317(3)	0.5323(5)	0.6626(7)	0.148(4)
C(28)	1.0921(3)	0.3115(3)	0.6104(4)	0.135(3)
C(29)	1.0319(3)	0.2440(3)	0.6104(4)	0.105(3)
C(30)	0.9820(3)	0.2158(3)	0.6314(4)	0.189(9)
C(31)	0.9525(3)	0.1713(3)	0.5878(4)	0.200(10)

C(32)	0.9729(3)	0.1549(3)	0.5233(4)	0.245(14)
C(33)	1.0227(3)	0.1831(3)	0.5024(4)	0.291(19)
C(34)	1.0522(3)	0.2276(3)	0.5459(4)	0.164(7)
C(41)	0.9100(7)	0.4747(6)	0.7025(11)	0.218(6)
C(42)	1.0325(6)	0.4234(5)	0.7202(9)	0.191(5)
C(43)	0.9417(6)	0.4156(7)	0.6709(11)	0.210(5)
C(44)	1.0000	0.3796(6)	0.6667	0.175(6)

II.5. References

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Chapter III. Cyclodextrin diphosphines as first and second coordination sphere cavitands

III. Cyclodextrin diphosphines as first and second coordination sphere cavitands

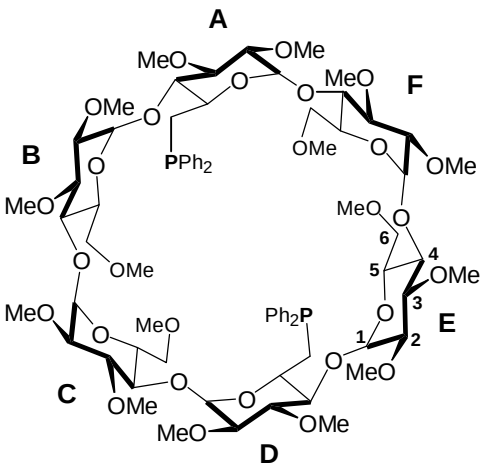
III.1. Introduction

Chemically-modified cyclodextrins (CDs) have largely contributed to the spectacular development of host-guest chemistry in the last 20 years.[1,2] The receptor properties of these macrocyclic compounds have been exploited in numerous applications such as, *e. g.*, the recognition and separation of chiral compounds,[3-5] the stabilisation of photo-isomerisable molecules,[6] the solubilisation of drugs (and their slow release in the human body)[7,8], or the construction of enzyme mimics.[9-14] Most of the supramolecular systems so far designed rely on the fact that the CDs and their chemically-modified analogues are scaffolds on which functional substituents can be assembled in a controlled manner, thus producing molecular cavities with enhanced recognition properties.[15,16]

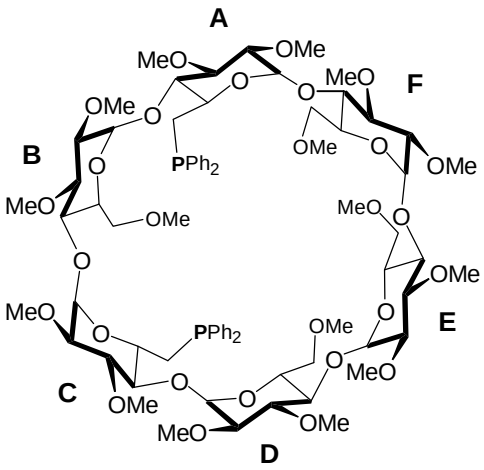
A relatively new field in cavitand chemistry focuses on the design and synthesis of CDs bearing appended transition metal centres.[17-32] Reetz *et al.*, for example, described a fascinating rhodium catalyst based on a β-CD-derivative which displays shape selectivity in hydrogenation and hydroformylation reactions, thus opening the way to supramolecular catalysis of industrial relevance.[33] Anchoring reactive coordination centres on CDs appears therefore a desirable goal. However, little has been reported on CDs in which the metal centre is rigidly held at the receptor entrance, nor have systems with free coordination sites that point towards the cavity interior been described. It may reasonably be anticipated that in such metallocyclodextrins the cavity, acting as a second coordination sphere, will strongly favour non-covalent interactions between a coordinated substrate and the inner cavity walls.

As part of our studies on phosphine- and amine-modified cavitands,[22,24,30,34] we now report on the synthesis and coordinative properties of the two α-CD-derived

ligands **L3** and **L4**. Both CDs have been prepared by anchoring phosphine ligands on non-adjacent glucose units, the phosphorus binding sites being closely linked to the CD skeleton. 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 **L3** and **L4**. This study also shows how the presence of the cavity, that to some extent, is wrapped around the first coordination sphere of a metal centre, favours the formation of an unprecedented cationic $[AgP_2(acetonitrile)_2]^+$ species (P = phosphine). Note that other cavitands, based on calix[4]-[34,35] and calix[6]arenes,[36-43] have recently been shown to act as second sphere ligands.



L3

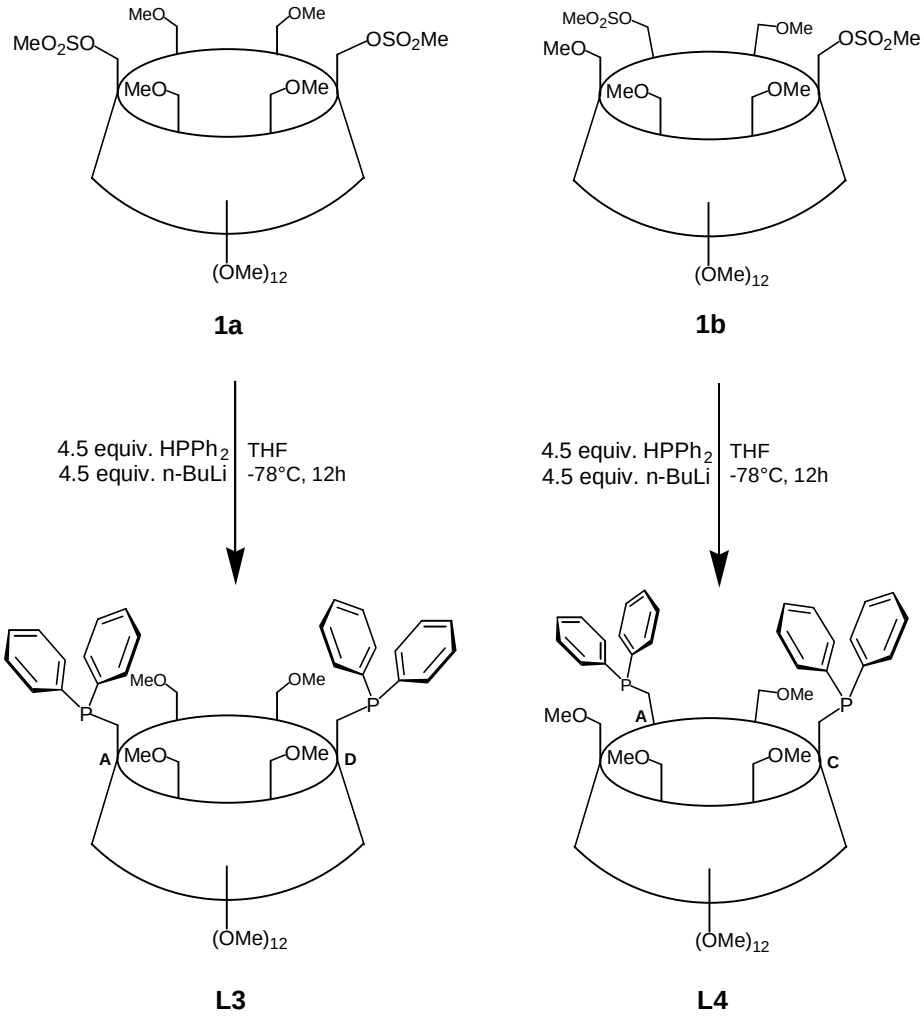


L4

III.2. Results and Discussion

III.2.1. Ligand synthesis and *trans*-binding properties

The two cyclodextrin-phosphines **L3** and **L4** were obtained in high yield by reaction of PPh_2Li with the precursors **1a**[23] and **1b**, respectively (Scheme 1). Both phosphines are fairly soluble in hexane. The ^{31}P NMR spectrum of **L3** shows a singlet

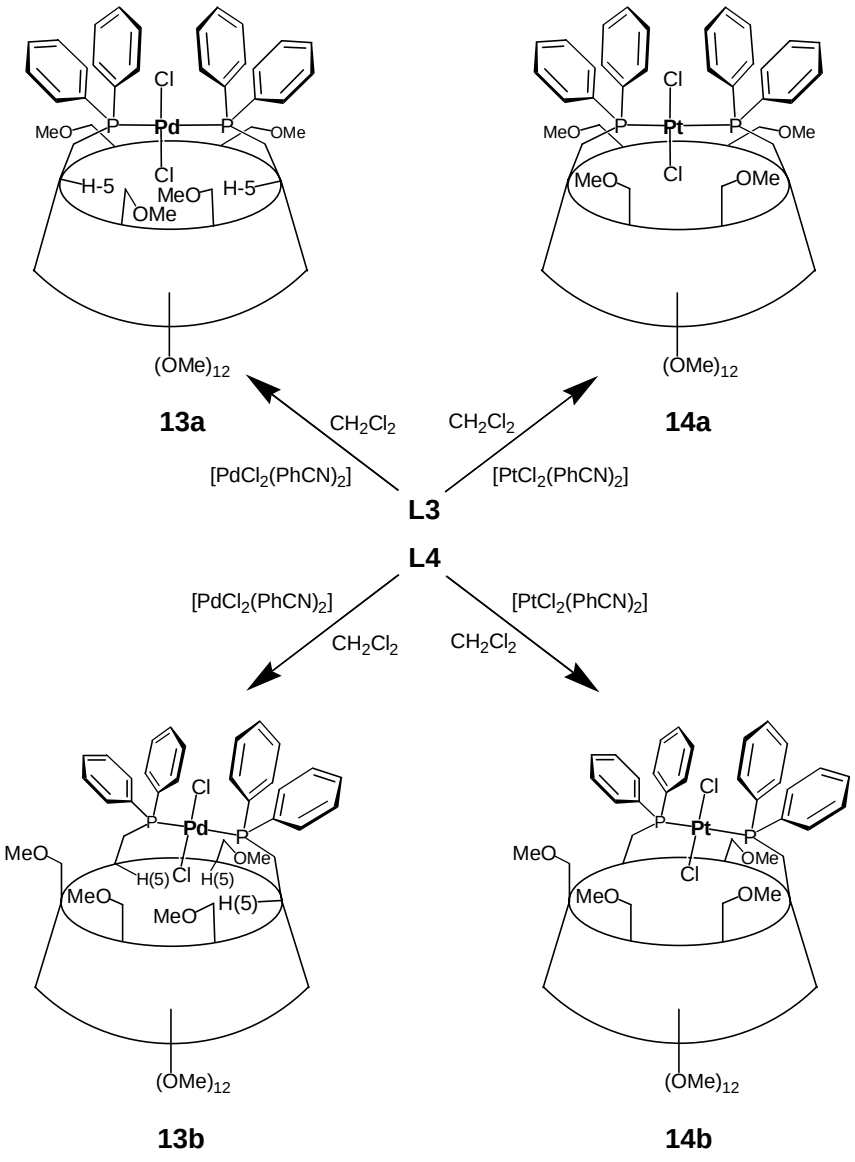


Scheme 1. Synthesis of two CD-based diphosphines

at -17.9 ppm, in keeping with a C_2-symmetrical compound, while the phosphorus signals of **L4**, which has no symmetry element, appear at -22.7 and -22.3 ppm. The C_2-symmetry of **L3** is further confirmed by the presence of 3 distinct doublets (*vs.* 6 for **L4**) for the H-1 protons and of 8 methoxy singlets (*vs.* 16 for **L4**) in the ^{1}H NMR spectrum. It is worth mentioning that the close proximity of the chiral CD core produces a strong differentiation between the geminal Ph rings carried by each phosphorus atom of **L3**, as revealed by ^{13}C NMR spectroscopy. Such a discrimination was not observed in other C_2-symmetrical CD-diphosphines where the phosphinyl units are further away from the cavtity.[20]

Molecular models show that both diphosphines are ideally suited for forming *trans*-chelate complexes. Thus, reaction of **L3** with $[PdCl_2(PhCN)_2]$ afforded after

work-up complex **13a** (*ca.* 40 %),[44] which is characterised by a ^{31}P NMR signal at 11.9 ppm. Again all ^{1}H 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(PC) + ^{3}J(PC) = 23 Hz) reflects the presence of *trans*-arranged phosphorus atoms.[45]



The platinum analogue **14a** 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(PPt) coupling constant of 2637 Hz, which lies in the range

expected for this stereochemistry.[46] The *trans*-spanning behaviour of **13a** and **14a** was confirmed by two X-ray diffraction studies (Figure 1 and 2). Both compounds are isostructural and possess C_2-symmetry. The P–M–P angles are close to 172°, the PM vectors being slightly bent towards the cavity. The P–M distances (2.362(1) Å for **13a** and 2.334(1) Å for **14a**) lie within the range found in the literature for this type of phosphine complexes.[45] The most interesting feature in each of these structures is undoubtedly the presence of a M–Cl bond that is directed towards the CD interior. Careful examination of the structure shows that the chlorine atom is located between the two inwardly pointing H-5 atoms belonging to the phosphine-substituted glucose units.

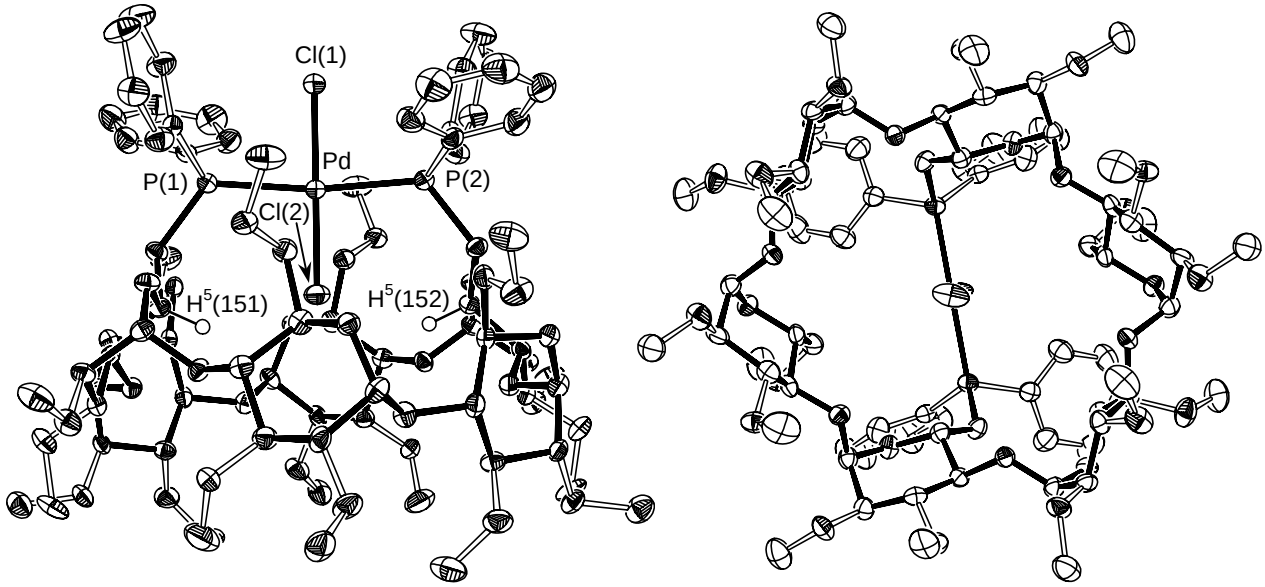


Figure 1. Ortep views of **13a**; side view(left) and bottom (right) view. Ellipsoids are drawn at the 50% probability level. The included butanone molecule has been omitted for clarity.

Table 1. Selected bond lengths and angles for **13a**

bond lengths (Å) [a]		angles (°)	
P(1)-Pd	2.362(1)	P(1)-Pd-P(2)	171.81(7)
P(2)-Pd	2.362(1)	Cl(1)-Pd-Cl(2)	180.00(3)
Pd-Cl(1)	2.291(2)	Cl(2)-Pd-P(1)	94.10(3)
Pd-Cl(2)	2.288(2)	Cl(2)-Pd-P(2)	94.10(3)
H(151)-Cl(2)	2.651		
H(152)-Cl(2)	2.656		

[a] the C-H(151) and C-H(152) distances have been fixed at 0.95 Å

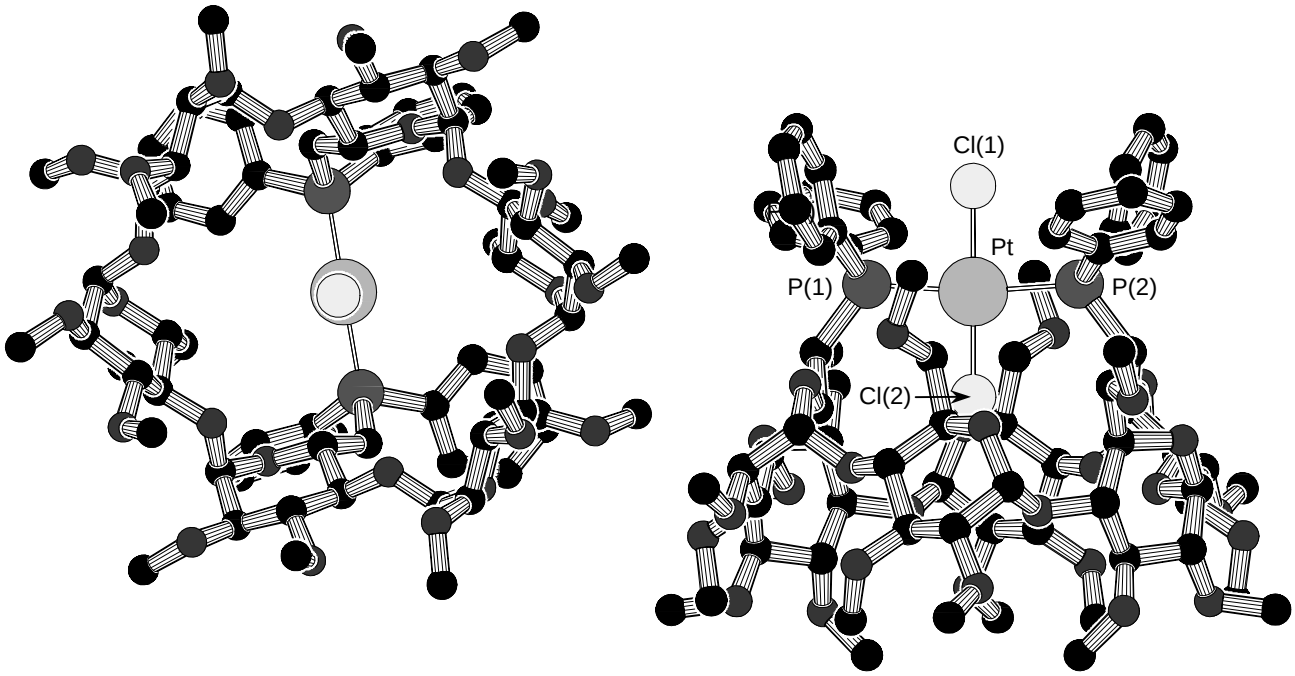


Figure 2. Platon drawing of **14a**; bottom view (left) and side view (right). The included butanone molecule has been omitted for clarity.

Table 2. Selected bond lengths and angles for **14a**

bond lengths (Å) [a]		angles (°)	
P(1)-Pt	2.334(1)	P(1)-Pt-P(2)	172.17(6)
P(2)-Pt	2.334(1)	Cl(1)-Pt-Cl(2)	180.00(0)
Pt-Cl(1)	2.299(2)	Cl(2) Pt P(1)	93.92(3)
Pt-Cl(2)	2.297(2)	Cl(2) Pt P(2)	93.92(3)
H(151)-Cl(2)	2.637		
H(152)-Cl(2)	2.642		

[a] the C-H(151) and C-H(152) distances have been fixed at 0.95 Å

Assuming a C-5–H-5 bond length of 0.95 Å, the H-5•••Cl separations are close to 2.65 Å in both complexes. A clear indication 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 lowfield shift, of *ca.* 0.8 ppm with respect to the free ligand.

Similar complexing properties were found for ligand **L4** from which the *trans*-MCl_2(**L4**) complexes **13b** (M = Pd) and **14b** (M = Pt) could be obtained (see

experimental part). The mass spectra (FAB) of **13a** and **14b** display peaks at *m/z* 1710.4 and 1799.5, respectively, revealing the presence of the corresponding $[M+H]^+$

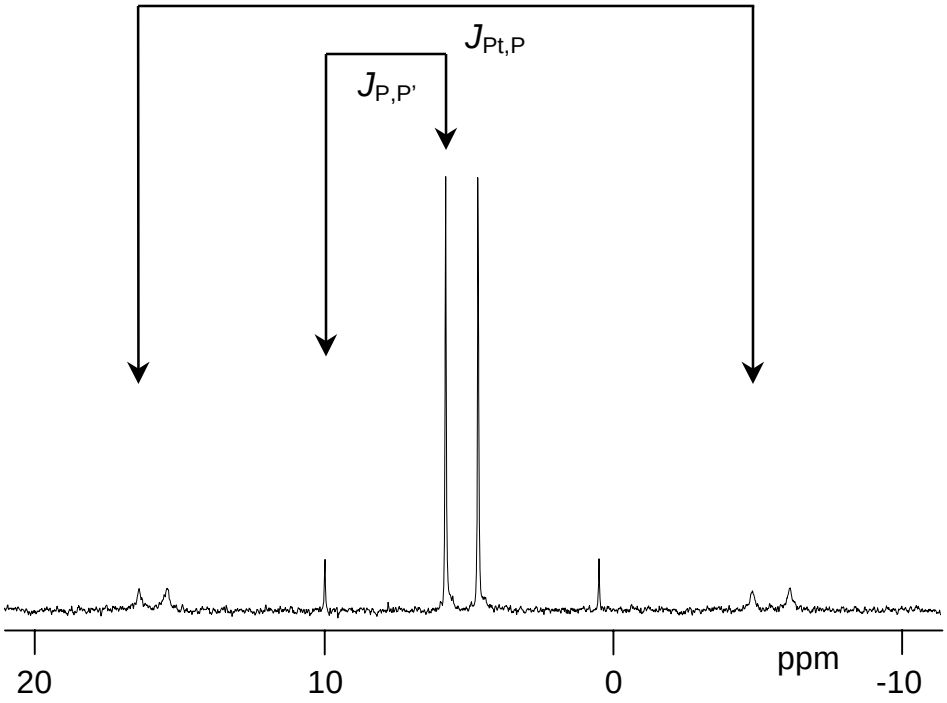


Figure 3. ^{31}P NMR spectrum of **14b** recorded in $CDCl_3$ at 121.5 MHz

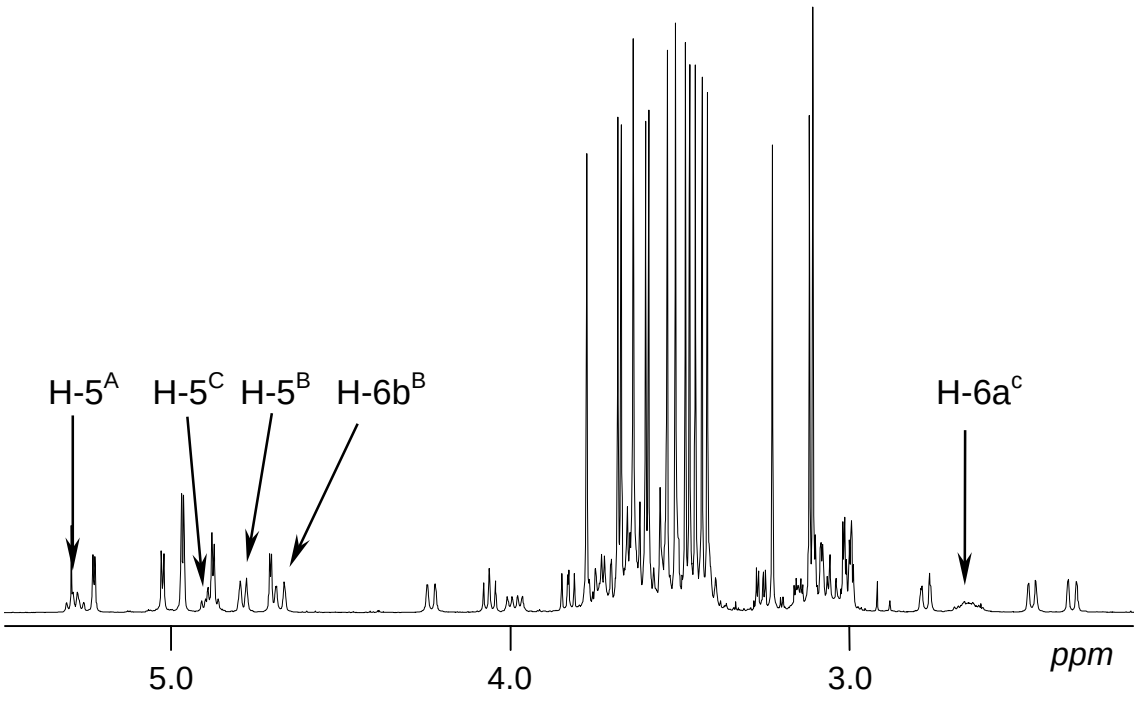
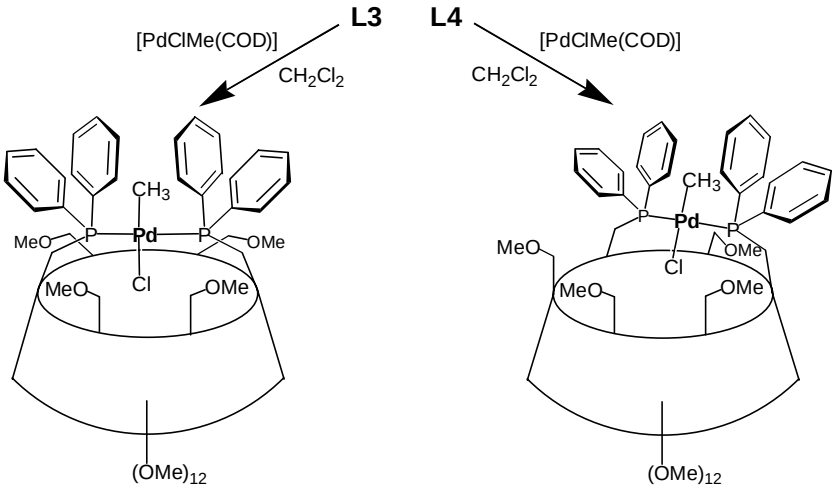


Figure 4. ^1H NMR spectrum of **14b** recorded in $CDCl_3$ at 500 MHz

ions. The *trans* configuration of **14b** was easily deduced from the ^{31}P NMR spectrum (Figure 3), which exhibits an ABX spectrum (X = Pt) pattern characterised by the following coupling constants: *J*(PP') = 509 Hz, *J*(PPt) = 2620 and 2577 Hz. Interestingly, the two phosphorus atoms of **13b** are equivalent by accident. In fact, the chemical shift of the corresponding signal (9.9 ppm in $CDCl_3$) is very close to that found for **13a** and therefore a *trans*-PP arrangement can reasonably be assigned to this complex. It should be mentioned, in addition, that the ^{1}H NMR spectra of **13b** and **14b** 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 **14b**, Figure 4), in agreement with the presence of weak interactions with an *endo*-oriented M–Cl unit.

A further illustration of the "chlorophillic" character of **L3** and **L4** was provided by their reactions with [PdClMe(COD)], which afforded **15a** and **15b** respectively, in high yield (Scheme 2). The ^{31}P NMR spectrum of the C_2-symmetrical complex **15a** shows a singlet at 19.4 ppm, whereas that of **15b** displays 2 doublets centred at 14.1 and 20.3 ppm, respectively, and reveals a *J*(PP') coupling constant 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 (^{3}J(PH) = 6.0 Hz for **15a** and 6.4 Hz for **15b**). As for complexes **13a** and **14a**, the two H-5 atoms of the phosphine-functionalised glucose rings of **15a** are significantly lowfield shifted when compared to

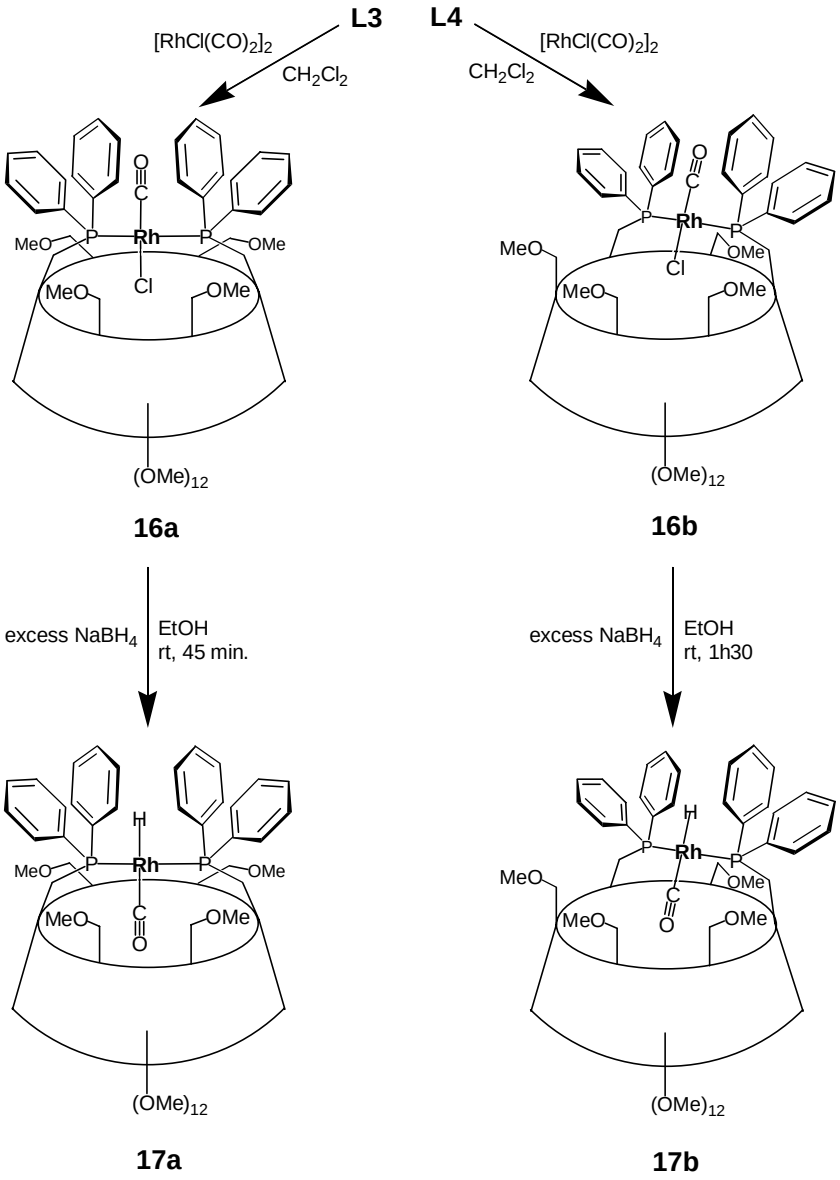


15a **15b**

their counterparts in free **L3** ($\Delta\delta$ = 1.35 ppm). Furthermore, 2D ROESY experiments unambiguously confirmed the spatial proximity of the methyl group and the PPh_2 groups, *i.e.* 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 **15b**, 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).

In order to check whether the particular orientation of the Cl–Pd–CH_3 rod in **15a** and **15b** has its origin in steric effects, we investigated the binding properties of **L3** and **L4** towards the smaller Cl–Rh–CO unit. Complexes **16a** and **16b** were obtained quantitatively by reaction of $[RhCl(CO)_2]_2$ with **L3** and **L4**, respectively (Scheme 2). A monomeric structure was assigned to both complexes on the basis of their ^{1}H NMR spectra which are very similar to those of **15a** and **15b**, respectively. This was confirmed in the case of **16b**, by the presence in the FAB mass spectrum of a peak corresponding to the $[M+H]^+$ ion (for **16a** the highest peak corresponds to $[M\text{-}Cl\text{-}CO]^+$). The *trans* phosphine arrangements could unambiguously be deduced from the corresponding NMR spectrum (typical PCH_2 pattern for **16a** in the ^{13}C NMR spectrum; large *J*(PP') coupling constant for **16b**, 370 Hz). The infrared spectra of both complexes show, as expected, a strong band in the terminal CO region (1975 cm^{-1}, **16a**; 1980 cm^{-1}, **16b**). Again the H-5 protons of the substituted glucose units show a marked downfield shift when compared to their free ligand counterparts, as expected for a weak CH•••Cl interaction (**16a**: $\Delta\delta$ = +0.96 ppm; **16b**: $\Delta\delta$ = +1.10 and +0.70 ppm).

Upon treatment of **16a** or **16b** with $NaBH_4$ in ethanol, the hydrido complexes **17a** and **17b** were formed respectively. Both ^{1}H NMR spectra show a symmetrical hydride signal near -5.0 ppm (see experimental part), while the infrared spectra confirm that the CO ligand is still present in the complexes (ν_{CO}: 1978 cm^{-1} (**17a**); ν_{CO}: 1969 cm^{-1} (**17b**)). As clearly revealed by ROESY experiments, the hydride lies outside the cavity, it only correlates 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, **17a**; +0.50 ppm [×2], **17b**) in both compounds. This could reflect some



Scheme 2. Binding of CO–Rh–Cl and CO–Rh–H rods by **L3** and **L4**

weak 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 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 **16a** and **16b** 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 against nucleophilic attack by the cavity. 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 (which were not isolated) could be detected by ^{31}P NMR spectroscopy (see experimental part). Despite the fact that the hydrides **17a** and **17b** are of medium stability, they constitute rare examples of hydrido rhodium bis(phosphine) complexes where the phosphines have a *trans*

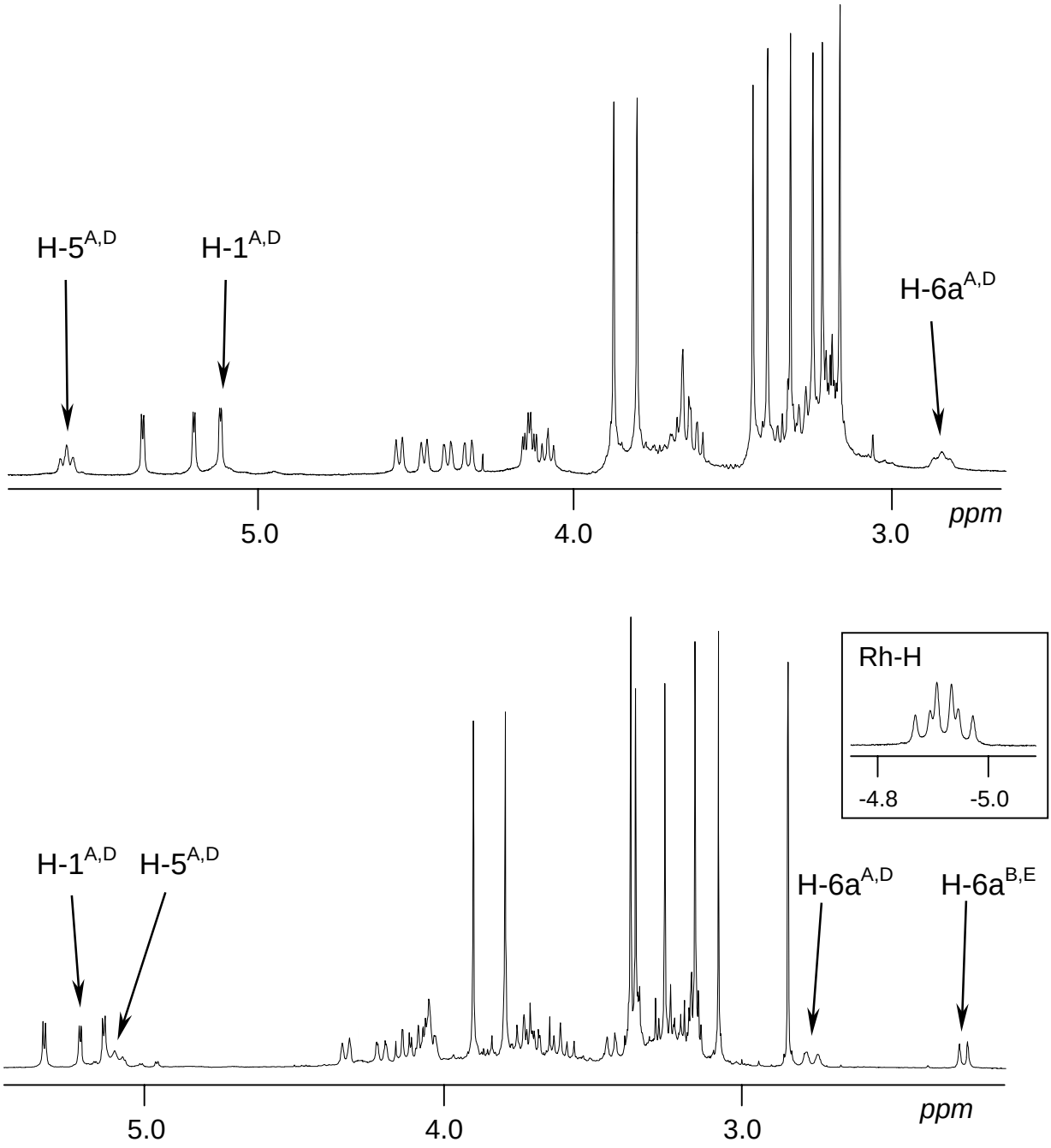
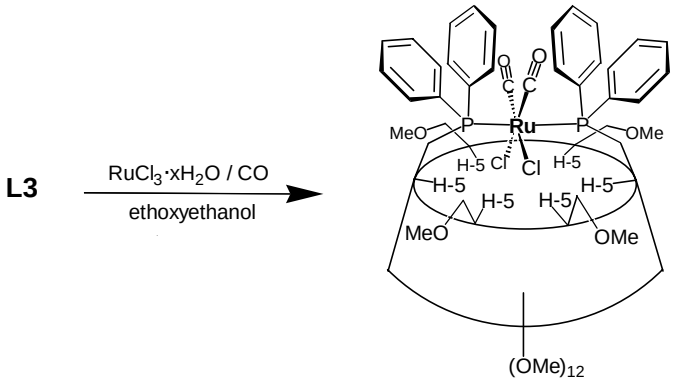


Figure 5. ^{1}H NMR spectra of **16a** (top) and **17a** (bottom) recorded in C_6D_6 at 500 MHz

arrangement. The only other known example is $RhH(CO)(PCy_3)_2$.[47] Preliminary catalytic studies with **17a** showed that in the oct-1-ene hydroformylation the l/b selectivity is identical to that obtained with conventional Rh/PPh_3 systems (see section



18a

III.5.1.). The propensity of cavitand **L3** to bind M–Cl moieties seems to be a general trend, even when the diphosphine is opposed to octahedral coordination spheres. Thus reaction of **L3** with $[RuCl_2(CO)_2]_n$ in boiling ethoxyethanol afforded the *trans,cis,cis*-

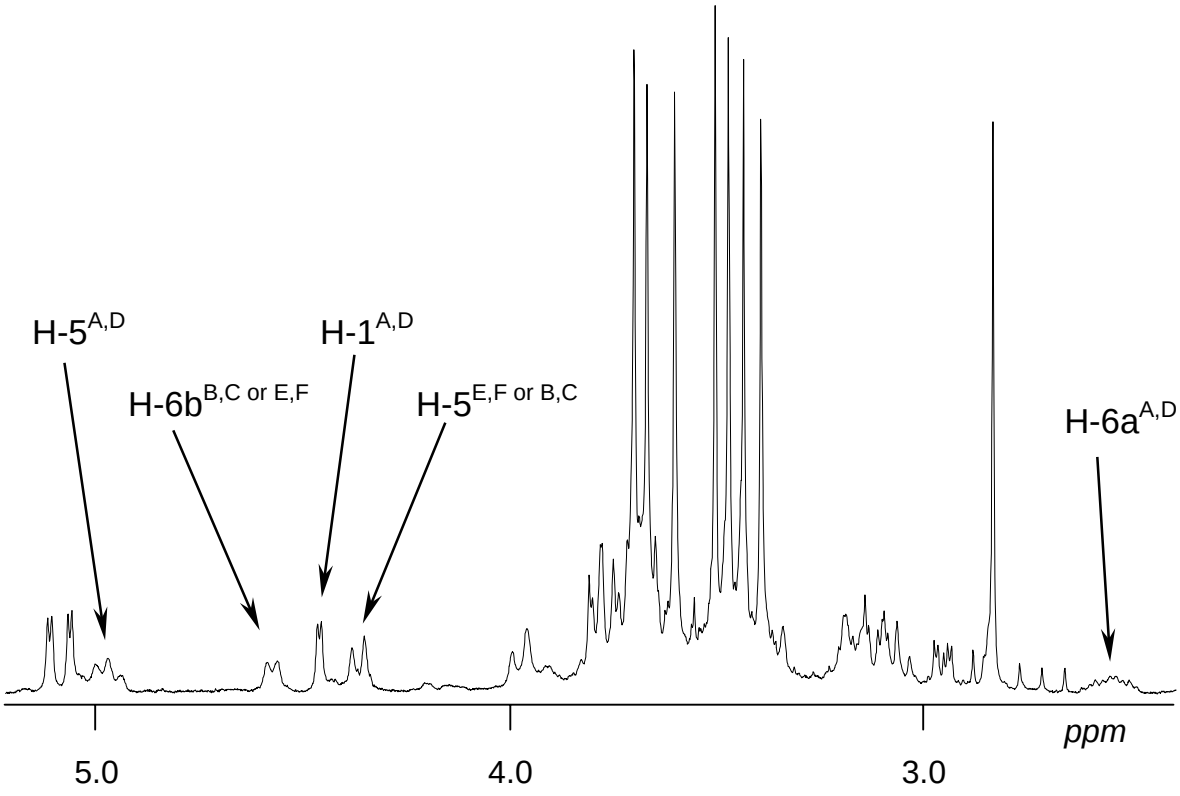


Figure 6. ^1H NMR spectra of **18a** recorded in $CDCl_3$ at 300 MHz

complex **18a** in *ca.* 70 % yield. The chelate is characterised by a singlet at 12.4 ppm in ^{31}P NMR spectroscopy and a peak with the isotopic profile corresponding to the $[M+H]^+$ ion in the FAB mass spectrum (*m/z* 1763.4). Trace amounts of another, unidentified complex were also detected. The infrared spectrum of **18a** displays two strong carbonyl bands, in accordance with two *cis*-coordinated COs. The ^1H NMR spectrum (Figure 6) is consistent with a C_2-symmetrical molecule and reveals that in this case *two* pairs of H-5 atoms are involved in hydrogen bonding with the Cl atoms. The stereochemistry of the complex and the presence of both M–Cl bonds inside the cavity was confirmed by an X-ray study (Figure 7). The solid state structure reveals some disorder characterised by the presence of two rotamers (ratio 80:20), both of which having the two Ru–Cl bonds pointing towards the cavity. Formally, one may switch from one isomer to the other by rotation of *ca.* 37° about the P–Ru–P axis. In other words, the chlorine atoms compete for occupying a central position inside the CD

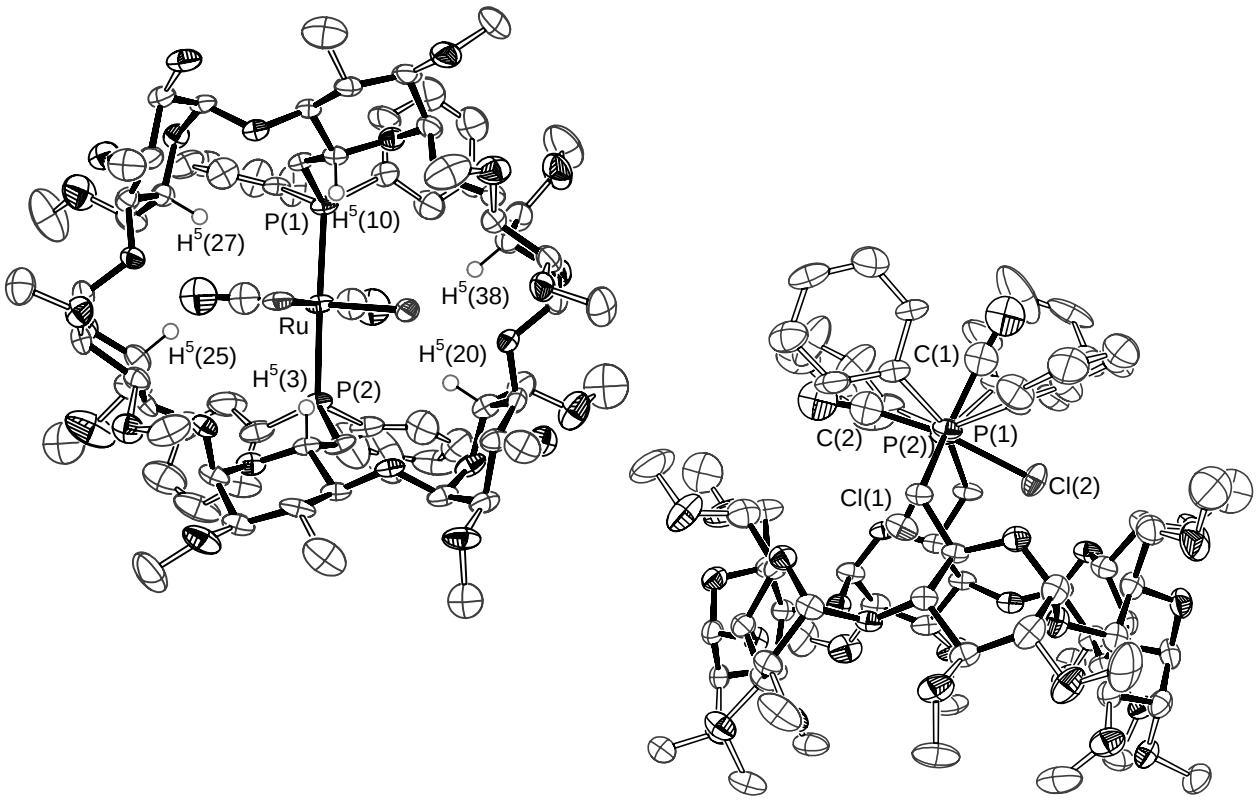


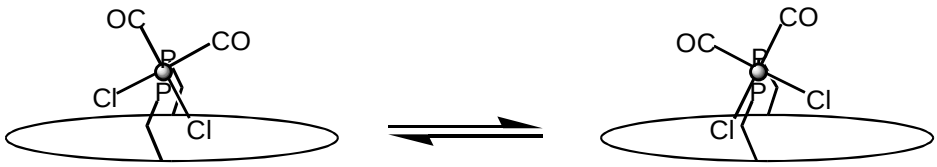
Figure 7. Ortep views of **18a**; bottom view (left) and side view along the P–P axis (right). Ellipsoids are drawn at the 30% probability level, the included benzene molecule has been omitted for clarity.

Table 3. selected bond lengths and angles for **18a**

bond lengths (Å)		C–H-5···Cl bond lengths (Å) [a]	
P(1)-Ru	2.425(2)	H(3)-Cl(1)	2.746
P(2)-Ru	2.423(2)	H(10)-Cl(1)	3.002
Ru-Cl(1)	2.408(3)	H(25)-Cl(1)	2.800
Ru-Cl(2)	2.355(3)	H(27)-Cl(1)	2.840
Ru-C(1)	1.950(1)	H(20)-Cl(2)	2.879
Ru-C(2)	1.951(1)	H(38)-Cl(2)	2.844
angles (°)			
P(1)-Ru-P(2)	175.33(6)		
Cl(1)-Ru-C(1)	178.3(5)		
Cl(2)-Ru-C(2)	171.1(3)		

[a] the C–H-5 distances have been fixed at 0.95 Å

so as to interact with the H-5 atoms of the A and D units. Both rotamers deviate a little from ideal C_2 symmetry. In the major one (Figure 7) 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). Obviously 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^- anions rather than with covalently bonded chlorine.[48] In the chloro complexes reported above, the chlorine atom possesses of course anionic character. It is noteworthy that **18a** does not isomerise in solution under visible light, unlike a related $RuCl_2(CO)_2P_2$ complex based on a calixarene-diphosphine 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.

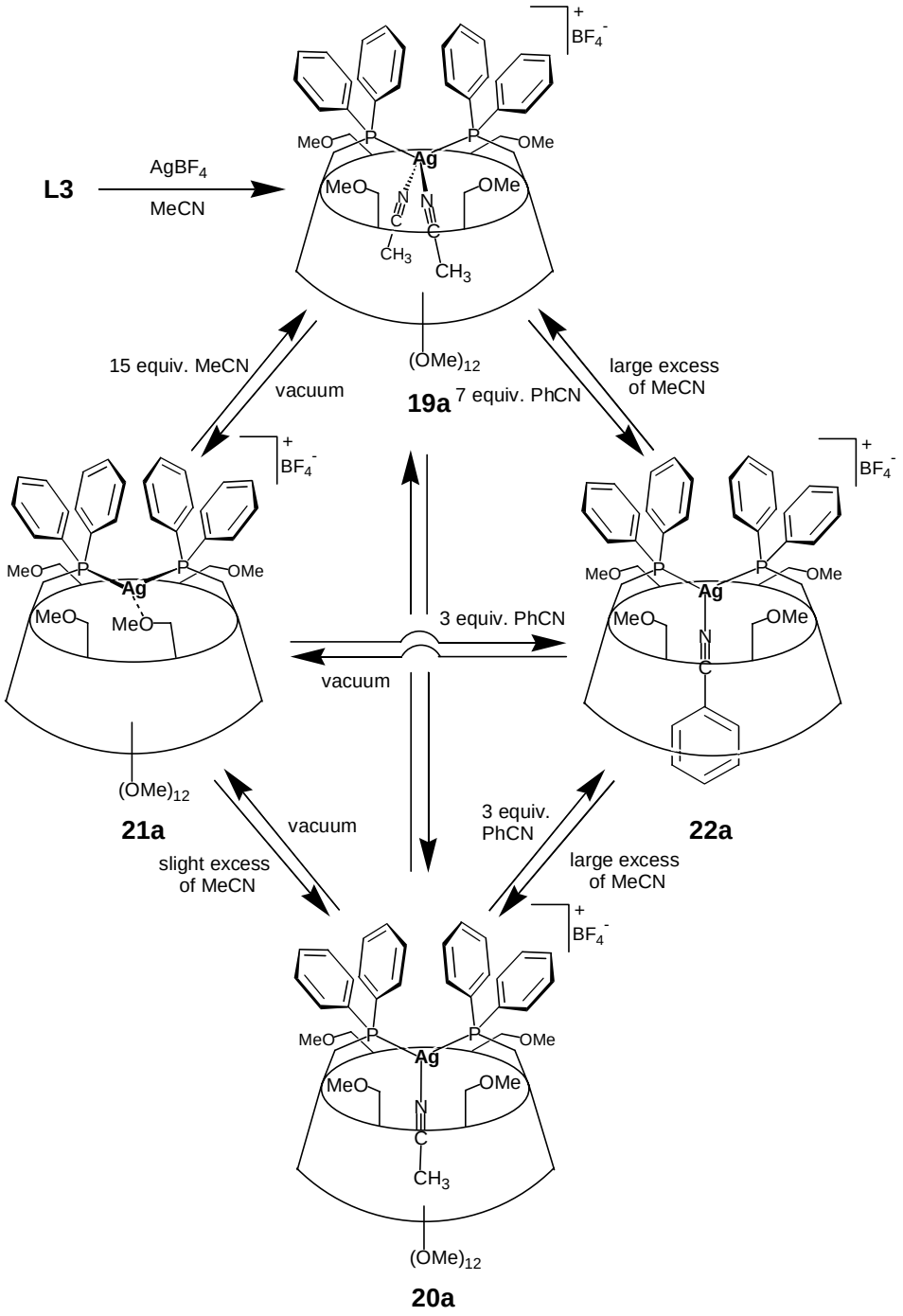
III.2.2. Reducing the bite angle of the diphosphines. Cyclodextrin cavities as probes for ligand exchange processes

The above described reactions, all involving metal chlorides, systematically afforded complexes where the diphosphines **L3** and **L4** behave as *trans*-spanning ligands. The questions whether smaller bite angles may be obtained with these ligands was investigated using the Ag^+ ion, a metal known to favour trigonal structures.

Reaction of **L3** with one equivalent of $AgBF_4$ in MeCN leads to the quantitative formation of the complex [Ag(**L3**)$(CH_3CN)_2$] (**19a**, Scheme 3) which is only stable in large excess of MeCN (> 15 equiv.) and therefore was not isolated as a solid. The formulation of **19a** was inferred from its ESI-MS spectrum which revealed the presence of a strong peak for the $[M\text{-}BF_4+H_2O]^+$ cation (*m/z* 1741.3)[49] 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 latter displays 2 doublets centred at 7.6 ppm ($^{107}J_{Ag,P}$ = 458 Hz, $^{109}J_{Ag,P}$ = 529 Hz). Furthermore, the 2D ROESY spectrum of **19a** in a $CDCl_3$ solution containing 15 equiv. of MeCN shows clearly cross-peaks corresponding to NOEs between the coordinated acetonitrile molecules[50] and all the H-3 CD protons as well as one type of H-5 CD proton but no through-space correlations between MeCN with protons lying outside the cavity (Figure 8).[51] These observations are fully consistent with coordinated acetonitrile molecules that are located inside the cavity.

Upon evaporation of MeCN, **19a** loses coordinated MeCN to produce complexes **20a** (δ = 6.1 ppm, $^{107}J_{Ag,P}$ = 417 Hz, $^{109}J_{Ag,P}$ = 480 Hz) and **21a** (δ = -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 **21a** could be achieved by adding some drops of acetone to the solution prior to evaporation (ketones are known to catalyse ligand substitution). Complex **21a** was characterised by microanalysis, NMR and FAB mass spectrometry.

At room temperature, the ^1H NMR spectrum of **21a**, recorded in $C_2D_2Cl_4$, reveals the presence of two distinctive species (45:55 ratio, identified by the symbols * and # in Figure 8) having both averaged C_2-symmetry. Upon heating, the signals first broaden,



Scheme 3. Ligand exchange processes occurring inside the cavity of **21a**

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 9. ((B,E) ⇌ (C,F) equilibration[52]). The energy barrier for this process is *ca.* 67.8 kJ.mol^{-1}.[53] Upon cooling down a CD_2Cl_2 solution of **21a** to 0°C, the room temperature spectrum no longer persists. Indeed, two new sets of signals emerge that correspond to two C_1-

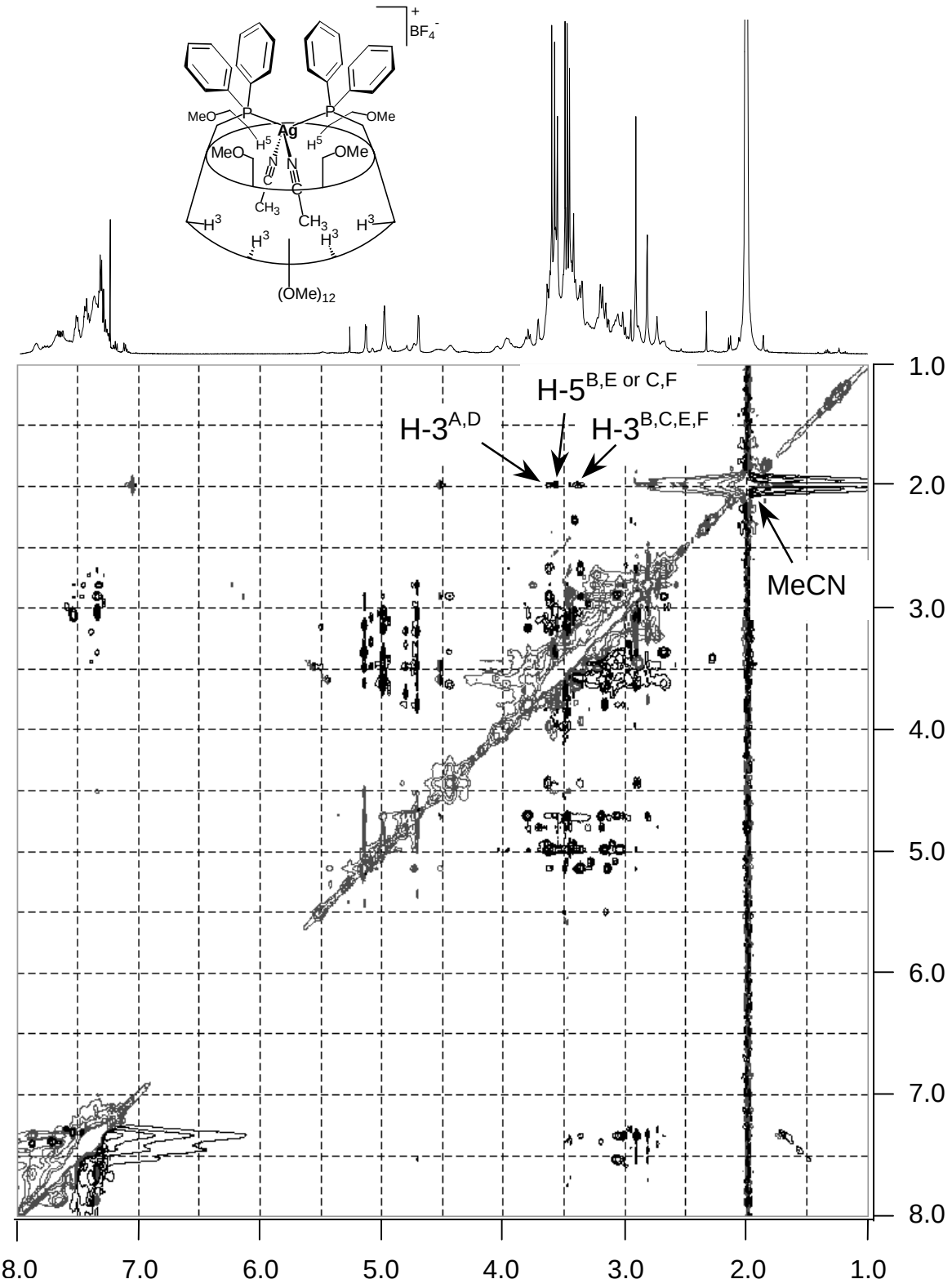


Figure 8. ROESY spectrum of **19a** (500 MHz, $CDCl_3/CH_3CN$, 300 K, **19a**:CH_3CN = *ca*. 1:15). The solution contains *ca*. 10 % of **20a**.

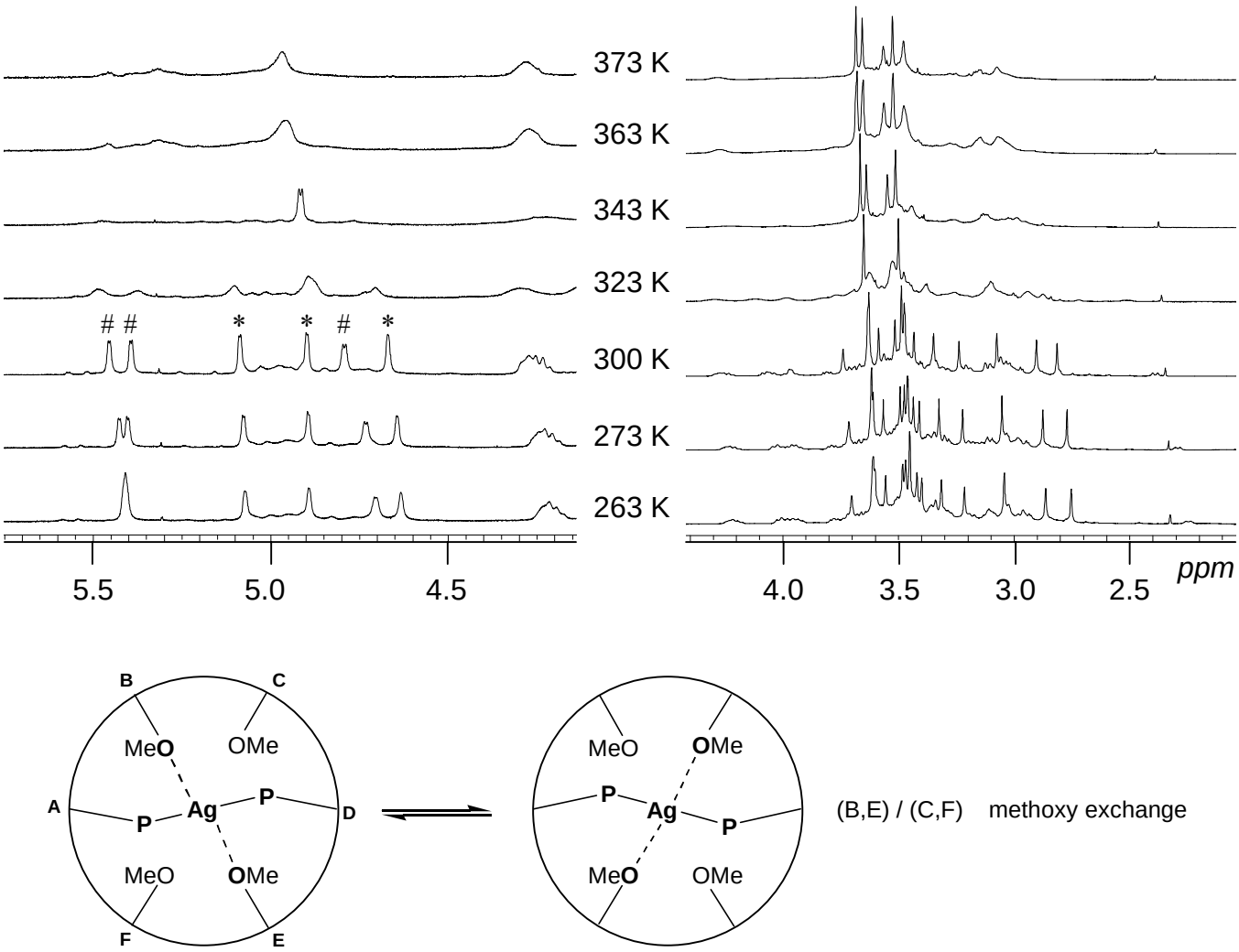
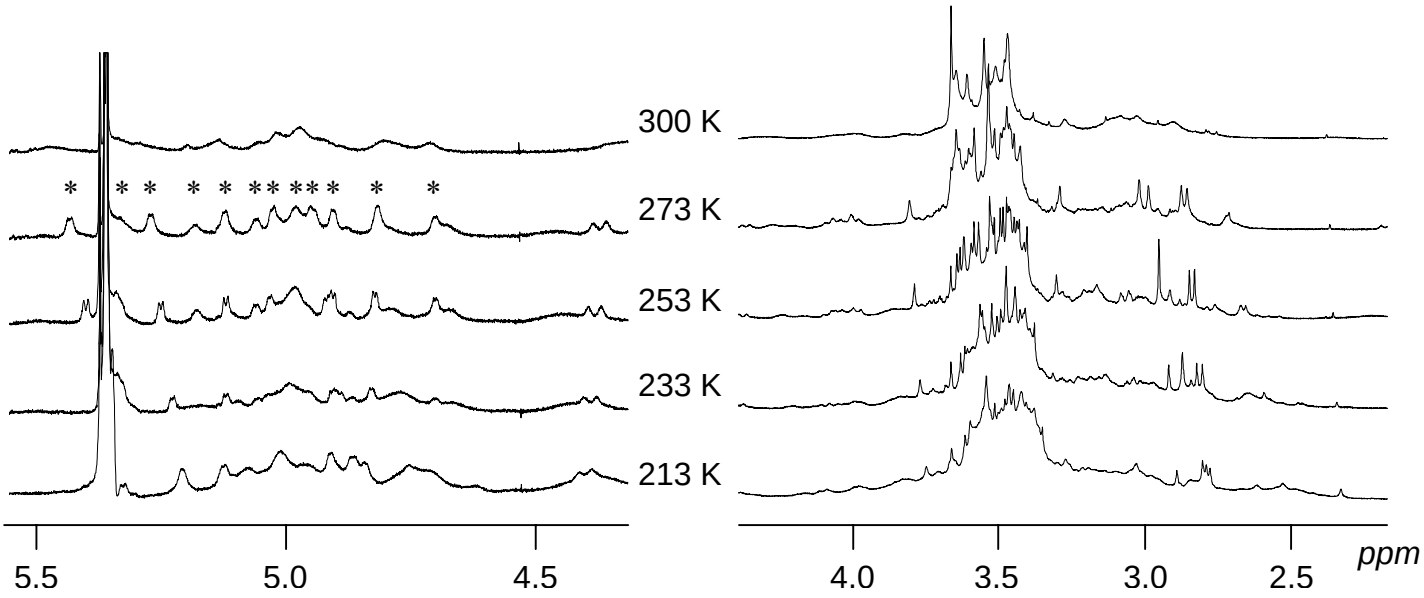


Figure 9. ^{1}H NMR spectra of **21a** in $C_2D_2Cl_4$ (400 MHz) in the range 263-373 K, reflecting the high energy exchange (B,E) $\rightleftharpoons$ (C,F) process. The two exchanging species are identified by the symbols * and # (left part, anomeric region; right part, MeO region. For clarity the left part has been magnified).

symmetrical species, reflecting a slow exchange on the ^{1}H NMR time scale between both pairs of diametrically opposed MeO-6 groups (Figure 10).[54] Overall, our observations are best rationalised in terms of ligand fluxionality about a tricoordinate silver ion, the dynamics involving alternative binding of each of the four ether groups located on the primary face. It should be mentioned here that hemilabile[55] behaviour has already been observed by Dunbar *et al.* for another phosphine being multiply-substituted by ether groups,[56,57] but in this case the binding oxygen donors were not arranged on a macrocycle. In view of the weak binding properties of the primary face



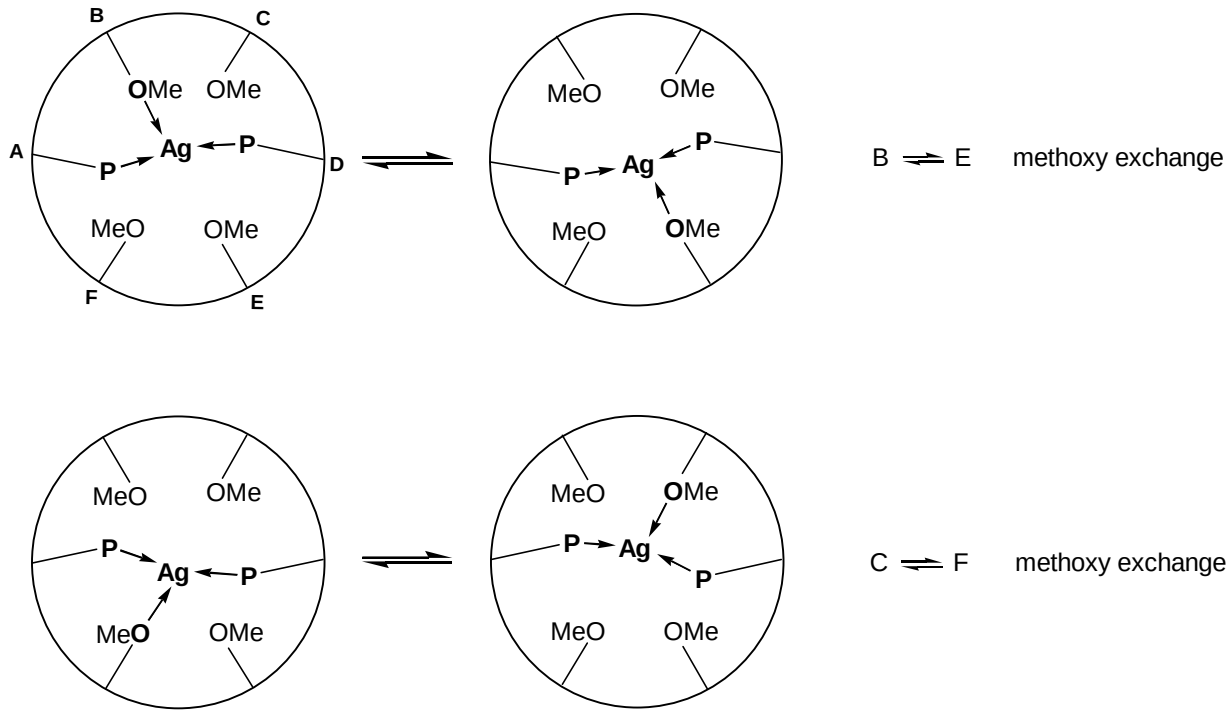


Figure 10. ^{1}NMR spectra of **21a** in CD_2Cl_2 (400 MHz) in the range 213-300 K, reflecting the two low-energy dynamics (left part, anomeric region; right part, MeO region. For clarity the left part has been magnified). The spectrum at 273 K shows distinctively 12 anomeric protons (marked with an *)

ether groups of **21a**, an easy substitution by stronger donors was anticipated.

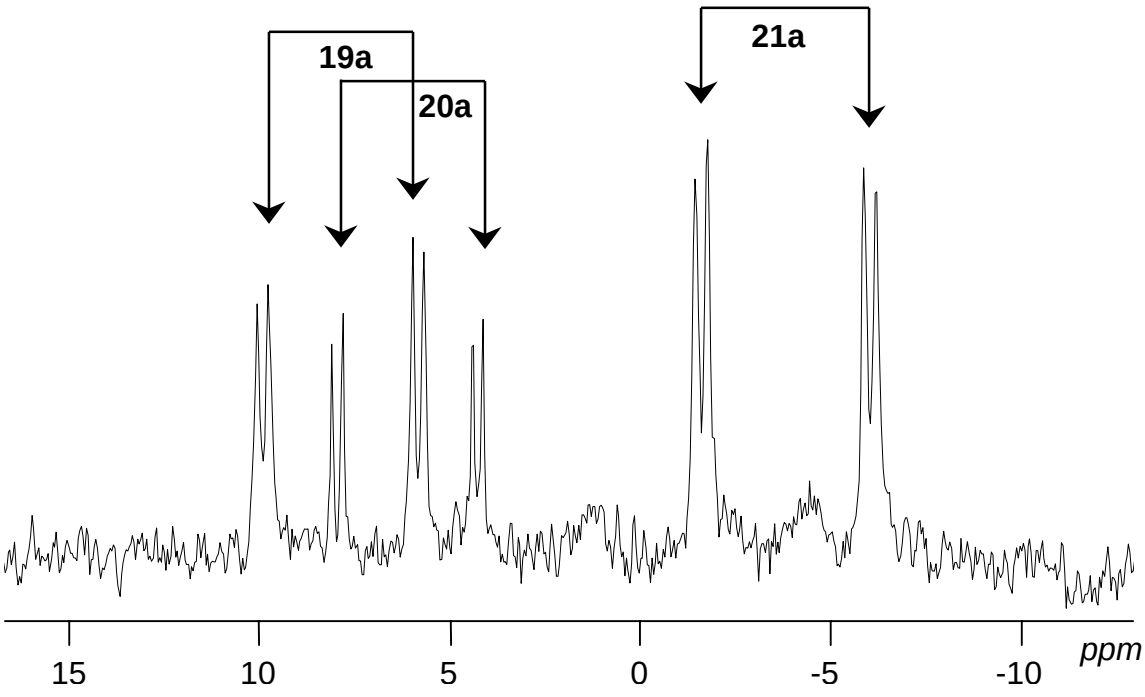


Figure 11. ^{31}P NMR spectrum (121.5 MHz, $CDCl_3$) obtained after addition of *ca.* 5 equiv. of MeCN to a solution of **21a**.

The addition of 5-10 equiv. of MeCN to a solution of **21a** was monitored by NMR (Figure 11) and found to lead reversibly to a mixture of complexes **19a** and **20a** (Scheme 3), as revealed by NMR experiments. A larger excess of MeCN causes **20a** to bind an extra MeCN molecule to give **19a** exclusively. Conversely, reducing the MeCN/CD ratio (by evaporation) regenerated compounds **20a** and **21a**. The C_2 symmetry of the trigonal complex **20a** was confirmed by NMR spectroscopy as well as in the solid state by a single crystal X-ray diffraction study (Figure 12). As 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 $[Ag(PPh_3)_2(NCMe)]BF_4$,[58] the Ag–P bonds of **20a** are unusually long (aver. 2.56 Å *vs.* 2.44 Å in the PPh_3-complex), reflecting the shortness of the two phosphine 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°. This geometry is comparable to those observed in trigonal planar silver complexes obtained with Venanzi's *trans*-spanning

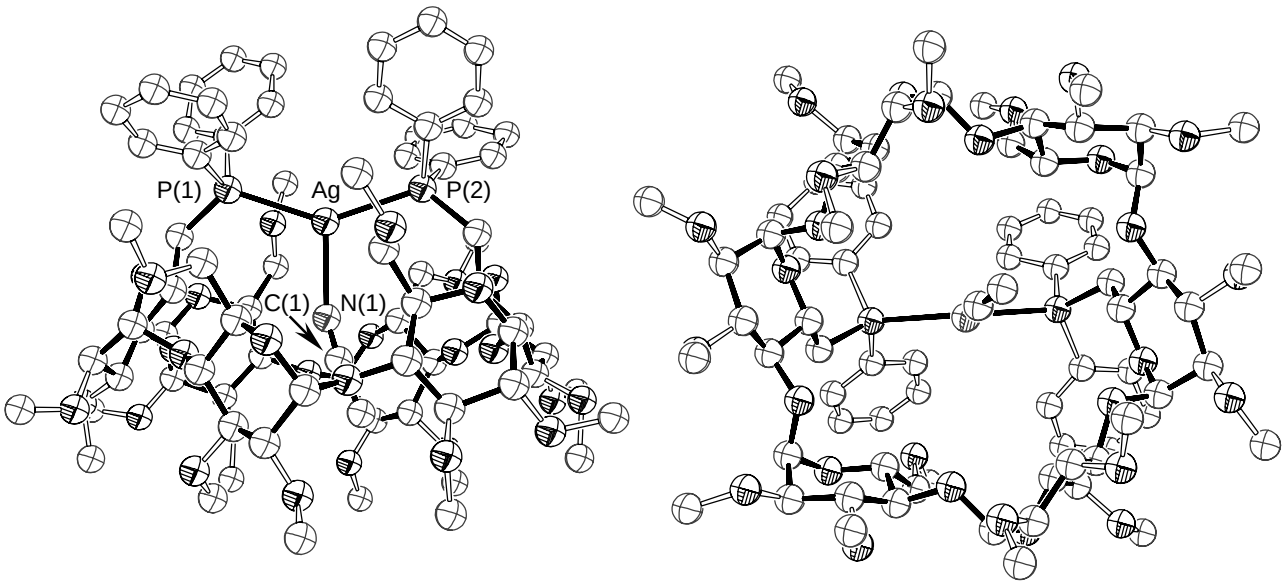
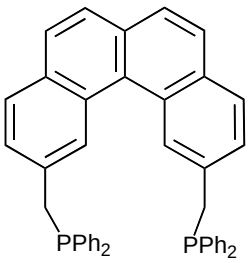


Figure 12. Ortep views of **20a**; side view (left) and bottom view (right). Ellipsoids are drawn at the 50% probability level, the BF_4^- counterion and has been omitted for clarity.

Table 4. Selected bond lengths and angles for **20a**

bond lengths (Å)	
P(1)-Ag	2.570(4)
P(2)-Ag	2.558(4)
N(1)-Ag	2.41(1)
angles (°)	
Ag-N(1)-C(1)	158.31
P(1)-Ag-P(2)	142.9(1)
P(1)-Ag-N(1)	108.9(4)
P(2)-Ag-N(1)	108.2(4)



Venanzi's *trans*-spanning benzo[*c*]phenanthrene-based diphosphine

diphosphines.[59] Interestingly, the Ag-N bond is also longer than usual (2.41(1) Å *vs.* 2.321(2) Å in $[Ag(PPh_3)_2(NCMe)]BF_4$), in keeping with a weakly bonded nitrile.

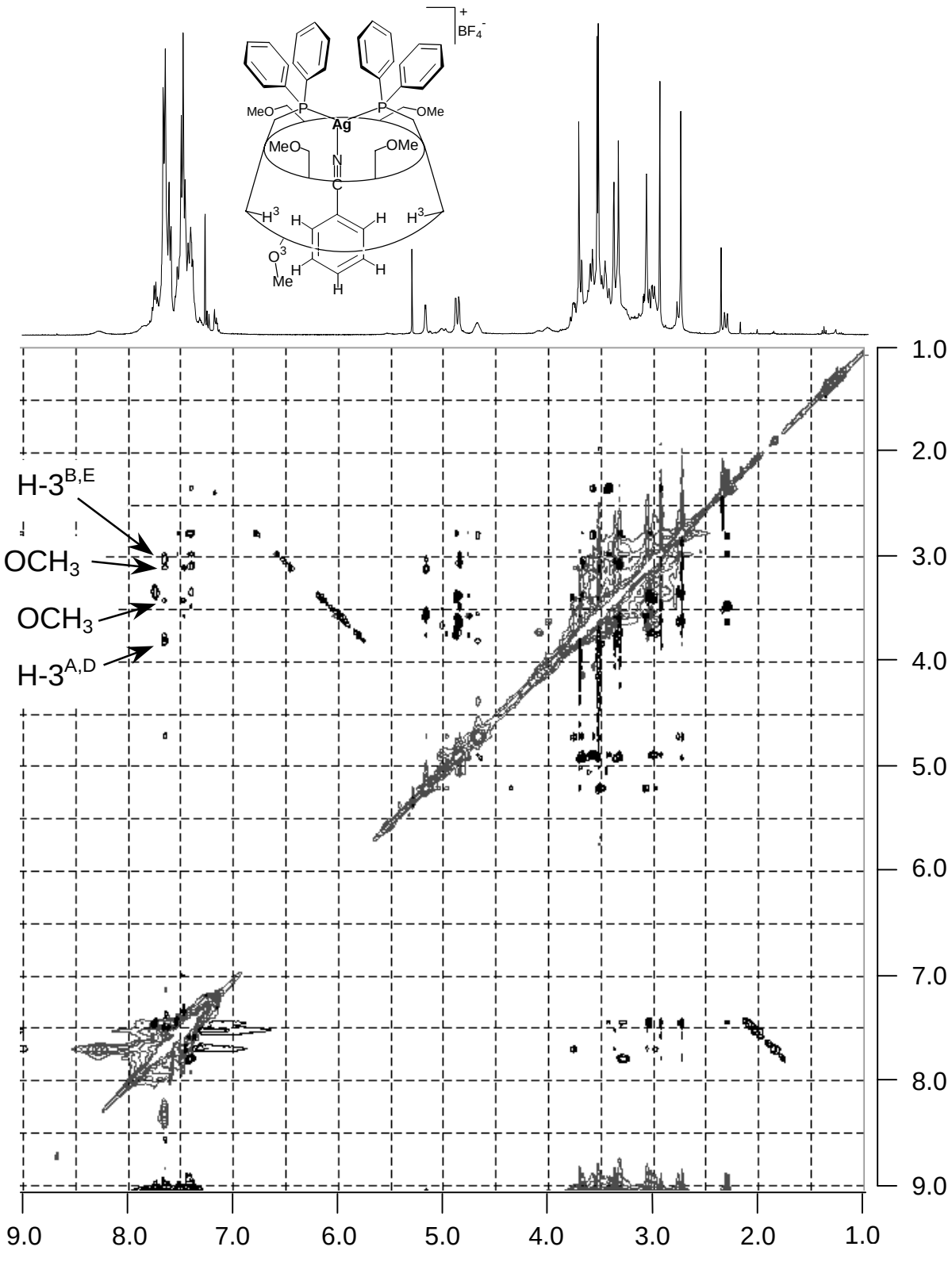


Figure 13. ROESY spectrum of **22a** (400 MHz, $CDCl_3$/PhCN, 300 K, **22a**:PhCN = *ca*. 1:5)

Finally, it is worth mentioning that the nitrile rod is slightly bent with respect to the Ag-N axis (Ag-N(1)-C(1) 158.3(2)°). The addition of benzonitrile (ca. 8 equiv.) to a solution of **19a** in a $CHCl_3$/MeCN mixture (**19a**:MeCN = 1:15) resulted in the *quantitative* formation of complex **22a** (δ = 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 $[M\text{-}BF_4]^+$ ion). A range of correlations between some H-3 as well as MeO-3 protons[60] and aromatic protons belonging to the entrapped guest in the 2D ROESY spectrum of **22a** 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 guest remaining close to the $H\text{-}3^{A,D}$ and $H\text{-}3^{B,C}$ 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 **22a** than in **19a** ($\Delta\delta$ = 0.65 ppm *vs.* 0.2 ppm, Figure 13). 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 **22a** compared to **20a**. The question whether the substitution occurs in an associative or a dissociative mechanism has not been investigated. Assistance of the methoxy group during this process cannot be ruled out.

The binding properties of the AC-substituted CD **L4** toward metallo-nitrile fragments were also investigated. Reaction between **L4** and $AgBF_4$ in CH_2Cl_2 affords compound **21b** quantitatively (Scheme 4), whose FAB mass spectrum displays the signal expected for the $[M\text{-}BF_4]^+$ ion (*m/z* 1641.5) The two phosphorus atoms resonate as two ABX systems in ^{31}P NMR (X = ^{107}Ag and ^{109}Ag, δ_A = 3.7 and δ_B = 8.3 ppm, $J(^{107}AgP)$ = 478 Hz, $J(^{109}AgP)$ = 556 Hz, $J(^{107}AgP')$ = 480 Hz, $J(^{109}AgP')$ = 558 Hz, $^2J(PP')$ = 147 Hz). Unlike its AD-counterpart, **21b** produces a ^{1}H NMR spectrum with sharp signals at room temperature, suggesting a non-fluxional ligand behaviour. Molecular models show that the primary methoxy groups of glucose unit B is perfectly positioned for binding to silver, but we have no formal proof for this coordination.

Addition of 15 equivalents of CD_3CN to a solution of **21b** in $CDCl_3$ causes both the ^1H and ^{31}P NMR spectra, to broaden (Figure 14), suggesting the occurrence of an equilibrium between **21b** and an acetonitrile adduct. Addition of 15 more equivalents of CD_3CN triggers the complete conversion to **20b**, which presents sharp signals in all NMR spectra (ABX systems (X = ^{107}Ag, ^{109}Ag) in ^{31}P NMR; δ_A = 5.1 and δ_B = 7.8 ppm, $J(^{107}AgP)$ = 475 Hz, $J(^{109}AgP)$ = 549 Hz, $J(^{107}AgP')$ = 470 Hz, $J(^{109}AgP')$ = 544 Hz, $^2J(PP')$ = 137 Hz). As shown unambiguously by ROESY/TOCSY experiments, the coordinated acetonitrile is here again located inside the cavity.[61] Evaporation of this solution regenerates **21b**.

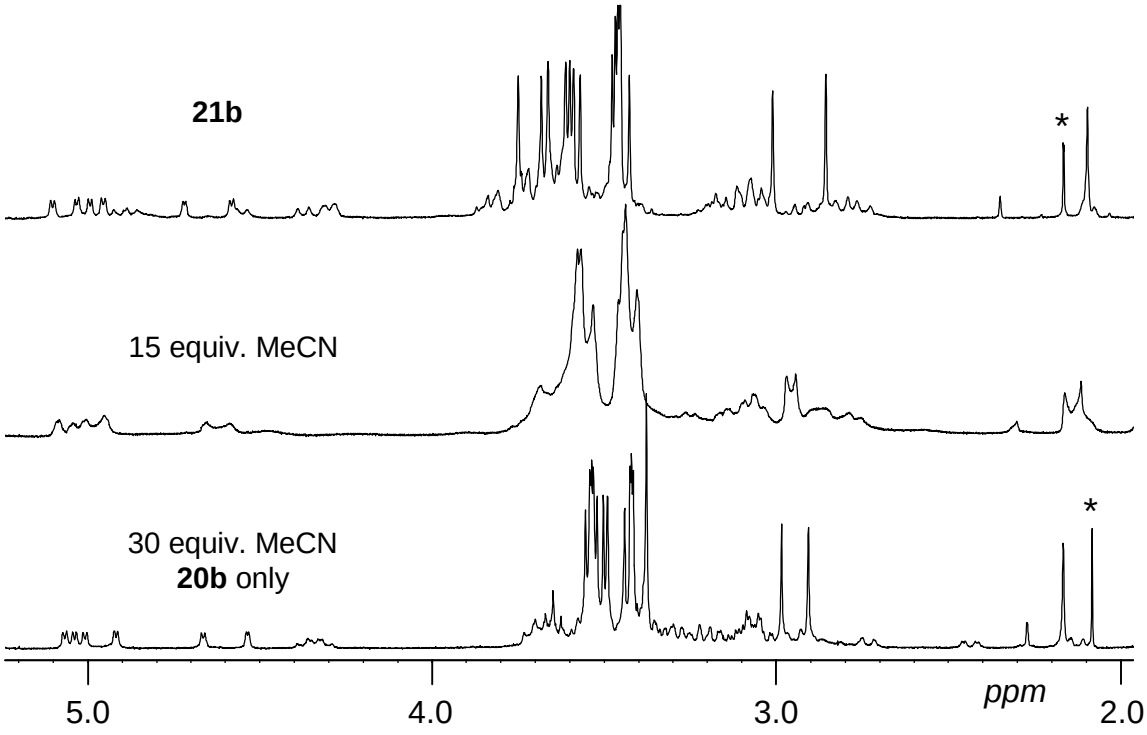
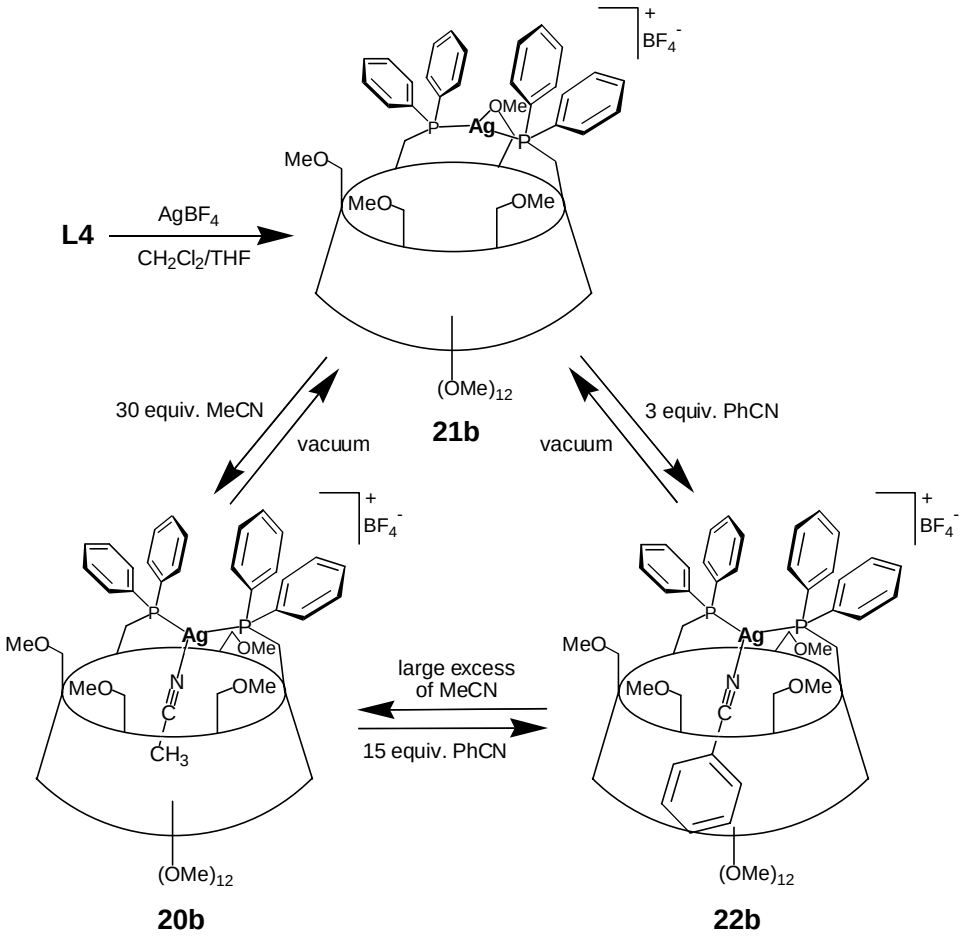


Figure 14. Monitoring the transformation of **21b** into **20b** upon gradual addition of MeCN (^1H NMR**,** 300 MHz, $CDCl_3/CD_3CN$, 300 K). The asterisk denotes residual acetone.

Unlike **20a**, complex **20b** does not coordinate a second acteonitrile despite the fact that there is no barrier of steric order for the formation of a tetrahedral $[Ag(\mathbf{L4})_2(CH_3CN)_2]^+$ cation. Molecular models clearly show that in such a hypothetical complex one coordinated acetonitrile would lie outside the cavity. This finding strongly suggests that formation of the double guest complex **19a** owes its existence to the presence of a cavity. Interestingly, there is no report in the literature on



Scheme 4. Ligand exchange processes occurring inside the cavity of **21b**

a $[AgP_2(CH_3CN)_2]^+$ species, although transient formation of such complexes has been suggested by Venanzi in 1976.[62] It is likely that the cavity walls of **19a** strongly favour recombination of the complex as soon as one of the two acetonitrile molecules dissociates. This *cavity effect* is reminiscent of the observations made by Reinhoudt *et al.* for another cavitand which ensures a high thermal stability to certain incarcerated guests[63].

Finally, we found that, as for the related complex **20a**, addition of PhCN in excess (*ca.* 15 equiv.) to a solution of **20b** resulted in complete nitrile substitution and formation of **22b** (see experimental part).

III.3. Conclusion

In summary, we have shown that the α-cyclodextrin derivatives **L3** displays a high propensity to form chelate complexes. In the complexes derived from this diphosphine, the ligand bite angle is comprised between *ca.* 145-180°. Together with the four primary methoxy groups, the two P(III) centres of **L3** form a circularly arranged P_2O_4 12-electron donor set able to complex the Ag^+ ion in a dynamic process involving alternative binding of the four oxygen atoms. The particular structure of **L3** and **L4**, characterised by the presence of two P(III) units lying close to the cavity entrance leads upon complexation to complexes where the first coordination sphere is partly entrapped in the CD. When opposed to complexes containing a M–Cl bond, both ligands systematically produce complexes in which the M–Cl unit is maintained inside the CD via weak Cl•••H-5 interactions. This finding 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, non-covalent interactions between a guest and the CD inner walls reflects the absence of stronger competing supramolecular forces, *e.g.* 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 **21a** is that ligand exchange processes involving metal centres confined inside a CD cavity are possible. This opens the way to catalytic reactions taking place in an optically active, cylindrical cavity. Finally, the present study provides the first identification of an $[Ag(phosphine)_2(acetonitrile)_2]^+$ species. The unexpected stabilisation of this species probably rests on the fact that the cavity walls strongly favour recombination of the complex after dissociation of the nitrile ligands. Future work is aimed at exploiting this *cavity effect*.

III.4. Experimental Section

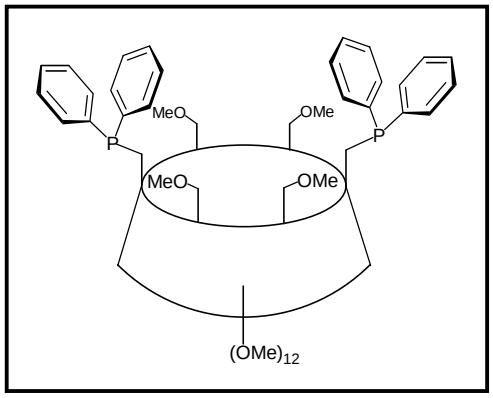
III.4.1. General procedures

All commercial reagents were used as supplied. All manipulations involving phosphines were performed in Schlenk-type flasks under argon. Solvents were dried by conventional methods and distilled immediately prior to use. Column chromatography was performed on silica gel 60 (particle size 40-63 μm, 230-240 mesh). $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under argon over molecular sieves (4 Å). Routine ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded with FT Bruker AC200 (^1H: 200.1 MHz, ^{13}C: 50.3 MHz) and AC300 (^1H: 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 (^1H: 400.1 MHz, ^{13}C: 100.6 MHz) and an Avance 500 (^1H: 500.1 MHz, ^{13}C: 125.8 MHz) Bruker instrument, respectively. ^1H NMR spectral data were referenced to residual protiated solvents (δ 7.26 for $CDCl_3$ and δ 7.16 for C_6D_6), ^{13}C chemical shifts are reported relative to deuterated solvents (δ 77.00 for $CDCl_3$ and δ 128.30 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 using *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. Diphenylphosphine as well as $[PtCl_2(PhCN)_2]$,[64] $[PdCl_2(PhCN)_2]$[64] and [PdClMe(COD)][65] were synthesised according to literature procedures.

We do not provide microanalytical data for the nitrile complexes reported in this study since these species are equilibrating with either one or two other species.

III.4.2. Synthesis of ligands and complexes

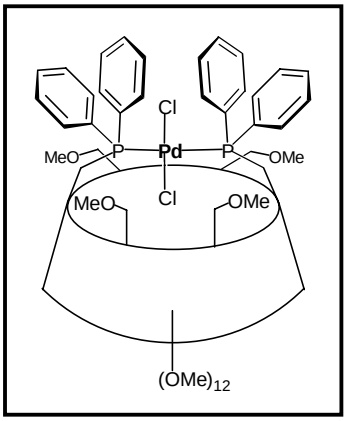
$6^A,6^D$-Bis-(diphenylphosphinyl)-$6^A,6^D$-dideoxy-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F$-hexadeca-*O*-methyl-$\alpha$-cyclodextrin (L3)



A solution of *n*-BuLi in hexane (1.6 M, 2.4 mL, 3.77 mmol) was added, at -78°C, to a solution of Ph_2PH (0.708 g, 3.77 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, 0.74 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, which allows removal of residual Ph_2PH. This operation was repeated 3 times to afford **L3** as a white powder (1.100 g, 97 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.31; Mp 112-114°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ (assignment by COSY) = 2.18 and 3.29 (AB, $^2J_{AB}$ = 10.4 Hz, 4H; H-$6^{C,F\ or\ B,E}$), 2.50 and 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-$2^{C,F\ or\ B,E}$), 3.15 (dd, 2H; H-$2^{B,E\ or\ C,F}$), 3.22 (dd, 2H; H-$2^{A,D}$), 3.28 and 4.05 (AB, $^2J_{AB}$ = 10.5 Hz, 4H; H-$6^{B,E\ or\ C,F}$), 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-$3^{C,F\ or\ B,E}$), 3.59 (t, 2H; H-$3^{B,E\ or\ C,F}$) 3.61 (s, 6H; OCH_3), 3.63 (s, 6H; OCH_3), 3.64 (t, 2H; H-$4^{C,F\ or\ B,E}$), 3.64 (t, 2H; H-$5^{C,F\ or\ B,E}$), 3.65 (s, 6H; OCH_3), 3.71

(t, ^{3}J = 8.9 Hz, 2H; H-4$^{B,E\text{ or }C,F}$), 3.79 (m, 2H, ^{3}J = 9.6 Hz, 2H; H-5$^{B,E\text{ or }C,F}$), 4.39 (m, ^{3}J = 8.8 Hz, 2H; H-5^{A,D}), 4.93 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 2H; H-1^{A,D}), 5.01 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 2H; H-1$^{B,E\text{ or }C,F}$), 5.03 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, 2H; H-1$^{C,F\text{ or }B,E}$), 7.22-7.64 (20H; arom. H); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 32.04 (d, $J_{C,P}$ = 14.8 Hz; C-6^{A,D}), 57.69, 57.79, 58.05, 58.22 and 58.58 (CH_3O-2, CH_3O-6), 61.53, 61.69 and 61.99 (CH_3O-3), 69.40 and 71.39 (C-6^{B,C,E,F}), 70.84 (C-4^{A,D}, tent. assignment), 71.66 and 72.11 (C-5^{B,C,E,F}), 81.25 [×3], 81.42, 81.83, 81.98, 82.47 and 82.79 (C-2, C-3, C-4^{B,C,E,F}), 88.54 (d, $^{2}J_{C,P}$ = 10.1 Hz; C-5^{A,D}), 98.93 and 100.40 [×2] (C-1), 128.01 (d, $^{3}J_{C,P}$ = 6.6 Hz; C_{meta}), 128.53 (d, $^{3}J_{C,P}$ = 6.6 Hz; C_{meta}), 131.84 (s; C_{para}), 132.17 (s; C_{para}), 134.29 (d, $^{2}J_{C,P}$ = 21.4 Hz; C_{ortho}), 134.35 (d, $^{2}J_{C,P}$ = 21.4 Hz; C_{ortho}), 140.30 (d, $J_{C,P}$ = 13.2 Hz; C_{ipso}), 141.53 (d, $J_{C,P}$ = 11.5 Hz; arom. C_{ipso}); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = -17.8 (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.

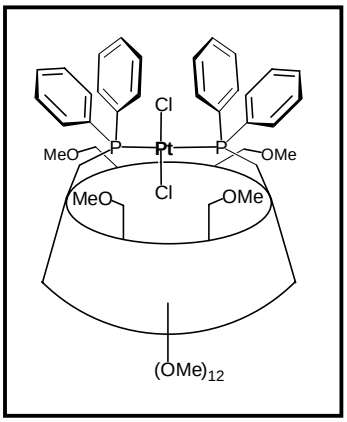
trans-P,P'-Dichloro-{6^{A},6^{D}-bis-(diphenylphosphinyl)-6^{A},6^{D}-dideoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin}palladium(II) (13a)



A solution of $[PdCl_2(PhCN)_2]$ (0.025 g, 0.065 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L3** (0.100 g, 0.065 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 **13a** as a yellow powder, which was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 94 : 6, v/v) (0.044 g, 40%).

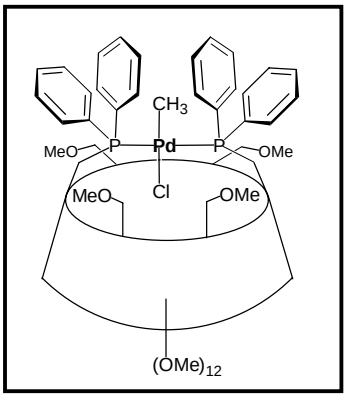
R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.31; Mp 185°C dec. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.67 (br d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 10.3 Hz; H-6a^{A,D}), 2.85 (s, 6H; CH_3O-6), 3.20 (s, 6H; CH_3O-6), 3.47 (s, 6H; OCH_3), 3.49 (s, 6H; OCH_3), 3.52 (s, 6H; OCH_3), 3.61 (s, 6H; OCH_3), 3.65 (s, 6H; 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 (4H; H_{ortho}); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 34.94 (virtual t, $^1J_{C,P} + {}^3J_{C,P'}$ = 23.0 Hz; C-6^{A,D}), 57.50 and 57.73 (CH_3O-6), 58.94 and 59.13 [×2] (CH_3O-2), 61.13, 61.50 and 61.82 (CH_3O-3), 70.02 (C-4^{A,D}), 70.61 and 70.80 (C-6^{B,C,E,F}), 71.33 and 71.46 (C-5^{B,C,E,F}), 80.28, 80.64, 80.77, 81.23 [×2], 81.69, 81.75 and 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 (virtual t, $^2J_{C,P} + {}^4J_{C,P'}$ = 13.2 Hz; C_{ortho}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 11.9 (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) (14a)



A solution of $[PtCl_2(PhCN)_2]$ (0.031 g, 0.065 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L3** (0.100 g, 0.065 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 **14a** 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; Mp 218°C dec. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.62 (br d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 10.7 Hz; 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 (4H; H$_{ortho}$); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 36.55 (virtual t, $^1J_{C,P} + {}^3J_{C,P'}$ = 21.5 Hz; C-6^{A,D}), 57.53 and 57.86 (CH_3O-6), 58.94, 59.20 and 59.30 (CH_3O-2), 61.13, 61.50 and 61.86 (CH_3O-3), 69.99 (C-4^{A,D}), 70.54 and 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] and 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 and 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 (virtual t, $^2J_{C,P} + {}^4J_{C,P'}$ = 11.5 Hz; C$_{ortho}$); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 7.8 (s with Pt satellites, $^1J_{Pt,P}$ = 2637 Hz); elemental analysis (%): calcd for $C_{76}H_{110}Cl_2O_{28}P_2Pt \bullet 0.5\ C_6H_6$ (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) $[M-Cl]^+$.

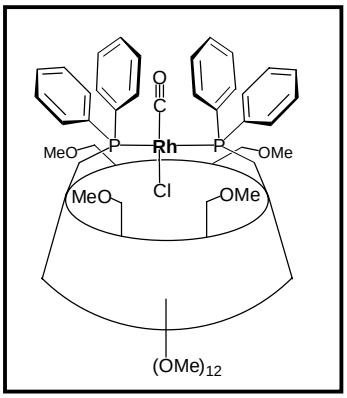
***trans*-*P*,*P'*-Chloro-methyl-{6^{A},6^{D}-bis-(diphenylphosphinyl)-6^{A},6^{D}-dideoxy-2^{A},2^{B},2^{C}, 2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin} palladium(II) (15a)**



A solution of [PdMeCl(COD)] (0.020 g, 0.076 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L3** (0.110 g, 0.072 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 was then filtered off over celite. Evaporation of the solvent afforded **15a** (0.080 g, 66%) as a yellow powder. R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.31; Mp 178°C dec. ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ = 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, $^3J_{H-1,H-2}$ = 2.6 Hz, 2H; H-1), 5.22 (d, $^3J_{H-1,H-2}$ = 3.1 Hz, 2H; H-1), 5.40 (d, $^3J_{H-1,H-2}$ = 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 (4H; H$_{ortho}$); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 4.51 ($PdCH_3$), 37.30 (virtual t, $^1J_{C,P} + {}^3J_{C,P'}$ = 24.7 Hz; C-6^{A,D}), 57.00 and 57.36 (CH_3O-6), 59.19, 59.56 and 60.05 (CH_3O-2), 60.96, 61.39 and 62.11 (CH_3O-3), 70.00 (C-4^{A,D}), 72.27 and 72.34 (C-5^{B,C,E,F}), 72.41 and 72.50 (C-6^{B,C,E,F}), 81.35, 81.58 [×2], 81.88, 82.30, 82.47, 82.83 and 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 and 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 (virtual t, $^1J_{C,P} + {}^3J_{C,P'}$ = 39.6 Hz; C$_{ipso}$); ^{31}P{^{1}H} NMR (121.5

MHz, $CDCl_3$): δ = 19.4 (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) $[M–CH_3–Cl]^+$.

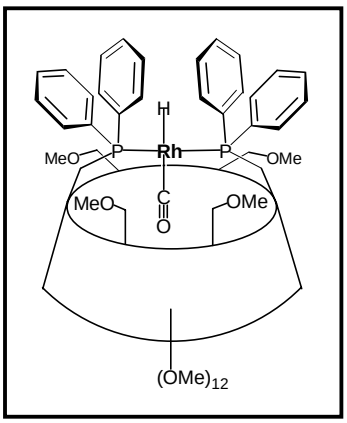
***trans*-*P*,*P'*-Chloro-carbonyl-{6^{A},6^{D}-bis-(diphenylphosphinyl)-6^{A},6^{D}-dideoxy-2^{A},2^{B}, 2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin} rhodium(I) (16a)**



A solution of $[Rh(CO)_2Cl]_2$ (0.013 g, 0.033 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L3** (0.100 g, 0.065 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 was filtered off over celite. Evaporation of the solvent afforded **16a** as an orange-yellow powder (0.070 g, 64%). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.31; Mp 182°C dec. IR (KBr) ν/cm^{-1}: 1975.5 (C≡O); ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ (assignment by COSY) = 2.84 and 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 and 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 and 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, $J_{H\text{-}1,H\text{-}2}$ = 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 (4H; H_{ortho}); $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 25°C): δ = 35.83

(virtual t, $^{1}J_{C,P} + {}^{3}J_{C,P'}$ = 22.4 Hz; C-$6^{A,D}$), 57.25 and 57.41 (CH_3O-6), 59.14, 59.30 and 59.44 (CH_3O-2), 61.25, 61.72 and 62.12 (CH_3O-3), 70.78 (C-$4^{A,D}$), 71.95 and 72.32 (C-$5^{B,C,E,F}$), 72.12 and 72.49 (C-$6^{B,C,E,F}$), 81.15, 81.63 and 81.70 [×2] , 81.88, 81.78, 82.84 and 84.12 (C-2, C-3, C-$4^{B,C,E,F}$), 89.23 (virtual t, $^{2}J_{C,P} + {}^{4}J_{C,P'}$ = 10.4 Hz; C-$5^{A,D}$), 98.31 and 98.81 (C-$1^{B,C,E,F}$), 101.37 (C-$1^{A,D}$), 127.97 (virtual t, $^{3}J_{C,P} + {}^{5}J_{C,P'}$ = 9.6 Hz; C_{meta}), 128.49 (virtual t, $^{3}J_{C,P} + {}^{5}J_{C,P'}$ = 9.6 Hz; C_{meta}), 129.69 (s; C_{para}), 130.36 (s; C_{para}), 133.35 (virtual t, $^{2}J_{C,P} + {}^{4}J_{C,P'}$ = 12.0 Hz; C_{ortho}), 134.54 (virtual t, $^{1}J_{C,P} + {}^{3}J_{C,P'}$ = 44.2 Hz; C_{ipso}), 135.58 (virtual t, $^{2}J_{C,P} + {}^{4}J_{C,P'}$ = 13.6 Hz; C_{ortho}), 140.68 (virtual t, $^{1}J_{C,P} + {}^{3}J_{C,P'}$ = 42.6 Hz; C_{ipso}); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6): δ = 17.9 (d, $^{1}J_{Rh,P}$ = 132 Hz); elemental analysis (%): calcd for $C_{77}H_{110}ClO_{29}P_2Rh \bullet C_6H_6$ (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'*-Hydrido-carbonyl-{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) (17a)**



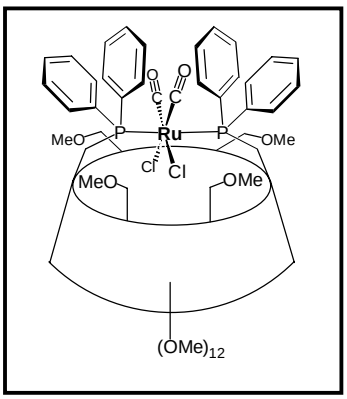
To a stirred, solution of **16a** (0.032 g, 0.019 mmol) in EtOH (10 mL) was added $NaBH_4$ (0.030 g, 0.793 mmol) as a solid. The suspension gradually turned orange-brown. After stirring at room temperature for 45 min. the mixture was evaporated to dryness. The residue was taken up in benzene (10 ml) and filtered through celite. Evaporation to dryness yielded **17a** as an orange-brown powder (0.029 g, 93%). IR (KBr) ν/cm^{-1}: 1978 (C≡O); ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ (assignments by ROESY and COSY) = -4.96 (dt, $^{1}J_{H,Rh}$ = 10.5 Hz, $^{2}J_{H,P}$ = 15.5 Hz, 1H; Rh-H), 2.22 and

4.00 (AB, $^{2}J_{AB}$ = 11.0 Hz, 4H; H-$6^{B,E}$), 2.73 and 3.26 (br AB, $^{2}J_{AB}$ = 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 and 4.17 (2m, $^{2}J_{AB}$ = 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, ^{3}J = 9.1 Hz, 2H; H-$5^{C,F}$), 4.29 (br d, ^{3}J = 9.7 Hz, 2H; H-$4^{C,F}$), 5.07 (br t, J = 11,0 Hz, 2H; H-$5^{A,D}$), 5.10 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.6 Hz, 2H; H-$1^{C,F}$), 5.18 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.6 Hz, 2H; H-$1^{A,D}$), 5.30 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 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 (4H; H_{ortho}); $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6, 25°C): δ = 36.25 (virtual t, $^{1}J_{C,P} + {}^{3}J_{C,P'}$ = 19.0 Hz; C-$6^{A,D}$), 56.78 and 56.88 (CH_3O-6), 58.29, 58.64 and 59.11 (CH_3O-2), 61.01, 61.18, and 61.98 (CH_3O-3), 70.6 (C-$4^{A,D}$), 70.84, 71.60, 71.69 and 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] and 83.71 (C-2, C-3, C-$4^{B,C,E,F}$), 87.39 (virtual t, $^{2}J_{C,P} + {}^{4}J_{C,P'}$ = 11.2 Hz; C-$5^{A,D}$), 98.44 and 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, $^{2}J_{C,P} + {}^{4}J_{C,P'}$ = 14.4 Hz; C_{ortho}), 134.47 (virtual t, $^{2}J_{C,P} + {}^{4}J_{C,P'}$ = 13.6 Hz; C_{ortho}); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6): δ = 37.6 (d, $^{1}J_{Rh,P}$ = 158 Hz).

During the formation of **17a**, a transient intermediate with the following spectroscopic data was observed : $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6): δ = 20.9 (d, $^{1}J_{Rh,P}$ = 123 Hz).

Samples of complex **17a** contained variable amounts of benzene which could not be removed at room temperature. This led to unsatisfactory microanalytical data.

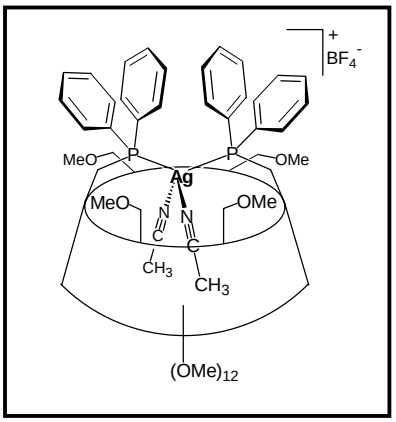
***trans*-*P*,*P*'-*cis*-Dichloro,*cis*-dicarbonyl-{6^{A},6^{D}-bis-(diphenylphosphinyl)-6^{A},6^{D}-dideoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin}ruthenium(II) (18a)**



CO was bubbled through a solution of commercial ruthenium trichloride (41.12% Ru, 0.018 g, *ca.* 0.075 mmol) in ethoxy-2-ethanol (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 **L3** (0.115 g, 0.0750 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 **18a** as a yellow powder (0.080 g, 61 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.31; Mp 145-147°C. IR (KBr) ν/cm^{-1}: 1986 and 2050 (C≡O); ^{1}H 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 (4H; H$_{ortho}$); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 33.50 (virtual t, $^1J_{C,P}$ + $^3J_{C,P'}$ = 28.0 Hz; C-6^{A,D}), 57.10 and 58.15 (CH_3O-6), 58.61, 58.84 and 59.07 (CH_3O-2), 61.20, 61.27 and 61.43 (CH_3O-3), 70.58 (C-4^{A,D}), 71.03 and 71.17 (C-6^{B,C,E,F}), 70.67 and 71.39 (C-5^{B,C,E,F}), 78.93, 79.95, 80.80 [×2] , 81.69, 81.98, 82.83 and 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 and 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, $^{1}J_{C,P} + {}^{3}J_{C,P'}$ = 46.2 Hz; C_{ipso}), 193.66 (virtual t, $^{2}J_{C,P} + {}^{2}J_{C,P'}$ = 23.0 Hz; CO); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 12.4 (s); elemental analysis (%): calcd for $C_{78}H_{110}Cl_2O_{30}P_2Ru \bullet 0.5\ CH_2Cl_2$ (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) $[M–Cl–CO)]^+$.

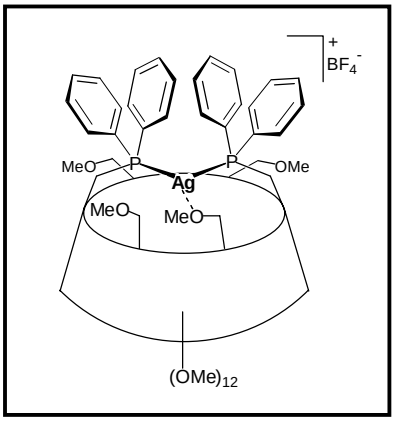
bis-Acetonitrile-{6^{A},6^{D}-bis-(diphenylphosphinyl)-6^{A},6^{D}-dideoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F}, 3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin}silver(I) tetrafluoroborate (19a)



A solution of $AgBF_4$ (0.027 g, 0.14 mmol) in MeCN (50 mL) was added to a solution of **L3** (0.210 g, 0.14 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 **19a**, **20a** and **21a** ($^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 7.7 (2d, $^{107}J_{Ag,P}$ = 458 Hz, $^{109}J_{Ag,P}$ = 529 Hz; **19a**), 6.1 (2d, $^{107}J_{Ag,P}$ = 417 Hz, $^{109}J_{Ag,P}$ = 480 Hz; **20a**) and -3.5 (2d, $^{107}J_{Ag,P}$ = 503 Hz, $^{109}J_{Ag,P}$ = 581 Hz; **21a**)). When the spectrum was recorded in pure CD_3CN, only **19a** was detected. ^{1}H NMR (400 MHz, CD_3CN, 25°C): δ = 2.52 (d, 2H, ^{2}J = 10.6 Hz; H-6b^{A,D}, tent. 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, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.6 Hz, 2H; H-1), 4.95 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.2 Hz, 2H; H-1), 5.14 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.2 Hz, 2H; H-1), 7.35-7.80 (20H; arom. H); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, CD_3CN): δ = 31.02

(virtual t, $^{1}J_{C,P} + {}^{3}J_{C,P'}$= 18.7 Hz, C-$6^{A,D}$), 58.39 [×2] ($CH_3O$-6), 59.01 and 59.24 [×2] (CH_3O-2), 61.44, 61.54 and 61.70 (CH_3O-3), 71.24 and 71.67 (C-$6^{B,C,E,F}$), 72.42 and 72.85 (C-$5^{B,C,E,F}$), 82.03 [×6], 82.55, 82.81 and 83.53 (C-2, C-3, C-4), 88.12 (virtual t, $^{2}J_{C,P} + {}^{4}J_{C,P'}$= 11.5 Hz; C-$5^{A,D}$), 98.05, 100.35 and 100.97 (C-1), 130.15 (virtual t, $^{3}J_{C,P} + {}^{5}J_{C,P'}$ = 9.8 Hz; C_{meta}), 130.64 (virtual t, $^{3}J_{C,P} + {}^{5}J_{C,P}$ = 9.8 Hz; C_{meta}), 132.24 and 132.60 (s, C_{para}), 133.23-134.15 (arom. C); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_3CN): δ = 7.6 [2d, $^{107}J_{Ag,P}$ = 458 Hz, $^{109}J_{Ag,P}$ = 529 Hz]; MS (ESI): *m/z* (%): 1741.3 (13) $[M\text{-}BF_4\text{+}H_2O]^+$. As deduced from 2D NMR experiments, the Me signals of free and coordinated MeCN are overlapping (1.90-2.10 ppm).

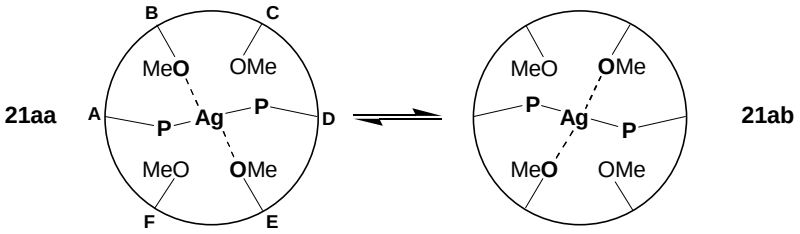
{6^{A},6^{D}-bis-(Diphenylphosphinyl)-6^{A},6^{D}-dideoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F}, 6^{B},6^{C},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin}silver(I) tetrafluoroborate (21a)



This complex was obtained by solvent removal *in vacuo* of the solution described above (**19a**). 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; Mp 151°C dec. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 100°C): δ = 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 signal, 2H; H-1), 5.35 (br signal, 2H; H-1), 5.50 (br signal, 2H; H-1), 7.40-7.70 (20H; arom. H); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 28.50 (C-$6^{A,D}$), 57.20, 57.40 [×2], 58.54 and 59.89 (CH_3O-2, CH_3O-6), 61.66 [×3] (CH_3O-3), 67.56, 70.50, 70.79 and 71.28 (C-$5^{B,C,E,F}$, C-$6^{B,C,E,F}$), 80.99 [×4] and 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 and 134.33 (arom. C); $^{31}P\{^{1}H\}$ (121.5 MHz, $C_2D_2Cl_4$,

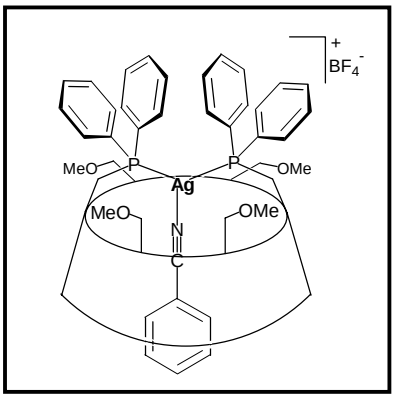
25°C): δ = 11.37 [2d, $^{107}J_{Ag,P}$ = 488 Hz, $^{109}J_{Ag,P}$ = 565 Hz; **21aa***] and 11.60 [2d, $^{107}J_{Ag,P}$ = 483 Hz, $^{109}J_{Ag,P}$ = 559 Hz; **21ab***]; elemental analysis (%): calcd for $C_{76}H_{110}AgBF_4O_{28}P_2$ (1728.30): C 52.82, H 6.41; found: C 53.08, H 6.45; MS (FAB): *m/z* (%): 1657.4 (60) [*M*-BF_4+O]$^+$, 1641.4 (100) [*M*-BF_4]$^+$.

***21aa** and **21ab** are two equilibrating isomers which both have C_2 symmetry on the NMR time scale.



In each of these species two diametrically-opposed methoxy groups bind the silver centre, but this exchange can only be evidenced at lower temperature.

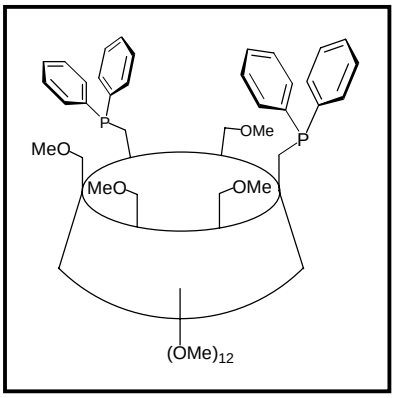
Benzonitrile-{6^A,6^D-bis-(diphenylphosphinyl)-6^A,6^D-dideoxy-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin}silver(I) tetrafluoroborate (22a)



This complex was formed by adding 2-3 equiv. of PhCN to a solution of **21a** in $CDCl_3$. It was only characterised in solution. ^{1}H NMR (400 MHz, $CDCl_3/C_6H_5CN$, 25°C): δ (assignment by COSY) = 2.28 and 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 and 3.30-3.35 (br AB [×2], 8H; H-6^{A,D} and 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-$5^{B,E\ or\ C,F}$), 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-$4^{B,E\ or\ C,F}$), 3.65 (d, 2H; H-$4^{C,F\ or\ B,E}$) 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-$1^{C,F\ or\ B,E}$), 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-$1^{B,E\ or\ C,F}$), 7.35-7.90 (20H, arom. H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3/C_6H_5CN$): δ = 30.94 (virtual t, $^1J_{C,P} + {}^3J_{C,P'}$ = 16.5 Hz; C-$6^{A,D}$), 57.59 and 58.18 (CH_3O-6), 58.90 [×2] and 59.17 (CH_3O-2), 61.13 [×2] and 61.69 (CH_3O-3), 70.08 [×2] (C-$6^{B,C,E,F}$), 71.30 and 71.89 (C-$5^{B,C,E,F}$), 79.46, 80.74, 80.84, 80.95, 81.26, 81.36, 81.65 and 82.18 [×2] (C-2, C-3, C-4), 86.90 (C-$5^{A,D}$), 98.31, 99.19 and 100.60 (C-1), 112.24 (C_{ipso} nitrile), 118.80 (CN) (free nitrile at 118.53), 128.92-133.18 (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3/C_6H_5CN$): δ = 8.7 [2d, $^{107}J_{Ag,P}$ = 458 Hz, $^{109}J_{Ag,P}$ = 529 Hz]; MS (ESI): *m/z* (%): 1744.7 (22) $[M\text{- }BF_4]^+$.

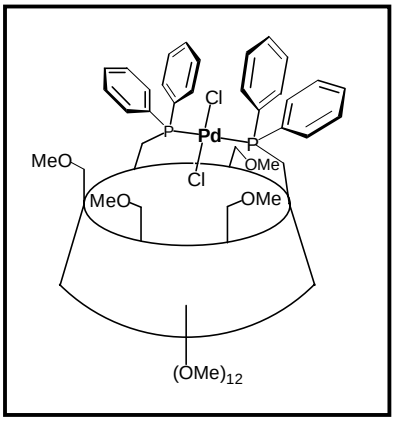
6^A,6^C-Bis-(diphenylphosphinyl)-6^A,6^C-dideoxy-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F, 6^B,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (L4)



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 (0.688 g, 3.69 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, 0.74 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, which allows removal of residual Ph_2PH. This operation was repeated 3 times to afford **L4** as a white powder (0.930 g, 82 %). R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.55; Mp 102-104°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 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 (20H; arom. H); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ = 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] and 59.04 (CH_3O-2, CH_3O-6), 61.50, 61.63, 61.72 [×2] and 61.79 [×2] (CH_3O-3), 69.66 [×2] and 70.18 [×2] (C-6^{B,D,E,F}), 71.10, 71.20 [×2] and 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 and 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 and 100.50 (C-1), 128.05-128.43 (4d; C_{meta}), 128.69, 128.96, 130.60 and 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 (d, $J_{C,P}$ = 14.6 Hz; C_{ipso}); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = -22.7 and -22.3 (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.

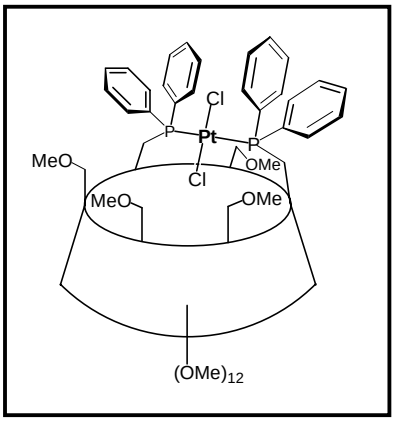
***trans*-*P*,*P*'-Dichloro-{6^{A},6^{C}-bis-(diphenylphosphinyl)-6^{A},6^{C}-dideoxy-2^{A},2^{B},2^{C},2^{D},2^{E}, 2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin}palladium(II) (13b)**



A solution of $[PdCl_2(PhCN)_2]$ (0.025 g, 0.065 mmol) in CH_2Cl_2 (50 mL) containing was added to a solution of containing **L4** (0.100 g, 0.065 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 **13a** (0.045 g, 41%). R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.55; Mp 178°C dec. ^{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, 6H; 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 (m, 2H; H_{ortho}); $^{13}C\{^1H\}$ 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] and 59.76 (CH_3O-6, CH_3O-2), 61.23 [×2], 61.33, 61.59, 61.79 and 61.89 (CH_3O-3), 67.43, 70.71, 71.23 and 72.38 (C-$5^{B,C,E,F}$), 68.77, 69.95, 70.61 and 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 and 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 and 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 (virtual t, $^2J_{C,P} + {}^4J_{C,P'}$ = 14.6 Hz; C_{ortho}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 9.9 (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) $[M\text{-Cl}]^+$, 1638.4 (42) $[M\text{-}2\text{Cl}]^+$.
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 strong roof effect.

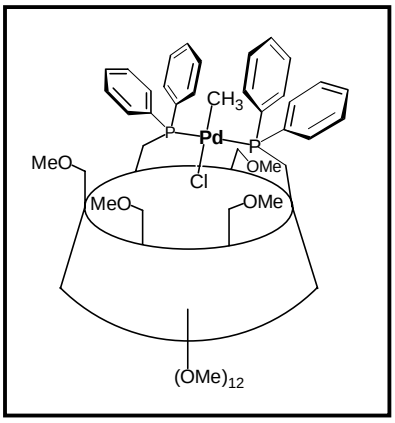
trans-_P,P'_-Dichloro-{6^A,6^C-bis-(diphenylphosphinyl)-6^A,6^C-dideoxy-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-_O_-methyl-α-cyclodextrin}platinum(II) (14b)



A solution of $[PtCl_2(PhCN)_2]$ (0.037 g, 0.078 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **L4** (0.120 g, 0.078 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 **14b** (0.053 g, 38%). R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.55; Mp 170-172°C. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ (assigment 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,F,C}, 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 (br t, J = 7.7 Hz, 2H; H_{ortho}), H-5^E and H-6^E not assigned; $^{13}C\{^1H\}$ 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] and 59.72 (CH_3O-6, CH_3O-2), 61.10, 61.20, 61.30, 61.50, 61.69 and 61.82 (CH_3O-3), 67.33, 70.35, 71.20 and 72.31 (C-5^{B,C,E,F}), 68.71, 69.66, 70.61 and 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 and 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 and 101.13 (C-1), 126.80-137.00 (arom. C); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 2.1 and 7.8 (2d with Pt satellites, $^{1}J_{Pt,P}$ = 2620 Hz, $^{1}J_{Pt,P'}$ = 2577 Hz, $^{2}J_{P,P'}$ = 509 Hz; P and P'); elemental analysis (%): calcd for $C_{76}H_{110}Cl_2O_{28}P_2Pt \bullet 0.5\ C_6H_6$ (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) $[M\text{-Cl}]^+$, 1727.6 (2.5) $[M\text{-}2Cl]^+$.

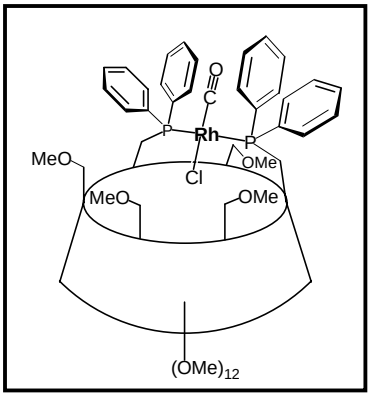
***trans*-*P*,*P'*-Chloro-methyl-{6^A,6^C-bis-(diphenylphosphinyl)-6^A,6^C-dideoxy-2^A,2^B,2^C, 2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin} palladium(II) (15b)**



A solution of [PdMeCl(COD)] (0.020 g, 0.075 mmol) in CH_2Cl_2 (30 mL) was added to a solution of **L4** (0.115 g, 0.075 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 was then filtered off over celite. Evaporation of pentane afforded **15b** as a yellow powder (0.090 g, 71%). R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.50; Mp 165°C dec. ^{1}H NMR (400 MHz, C_6D_6, 25°C): δ (assignment by COSY) = -0.04 (t, $^{3}J_{H,P}$ = 6.4 Hz, 3H; $PdCH_3$), 2.65 and 3.34 (AB, $^{2}J_{AB}$ = 13.3 Hz, 2H, H-6), 2.79 and 4.14 (AB, $^{2}J_{AB}$ = 10.6 Hz, 1H; H-6), 2.87 and 3.92 (AB, 2H; H-$6^{A \text{ or } C}$), 2.90 and 3.14 (AB, 2H; H-$6^{C \text{ or } A}$), 3.05 (dd, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, $^{3}J_{H\text{-}3,H\text{-}2}$ = 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;

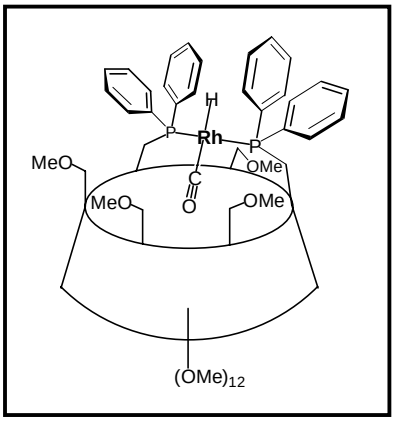
OCH_3), 3.88 (s, 3H; OCH_3), 3.10-4.23 (23H; H-2, H-3, H-4, H-5, H-6), 4.38 and 5.09 (AB, ^3J = 8.4 Hz, $^2J_{AB}$ = 9.3 Hz,1H; H-6), 5.03 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.5 Hz, 1H; H-1), 5.05 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1), 5.05 (m, 1H; H-5, tent. assignment), 5.07 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 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 (br t, J = 9.0 Hz, 2H; H_{ortho}); $^{13}C\{^1H\}$ 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, 58.83, 59.03, 59.19 and 60.05 (CH_3O-6, CH_3O-2), 61.29, 61.46 [×2], 61.65 [×2] and 61.85 (CH_3O-3), 68.77, 71.26, 72.11 and 72.97 (C-$5^{B,C,E,F}$), 70.14, 70.64, 71.98 and 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 and 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 and 101.55 (C-1), 127.77-137.83 (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 14.1 and 20.3 (2d, $^2J_{P,P'}$ = 443 Hz; P and 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) $[M\text{-}CH_3]^+$, 1653.7 (15) $[M\text{-}Cl]^+$, 1638.6 (9) $[M\text{-}CH_3\text{-}Cl]$.

trans-_P,P'_-Chloro-carbonyl-{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) (16b)



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 **L4** (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 **16b** as a yellow powder (0.100 g, 72%). R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.55; Mp 175°C dec. IR (KBr) ν/cm^{-1}: 1979.9 (C≡O); ^{1}H 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, tent. 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 (br m, 2H; H_{ortho}); ^{13}C{^{1}H} 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 [×2], 58.67 [×2], 58.83, 59.23 and 60.05 (CH_3O-6, CH_3O-2), 61.29, 61.39, 61.49, 61.59, 61.69 and 61.88 (CH_3O-3), 68.96, 71.26, 72.18 and 73.00 (C-5^{B,C,E,F}), 69.95, 70.14, 71.98 and 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 and 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 and 101.65 (C-1), 127.67-137.87 (arom. C), 138.80 (d, $J_{C,P}$ = 41.2 Hz; C_{ipso}), 143.14 (d, $J_{C,P}$ = 42.9 Hz; C_{ipso}); ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 8.4 and 20.3 (2dd, $^1J_{Rh,P}$ = $^1J_{Rh,P'}$ = 126 Hz, $^2J_{P,P'}$ = 370 Hz; P and 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) $[M\text{-CO}]^+$, 1635.8 (5) $[M\text{-CO-Cl}]^+$.

***trans*-*P*,*P'*-Hydrido-carbonyl-{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) (17b)**

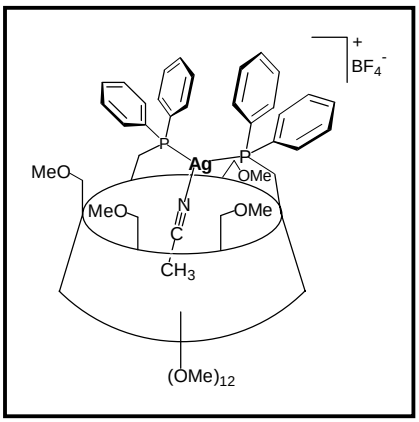


To a stirred solution of **16b** (0.065 g, 0.0382 mmol) in EtOH (10 mL) was added $NaBH_4$ (0.040 g, 1.057 mmol) as a solid. The resulting suspension gradually turned orange-brown. After stirring for 1 h, the mixture was evaporated to dryness. The residue was taken up in toluene (10 ml) and filtered through celite. Evaporation to dryness of the solution yielded **17b** (orange brown) along with small amounts of an isomeric compound (0.060 g, 94%). IR (nujol) ν/cm^{-1}: 1969.0 (C≡O); ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ (assignment by COSY) = -5.48 (dt, $^{1}J_{H,Rh}$ = 10.2 Hz, $^{2}J_{H,P}$ = 17.9 Hz, 1H; Rh-H), 2.53 and 4.20 (AB, ^{3}J = 2.5 Hz, $^{2}J_{AB}$ = 11.2 Hz, 2H; H-6), 2.67 (s, 3H; CH_3O-6), 2.94 and 3.31 (AB, $^{2}J_{AB}$ = 12.1 Hz, 2H; H-6), 3.11 (dd, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, $^{2}J_{H\text{-}3,H\text{-}2}$ = 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 and 4.80 (br AB, $^{2}J_{AB}$ = 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 and 4.97 (2 overlapping m, 2H; H-5^{A,C}), 5.01 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.1 Hz, 1H; H-1), 5.10 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.6 Hz, 1H; H-1), 5.13 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 1H; H-1), 5.14 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 1H; H-1), 5.19 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, 1H; H-1), 5.25 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 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 (m, 2H, H$_{ortho}$); NMR ^{31}P{^{1}H} (121.5 MHz, C_6D_6): δ = 33.6 and 39.24 (2dd, $^{1}J_{Rh,P}$ = $^{1}J_{Rh,P'}$ = 158 Hz, $^{2}J_{P,P'}$ = 280 Hz, P and 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 and 24.9 (2dd, $^1J_{Rh,P} = {}^1J_{Rh,P'}$ = 118 Hz, $^2J_{P,P'}$ = 326 Hz, P and P').

Samples of complex **17b** contained variable amounts of benzene which could not be removed at room temperature. This led to unsatisfactory microanalytical data.

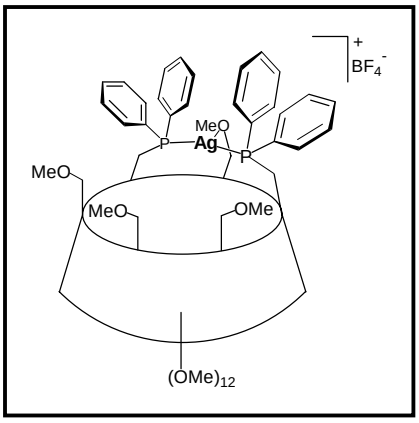
Acetonitrile-{6^A,6^C-bis-(diphenylphosphinyl)-6^A,6^C-dideoxy-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin}silver(I) tetrafluoroborate (20b)



Addition of a large excess of MeCN (*ca.* 30 equiv.) to a solution of **21b** (see below) in $CDCl_3$ afforded **20b** quantitatively. Solvent evaporation regenerated **21b**. ^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 (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 (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3/CD_3CN$): δ = 5.1 and 7.8 (ABX, $^{107}J_{Ag,P}$ = 475 Hz, $^{109}J_{Ag,P}$ = 549 Hz and $^{107}J_{Ag,P'}$ = 470 Hz, $^{109}J_{Ag,P'}$ = 544 Hz, $^2J_{P,P'}$ = 137 Hz; P and P').

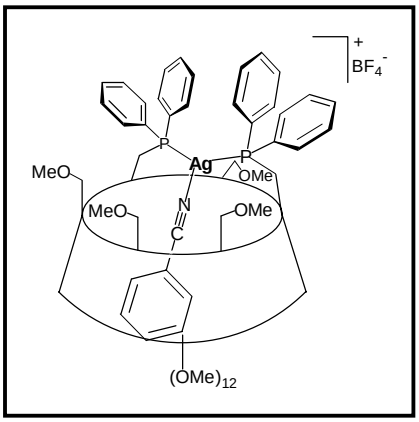
{6^A,6^C-Bis-(diphenylphosphinyl)-6^A,6^C-dideoxy-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F, 6^B,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin}silver(I) tetrafluoroborate (21b)



A solution of $AgBF_4$ (0.020 g, 0.11 mmol) in THF (50 mL) was added to a solution of **L3** (0.155 g, 0.11 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 **21b** as a white precipitate which was filtered off (0.080 g, 46%). R_f (CH_2Cl_2/MeOH, 9 : 1, v/v) = 0.40; Mp 125°C dec. ^1H NMR (300 MHz, $CDCl_3$): δ (assignment by COSY) = 2.09 and 3.67 (AB, $^2J_{AB}$ = 10.0 Hz, 2H; H-6), 2.10 (s, 3H; CH_3O-6), 2.75 and 2.93 (AB, $^2J_{AB}$ = 11.5 Hz, 2H; H-6), 2.81 and 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 and 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 (2 br 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}, tent. assignment), 4.95 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1), 4.99 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H; H-1), 5.03 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1), 5.10 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1), 7.23-7.55 (18H; arom. H), 7.82-7.89 (m, 2H; H_{ortho}); $^{13}C\{^{1}H\}$ 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 and 59.26 (CH_3O-6, CH_3O-2), 61.17 [×2], 61.50, 61.76, 62.02 and 62.15 (CH_3O-3), 69.79, 70.05, 70.19 [×2], 70.40, 70.51 [×2] and 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] and 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 and 101.22 (C-1), 128.50-135.09 (arom. C); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 3.7 and 8.3 (ABX, $^{107}J_{Ag,P}$ = 478 Hz, $^{109}J_{Ag,P}$ = 556 Hz and $^{107}J_{Ag,P'}$ = 480 Hz, $^{109}J_{Ag,P'}$ = 558 Hz, $^{2}J_{P,P'}$ = 147 Hz; P and 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 (22b)

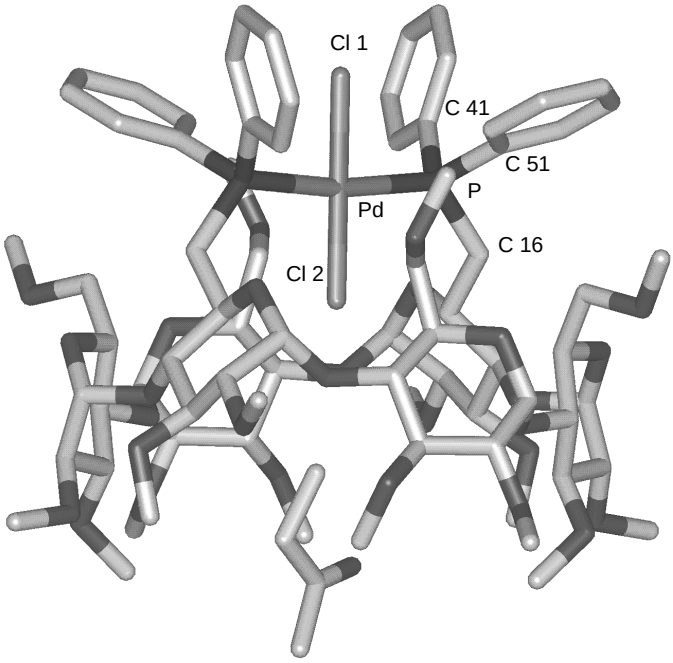


Complex **22b** was obtained after addition of an excess of PhCN (*ca.* 15 equiv.) to a solution of **21b** in $CDCl_3$. Solvent evaporation regenerated **21b**. ^{1}H NMR (300 MHz, $CDCl_3/C_6H_5CN$): δ = 2.13 (d, ^{2}J = 8.8 Hz, 1H, H-6), 2.17 (s, 3H; CH_3O-6), 2.91 (s, 3H; CH_3O-6), 3.01 (s, 3H; CH_3O-6), 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 (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 and 59.37, (CH_3O-6 and CH_3O-2), 61.14 [×2], 61.40, 61.47 and 61.87 [×2] (CH_3O-3), 69.93, 70.16 [×2] and 71.28 (C-$6^{B,D,E,F}$), 70.34 [×2], 70.77 and 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 and 82.80 (C-2, C-3, C-4), 89.31 (d, $^2J_{C,P}$ = 11.3 Hz; C-$5^{A \text{ or } C}$), 90.42 (d, $^2J_{C,P}$ = 12.8 Hz; C-$5^{C \text{ or } A}$), 98.14, 99.02, 99.18, 99.78, 100.90 and 101.08 (C-1), 128.64-134.72 (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3/C_6H_5CN$): δ = 4.3 and 8.0 (ABX, $^{107}J_{Ag,P} = {}^{107}J_{Ag,P'}$ = 500 Hz and $^{109}J_{Ag,P} = {}^{109}J_{Ag,P'}$ = 580 Hz, $^2J_{P,P'}$ = 142 Hz; P and P').

III.4.3. X-ray crystallographic data

III.4.3.1. X-ray crystallographic data of 13a •C_4H_8O



Crystals of **13a** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a butanone solution of the complex. Data were collected on a Bruker SMART 1000 CCD system at 133(2) K (graphite-monochromated MoKα radiation, λ = 0.71073 Å). The structure was solved by direct methods and refined on F_o^2 by full-matrix least squares (program SHELXL-97, G.M. Sheldrick, University of Göttingen). All non-hydrogen atoms were refined anisotropically; hydrogens were included using a riding model. The absolute configuration (and thus the enantiomeric space group assignment) was determined by a *Flack* x parameter of -0.07(3). A summary of the crystallographic data is given in Table 5.

Table 5. Crystallographic data for compound **13a**•C_4H_8O

Crystal Data	
Crystal size	0.44 x 0.20 x 0.12 mm^3
Empirical formula	$C_{80}H_{118}Cl_2O_{29}P_2Pd$
M_r	1782.98
Crystal system	Hexagonal
Space group	$P6_522$
Temperature	133(2) K
Unit cell parameters	
a	14.8846(3) Å
b	14.8846(3) Å
c	67.0615(15) Å
α	90°
β	90°
γ	120°
V	12867.0(5) $Å^3$
Z	6
D (calculated)	1.381 Mg/m^3
F(000)	5640
μ	0.395 mm^{-1}
Data Processing and Reduction	
θ range for data collection	1.58 to 23.23°
Index ranges	$-14 \leq h \leq 16$, $-16 \leq k \leq 15$, $-68 \leq l \leq 64$
Reflections collected	66529
Independent reflections	5529 [R(int) = 0.0699]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5529 / 148 / 517
Goodness-of-fit on F^2	1.071
Final R indices [$I>2\sigma(I)$]	R1 = 0.0413, *w*R2 = 0.0999
R indices (all data)	R1 = 0.0476, *w*R2 = 0.1025
Largest diff. peak and hole	0.791 and -0.396 e.$Å^{-3}$

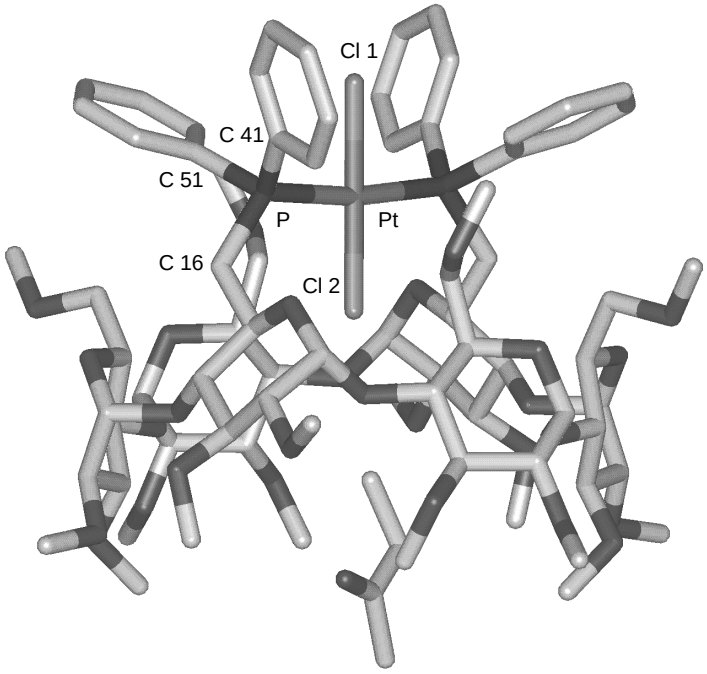
Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **13a**. U(eq) is defined as one third of the trace of the orthogonalised Uij tensor

	x	y	z	U(eq)
Pd	7121.0(4)	8560.5(2)	9167	21.3(2)
P	7251.9(9)	9018.2(9)	9507.0(2)	20.5(3)
Cl(1)	8898.2(14)	9449.1(7)	9167	50.0(6)
Cl(2)	5346.4(13)	7673.2(7)	9167	39.6(5)
O(11)	4149(2)	5376(2)	9629.2(5)	21.2(8)
C(11)	4787(4)	5860(4)	9794.6(7)	21.7(11)
C(12)	4114(4)	5868(4)	9966.2(7)	22.4(11)
C(13)	3578(4)	6442(4)	9899.2(7)	21.8(10)
C(14)	4366(3)	7534(4)	9832.1(7)	19.3(11)
O(15)	5552(2)	6896(2)	9754.0(5)	22.6(7)
C(15)	5158(3)	7553(4)	9683.4(7)	20.8(11)
C(16)	6106(3)	8651(4)	9668.0(7)	22.3(11)
O(17)	3369(3)	4871(2)	10033.1(5)	27.3(8)
C(17)	3794(4)	4367(4)	10145.8(9)	39.2(15)
O(18)	2985(2)	6530(2)	10055.1(4)	28.4(8)
C(18)	1910(4)	5821(4)	10035.2(8)	37.5(14)
O(21)	3430(2)	3781(2)	9057.3(4)	22.4(8)
C(21)	3840(4)	3311(3)	9181.0(7)	23.9(11)
O(22)	2128(3)	2118(3)	9293.1(5)	30.4(8)
C(22)	3122(4)	2848(4)	9359.3(7)	23.1(11)
O(23)	2513(2)	3280(3)	9656.8(4)	26.9(8)
C(23)	3111(4)	3706(4)	9480.5(7)	24.2(11)
C(24)	4206(4)	4537(3)	9536.0(7)	20.6(11)
O(25)	4847(2)	4037(2)	9252.6(4)	21.6(7)
C(25)	4887(4)	4911(4)	9351.3(7)	21.4(11)
O(26)	6417(2)	5301(3)	9536.4(5)	29.3(8)
C(26)	6010(4)	5682(4)	9387.4(7)	24.6(12)
C(27)	1620(4)	1198(4)	9410.9(8)	36.4(14)
C(28)	1587(4)	3300(5)	9658.9(9)	49.2(16)
C(29)	7389(4)	5422(5)	9488.2(9)	43.9(16)
C(31)	3796(4)	4983(4)	8495.9(7)	22.4(12)
O(31)	3798(2)	5824(2)	8595.1(4)	20.3(7)
O(32)	1905(2)	4002(2)	8455.5(4)	25.4(8)
C(32)	2777(3)	3995(3)	8535.9(7)	20.7(11)
O(33)	1742(3)	2763(3)	8783.6(5)	31.7(9)
C(33)	2629(3)	3768(4)	8757.4(7)	21.8(11)
C(34)	3556(4)	3763(4)	8844.3(7)	21.9(11)
O(35)	4615(2)	4842(2)	8566.1(4)	21.7(8)
C(35)	4604(4)	4698(3)	8779.0(6)	19.0(11)
O(36)	5310(3)	3560(3)	8786.9(5)	34.3(9)
C(36)	5544(4)	4599(4)	8821.7(7)	23.3(11)
C(37)	1766(4)	3754(4)	8248.1(7)	35.6(13)
C(38)	986(4)	2724(5)	8917.1(9)	43.1(15)

C(39)	6119(4)	3392(4)	8850.4(9)	41.0(15)
C(41)	8141(3)	8746(4)	9646.8(7)	21.8(11)
C(42)	9184(4)	9525(4)	9670.5(7)	34.6(13)
C(43)	9880(4)	9311(5)	9767.5(9)	45.7(16)
C(44)	9547(4)	8332(4)	9841.9(9)	42.4(15)
C(45)	8543(4)	7567(4)	9818.9(8)	36.4(14)
C(46)	7844(4)	7773(4)	9720.5(8)	31.0(12)
C(51)	7855(4)	10425(4)	9530.6(7)	22.8(11)
C(52)	8107(4)	11063(4)	9363.7(8)	33.3(13)
C(53)	8569(4)	12131(4)	9384.9(9)	45.2(15)
C(54)	8795(4)	12566(4)	9571.8(9)	45.8(15)
C(55)	8565(4)	11958(4)	9738.1(9)	41.0(14)
C(56)	8100(4)	10895(4)	9717.5(8)	34.4(13)
C(91)	-175(19)	4720(30)	9076(5)	259(9)
C(92)	880(16)	5172(18)	9167(4)	259(9)
C(93)	1560(20)	5630(30)	8984(4)	259(9)
C(94)	2610(20)	6400(30)	9064(4)	259(9)
O(91)	1130(17)	5237(19)	9340(4)	259(9)

Symmetry transformation used to generate equivalent atoms:
#1 x,x-y+1,-z+11/6

III.4.3.2. X-ray crystallographic data of 14a•C_4H_8O



Crystals of **14a** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a butanone solution of the complex. Data were collected on a Bruker SMART 1000 CCD system at 133(2) K (graphite-monochromated MoKα radiation, λ = 0.71073 Å). The structure was solved by direct methods and refined on F_o^2 by full-matrix least squares (program SHELXL-97, G.M. Sheldrick, University of Göttingen). All non-hydrogen atoms were refined anisotropically; hydrogens 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). A summary of the crystallographic data is given in Table 7.

Table 7. Crystallographic data for compound **14a**•C_4H_8O

Crystal Data	
Crystal size	0.16 x 0.16 x 0.12 mm^3
Empirical formula	$C_{80}H_{118}Cl_2O_{29}P_2Pt$
M_r	1871.67
Crystal system	Hexagonal
Space group	$P6_522$
Temperature	133(2) K
Unit cell parameters	
a	14.8955(3) Å
b	14.8955(3) Å
c	67.009(3) Å
α	90°
β	90°
γ	120°
V	12875.8(7) $Å^3$
Z	6
D (calculated)	1.448 g/cm^3
F(000)	5832
μ	1.813 mm^{-1}
Data Processing and Reduction	
θ range for data collection	1.61 to 30.04°
Index ranges	$-20 \leq h \leq 20$, $-20 \leq k \leq 20$, $-88 \leq l \leq 94$
Reflections collected	192791
Independent reflections	12553 [R(int) = 0.0879]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12553 / 148 / 517
Goodness-of-fit on F^2	1.062
Final R indices [$I>2\sigma(I)$]	R1 = 0.0485, *w*R2 = 0.1093
R indices (all data)	R1 = 0.0567, *w*R2 = 0.1122
Largest diff. peak and hole	1.049 and -2.258 $e.Å^{-3}$

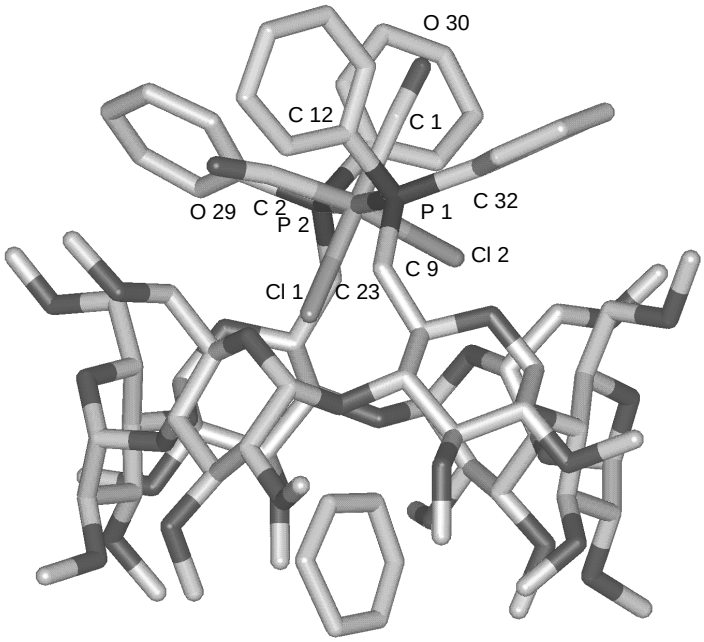
Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **14a**. U(eq) is defined as one third of the trace of the orthogonalised Uij tensor

	x	y	z	U(eq)
Pt	7131.5(2)	8565.8(1)	9167	18.3(1)
P	7255.1(9)	9022.3(9)	9502.9(2)	17.3(2)
Cl(1)	8913.9(13)	9457.0(7)	9167	47.0(6)
Cl(2)	5351.2(12)	7675.6(6)	9167	33.4(4)
O(11)	4157(2)	5374(2)	9629.0(5)	19.6(6)
C(11)	4800(3)	5867(4)	9794.5(7)	18.3(8)
C(12)	4131(4)	5875(4)	9966.8(6)	19.1(8)
C(13)	3584(4)	6444(4)	9896.4(6)	19.3(7)
C(14)	4369(3)	7544(3)	9829.8(6)	16.7(8)
O(15)	5559(2)	6903(2)	9751.7(5)	20.3(6)
C(15)	5164(3)	7554(4)	9680.8(6)	18.9(8)
C(16)	6101(3)	8657(4)	9664.0(7)	21.8(9)
O(17)	3378(3)	4875(3)	10032.3(5)	25.2(7)
C(17)	3805(4)	4373(5)	10144.2(10)	35.7(13)
O(18)	2996(2)	6537(3)	10054.9(5)	26.6(7)
C(18)	1917(4)	5813(4)	10035.1(8)	32.8(12)
O(21)	3430(2)	3774(3)	9057.5(5)	20.1(6)
C(21)	3837(3)	3301(3)	9180.8(7)	20.8(8)
O(22)	2125(3)	2116(3)	9293.6(5)	27.6(7)
C(22)	3127(3)	2845(4)	9360.2(6)	20.9(9)
O(23)	2520(3)	3280(3)	9657.4(4)	24.6(7)
C(23)	3118(3)	3705(4)	9481.6(6)	19.6(8)
C(24)	4214(3)	4535(3)	9535.4(7)	17.7(8)
O(25)	4850(3)	4032(2)	9252.1(5)	19.3(6)
C(25)	4889(3)	4907(3)	9350.2(6)	17.8(8)
O(26)	6429(3)	5299(3)	9535.6(5)	25.8(7)
C(26)	6020(4)	5675(4)	9386.6(7)	21.6(9)
C(27)	1625(4)	1198(4)	9411.5(8)	32.9(12)
C(28)	1589(5)	3299(5)	9659.9(9)	45.0(15)
C(29)	7396(4)	5420(5)	9485.3(10)	38.3(13)
C(31)	3799(4)	4990(3)	8496.9(7)	19.5(9)
O(31)	3798(2)	5828(2)	8596.7(4)	18.1(6)
O(32)	1902(3)	4004(3)	8455.7(5)	24.3(7)
C(32)	2776(3)	3996(3)	8536.3(6)	18.7(8)
O(33)	1736(3)	2759(3)	8781.7(5)	27.1(7)
C(33)	2623(3)	3763(4)	8757.2(7)	19.1(9)
C(34)	3564(4)	3760(4)	8844.5(7)	20.1(9)
O(35)	4615(2)	4844(2)	8565.7(5)	20.2(6)
C(35)	4599(4)	4692(3)	8778.4(6)	18.9(8)
O(36)	5307(3)	3557(3)	8787.9(6)	32.6(9)
C(36)	5543(4)	4588(4)	8823.2(7)	21.9(9)
C(37)	1756(4)	3753(4)	8247.6(7)	29.8(10)
C(38)	990(4)	2720(5)	8914.9(10)	41.2(14)

C(39)	6114(5)	3387(5)	8851.8(10)	40.2(14)
C(41)	8142(3)	8747(3)	9645.9(7)	19.6(9)
C(42)	9184(4)	9531(4)	9671.4(8)	30.3(11)
C(43)	9874(4)	9312(5)	9769.4(9)	38.6(13)
C(44)	9544(4)	8330(4)	9840.9(10)	41.0(15)
C(45)	8534(4)	7556(4)	9814.5(8)	31.5(11)
C(46)	7838(4)	7761(4)	9715.0(7)	25.8(9)
C(51)	7854(3)	10428(4)	9529.6(6)	19.7(9)
C(52)	8113(4)	11074(4)	9363.5(8)	28.8(11)
C(53)	8583(5)	12145(4)	9388.0(9)	43.2(13)
C(54)	8804(5)	12572(5)	9576.0(9)	39.2(13)
C(55)	8565(4)	11955(4)	9741.3(9)	36.3(12)
C(56)	8093(4)	10893(4)	9719.0(8)	32.1(12)
C(91)	-130(20)	4750(40)	9059(5)	228(10)
C(92)	925(18)	5197(19)	9148(5)	228(10)
C(93)	1600(20)	5670(40)	8967(4)	228(10)
C(94)	2660(20)	6420(30)	9051(5)	228(10)
O(91)	1170(20)	5220(20)	9319(5)	228(10)

Symmetry transformations used to generate equivalent atoms:
#1 x,x-y+1,-z+11/6

III.4.3.3. X-ray crystallographic data of 18a•C_6H_6



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Crystals of **18a** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a benzene solution of the complex; Data were collected on a Kappa CCD Enraf Nonius system at 173(2) K (graphite-monochromated MoKα radiation, λ = 0.71073 Å). The structure was solved by direct methods and refined on F_o^2 by full-matrix least squares (program SHELXL-97, G.M. Sheldrick, University of Göttingen). All non-hydrogen atoms were refined anisotropically; hydrogens were included using a riding model. The absolute structure was determined by refining Flack's x parameter (x = -0.01(4)). The included benzene molecule is disordered over two positions (interplane angle ca. 30°). A summary of the crystallographic data is given in Table 9.

Table 9. Crystallographic data for compound **18a**•C_6H_6

Crystal Data	
Crystal size	0.10 x 0.08 x 0.06 mm
Empirical formula	$C_{84}H_{116}Cl_2O_{30}P_2Ru$
M_r	1839.68
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Temperature	173(2) K
Unit cell parameters	
a	15.353(2) Å
b	24.313(2) Å
c	26.952(3) Å
α	90°
β	90°
γ	90°
V	10060.9(19) Å^3
Z	4
D (calculated)	1.211 g/cm^3
F(000)	3872
μ	0.311 mm^{-1}
Data Processing and Reduction	
θ range for data collection	2.82 to 27.49°
Index ranges	$0 \leq h \leq 19$, $0 \leq k \leq 31$, $-34 \leq l \leq 34$
Reflections collected	22786
Reflections [$I>2\sigma(I)$]	12112
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	22786 / 34 / 1027
Goodness-of-fit on F^2	0.971
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0830, $wR2$ = 0.2096
R indices (all data)	$R1$ = 0.1522, $wR2$ = 0.2421
Largest diff. peak and hole	1.447 and –0.645 e.Å^{-3}

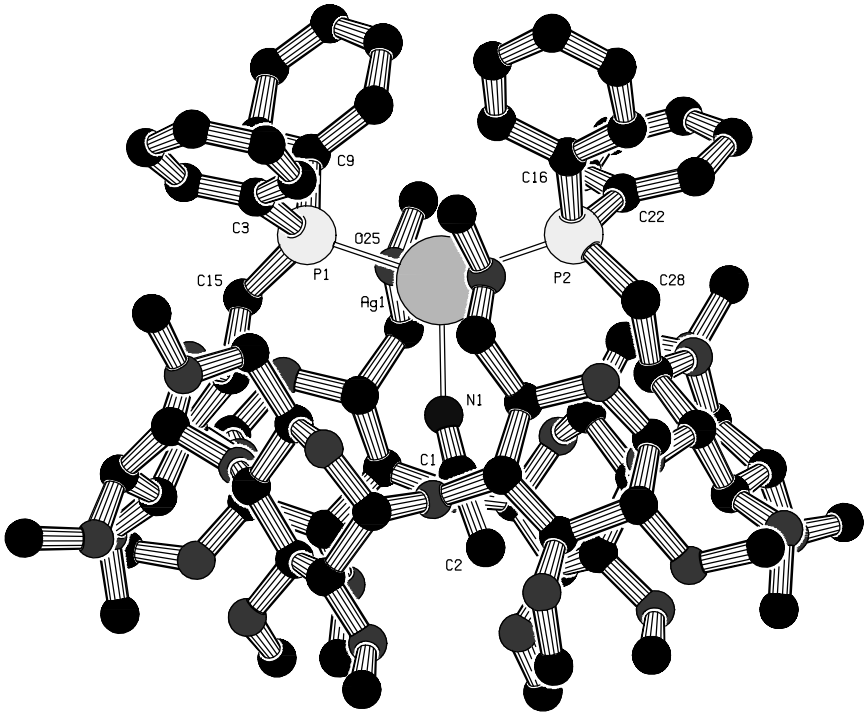
Table 10. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **18a**. U(eq) is defined as one third of the trace of the orthogonalised Uij tensor

	x	y	z	U(eq)
Ru(1)	-0.21342(4)	-0.62443(2)	-0.936802(18)	0.05277(17)
Cl(1)	-0.1831(2)	-0.52726(12)	-0.93494(10)	0.0637(8)
Cl(1A)	-0.1053(9)	-0.5633(5)	-0.9287(3)	0.086(4)
Cl(2)	-0.36154(18)	-0.60240(14)	-0.94780(10)	0.0716(8)
Cl(2A)	-0.3149(10)	-0.5447(6)	-0.9401(4)	0.107(4)
Cl(1B)	-0.2003(6)	-0.7210(4)	-0.9356(3)	0.087(2)
C(1)	-0.2392(10)	-0.70297(14)	-0.9363(6)	0.104(3)
O(30)	-0.2586(8)	-0.74856(14)	-0.9391(5)	0.147(2)
C(2A)	-0.1466(6)	-0.6926(2)	-0.9341(15)	0.104(3)
O(29A)	-0.107(3)	-0.7326(10)	-0.9303(16)	0.147(2)
C(2)	-0.08775(12)	-0.6304(4)	-0.9275(4)	0.104(3)
O(29)	-0.01345(13)	-0.6264(4)	-0.9230(4)	0.147(2)
P(1)	-0.22795(12)	-0.62852(7)	-0.84730(5)	0.0483(4)
P(2)	-0.20029(13)	-0.62842(7)	-1.02633(6)	0.0535(4)
O(1)	-0.1934(3)	-0.44337(15)	-0.79044(15)	0.0448(10)
O(2)	-0.5529(3)	-0.46593(19)	-0.98206(16)	0.0531(11)
O(3)	-0.0962(3)	-0.43023(18)	-1.04096(16)	0.0515(11)
O(4)	-0.3617(3)	-0.47295(18)	-1.08472(15)	0.0513(11)
O(5)	-0.6294(3)	-0.3724(2)	-0.94101(19)	0.0665(13)
O(6)	-0.6102(3)	-0.4026(2)	-1.0666(2)	0.0680(13)
O(7)	-0.3171(4)	-0.4076(2)	-0.71851(19)	0.0729(16)
O(8)	-0.2808(4)	-0.4047(2)	-1.15727(17)	0.0731(15)
O(9)	-0.0162(3)	-0.3902(18)	-0.89550(16)	0.0507(11)
O(10)	-0.4518(3)	-0.4808(2)	-0.83650(17)	0.0571(12)
O(11)	0.0194(3)	-0.28828(18)	-0.9415(2)	0.0647(13)
O(12)	-0.0163(4)	-0.3150(2)	-0.81373(19)	0.0706(15)
O(13)	-0.0301(4)	-0.3184(2)	-1.0386(2)	0.0695(14)
O(14)	-0.1054(5)	-0.3788(3)	-1.1349(2)	0.097(2)
O(15)	-0.4832(4)	-0.4081(2)	-1.14391(18)	0.0807(18)
O(16)	-0.4904(4)	-0.4365(3)	-0.7395(2)	0.0843(18)
O(17)	-0.5643(4)	-0.3850(3)	-0.8428(2)	0.0834(17)
O(18)	-0.1279(4)	-0.3498(2)	-0.73660(18)	0.0727(16)
O(19)	-0.1314(3)	-0.51401(18)	-1.07682(16)	0.0555(12)
O(20)	-0.6231(3)	-0.5219(2)	-0.92505(19)	0.0659(14)
O(21)	0.0841(3)	-0.4324(2)	-0.95025(19)	0.0626(13)
O(22)	-0.3684(3)	-0.54692(19)	-0.79773(17)	0.0549(12)
O(23)	-0.4652(4)	-0.5434(2)	-1.08730(18)	0.0636(14)
O(24)	-0.0533(3)	-0.48021(19)	-0.78738(17)	0.0545(12)
O(25)	-0.6152(5)	-0.5831(3)	-0.8340(3)	0.109(2)
O(26)	-0.6185(5)	-0.5933(3)	-1.0449(3)	0.104(2)
O(27)	0.1143(7)	-0.4946(4)	-1.0390(3)	0.153(4)
O(28)	0.1137(5)	-0.4953(3)	-0.8295(3)	0.115(3)
C(3)	-0.2210(5)	-0.5143(2)	-1.0635(2)	0.0475(15)

C(4)	-0.5510(6)	-0.5830(4)	-0.8714(3)	0.077(2)
C(5)	-0.5404(6)	-0.5862(3)	-1.0210(3)	0.075(2)
C(6)	0.0477(7)	-0.5073(4)	-1.0030(4)	0.089(3)
C(7)	0.0367(7)	-0.5066(4)	-0.8552(3)	0.080(3)
C(8)	-0.3406(5)	-0.4384(3)	-0.7597(2)	0.0521(17)
C(9)	-0.2168(5)	-0.5646(2)	-0.8108(2)	0.0439(14)
C(10)	-0.2869(5)	-0.5208(2)	-0.8110(2)	0.0426(14)
C(11)	-0.2595(5)	-0.6875(2)	-1.0513(2)	0.069(2)
C(12)	-0.1365(4)	-0.6676(2)	-0.8241(2)	0.0524(17)
C(13)	-0.4202(5)	-0.4724(4)	-0.7497(2)	0.068(2)
C(14)	-0.2743(5)	-0.4820(2)	-1.1030(2)	0.0504(17)
C(15)	-0.4331(5)	-0.4967(3)	-1.1112(3)	0.062(2)
C(16)	-0.2646(4)	-0.4769(3)	-0.7723(2)	0.0449(15)
C(17)	-0.1247(8)	-0.3594(4)	-0.6830(3)	0.093(3)
C(18)	-0.2342(6)	-0.4266(3)	-1.1137(2)	0.064(2)
C(19)	-0.5944(6)	-0.3451(3)	-1.0692(4)	0.083(3)
C(20)	-0.4975(5)	-0.5337(3)	-1.0369(3)	0.0594(19)
C(21)	-0.1131(5)	-0.4452(3)	-0.7645(2)	0.0486(16)
C(22)	-0.0297(5)	-0.3555(3)	-0.9985(3)	0.0537(17)
C(23)	-0.2521(5)	-0.5744(2)	-1.0645(2)	0.0562(18)
C(24)	-0.1063(8)	-0.2845(4)	-1.0414(4)	0.094(3)
C(25)	0.0142(5)	-0.4550(3)	-0.9797(3)	0.0604(19)
C(26)	-0.0939(5)	-0.4621(3)	-1.0839(3)	0.0597(19)
C(27)	-0.0337(4)	-0.4666(3)	-0.8388(2)	0.0491(16)
C(28)	-0.0056(4)	-0.4061(3)	-0.8445(3)	0.0517(16)
C(29)	-0.3000(8)	-0.3465(4)	-1.1514(4)	0.107(4)
C(30)	-0.5069(5)	-0.4558(3)	-1.1168(3)	0.065(2)
C(31)	-0.3423(9)	-0.7789(4)	-1.0897(4)	0.130(6)
C(32)	-0.3181(5)	-0.6665(3)	-0.8199(2)	0.065(2)
C(33)	-0.5386(5)	-0.4794(3)	-0.8579(3)	0.0576(18)
C(34)	-0.2139(7)	-0.7334(3)	-1.0687(6)	0.166(7)
C(35)	-0.5327(5)	-0.4358(3)	-1.0648(3)	0.0572(17)
C(36)	-0.0615(5)	-0.3663(3)	-0.8141(2)	0.0547(17)
C(37)	-0.0151(4)	-0.4128(3)	-1.0189(3)	0.0527(17)
C(38)	-0.5450(5)	-0.5278(3)	-0.8954(3)	0.0568(18)
C(39)	-0.4392(5)	-0.5112(3)	-0.7929(3)	0.062(2)
C(40)	-0.5562(4)	-0.4851(3)	-1.0328(3)	0.0509(16)
C(41)	-0.0750(5)	-0.3877(3)	-0.7615(2)	0.0543(17)
C(4)	-0.1399(6)	-0.4326(3)	-1.1256(3)	0.067(2)
C(43)	-0.6272(5)	-0.4706(3)	-0.9506(3)	0.061(2)
C(44)	-0.2530(9)	-0.7838(5)	-1.0803(8)	0.292(18)
C(45)	-0.3199(6)	-0.6730(4)	-0.7683(2)	0.090(3)
C(46)	0.0598(4)	-0.3841(3)	-0.9245(3)	0.0572(19)
C(47)	-0.1411(5)	-0.7250(2)	-0.8204(5)	0.105(4)
C(48)	-0.5104(10)	-0.3401(5)	-0.8449(4)	0.117(4)
C(49)	-0.0933(5)	-0.6408(3)	-1.0503(2)	0.076(2)
C(50)	-0.3388(9)	-0.3513(4)	-0.7228(4)	0.107(4)
C(51)	-0.6293(5)	-0.4245(3)	-0.9167(3)	0.062(2)

C(52)	-0.0326(7)	-0.6720(6)	-1.0237(3)	0.132(5)
C(53)	-0.3842(6)	-0.7049(4)	-0.7453(4)	0.117(4)
C(54)	-0.4437(7)	-0.7256(4)	-0.8260(4)	0.112(4)
C(55)	-0.0572(4)	-0.6437(3)	-0.8104(4)	0.083(3)
C(56)	-0.4483(8)	-0.7304(4)	-0.7743(4)	0.108(4)
C(57)	-0.5516(5)	-0.4247(3)	-0.8818(3)	0.0576(18)
C(58)	-0.3505(5)	-0.6881(3)	-1.0545(4)	0.101(3)
C(59)	0.0776(9)	-0.6676(6)	-1.0893(4)	0.149(6)
C(60)	-0.0667(6)	-0.6242(4)	-1.0977(3)	0.107(4)
C(61)	-0.3800(5)	-0.6935(4)	-0.8493(3)	0.094(3)
C(62)	-0.0717(7)	-0.2684(3)	-0.8263(3)	0.083(3)
C(63)	0.0913(6)	-0.2618(4)	-0.9190(4)	0.085(3)
C(64)	-0.7144(6)	-0.3586(4)	-0.9603(4)	0.092(3)
C(65)	0.0438(4)	-0.3388(3)	-0.9631(3)	0.0564(18)
C(66)	-0.3929(7)	-0.7347(3)	-1.0732(4)	0.110(4)
C(67)	-0.0253(8)	-0.3763(6)	-1.1601(5)	0.137(5)
C(68)	0.0133(7)	-0.6412(5)	-1.1174(4)	0.135(5)
C(69)	-0.4810(7)	-0.4184(5)	-1.1960(4)	0.106(3)
C(70)	-0.0686(5)	-0.7573(4)	-0.8087(5)	0.120(4)
C(71)	0.0079(6)	-0.7310(3)	-0.7934(3)	0.089(3)
C(72)	0.0170(5)	-0.6739(3)	-0.7973(4)	0.102(3)
C(73)	0.0498(7)	-0.6853(8)	-1.0424(4)	0.172(8)
C(74)	-0.5585(7)	-0.4660(6)	-0.7124(5)	0.128(5)
C(75)	-0.6167(10)	-0.6326(7)	-0.8088(6)	0.162(6)
C(76)	0.1826(9)	-0.5293(6)	-0.8456(8)	0.176(7)
C(77)	0.1750(12)	-0.5275(8)	-1.0506(7)	0.176(6)
C(78)	-0.6615(14)	-0.6386(9)	-1.0251(8)	0.197(8)
C(80)	-0.3328(11)	-0.3908(7)	-0.9591(6)	0.150
C(81)	-0.3816(11)	-0.3482(8)	-0.9721(6)	0.150
C(82)	-0.3720(11)	-0.2976(7)	-0.9601(6)	0.150
C(83)	-0.3096(11)	-0.2796(6)	-0.9368(6)	0.150
C(84)	-0.2456(10)	-0.3266(7)	-0.9269(6)	0.150
C(85)	-0.2634(11)	-0.3779(7)	-0.9332(6)	0.150

III.4.3.4. X-ray crystallographic data of 20a•3CH$_3$CN•H$_2$O



The counter-anion (BF_4^-) as well as the solvent molecules have been omitted for clarity.

Crystals of **20a** suitable for X-ray diffraction were obtained by slow diffusion of diisopropylether into a butanone-acetonitrile (100:1, v/v) solution of the complex. Data were collected on a Kappa CCD Enraf Nonius system at 173 K (graphite-monochromated MoKα radiation, λ = 0.71073 Å). The structure was solved by direct methods and refined on F_o^2 by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. The absolute structure was determined by refining Flack's x parameter. A summary of the crystallographic data is given in Table 11.

Table 11. Crystallographic data for compound **20a**•3CH_3CN•H_2O

Crystal Data	
Crystal size	0.20 x 0.20 x 0.18 mm
Empirical Formula	$C_{84}H_{124}AgBF_4N_4O_{29}P_2$
M_r	1910.56
Crystal system	Triclinic
Space group	P1
Temperature	173 K
Unit cell parameters	
a	13.7530(4) Å
b	14.4944(6) Å
c	15.0189(6) Å
α	118.057(5)°
β	98.133(5)°
γ	103.960(5)°
V	2447.8(6) $Å^3$
Z	1
D (calculated)	1.30 g /cm^3
F(000)	1006
$\mu(mm^{-1})$	0.321
Data Processing and Reduction	
Scan mode	'φ scans'
θ range for data collection	2.5 to 27.46°
Index ranges	$-13 \leq h \leq 17$, $-18 \leq k \leq 18$, $-18 \leq l \leq 19$
Reflections collected	15874
Reflections [$I > 3\ \sigma(I)$]	5753
Number of variables	1121
Goodness-of-fit on F^2	1.589
R	0.069
R*w*	0.089
Largest diff. peak and hole	1.408 and -0.129 e.$Å^{-3}$

Table 12. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **20a**. U(eq) is defined as one third of the trace of the orthogonalised Uij tensor

	x	y	z	U(eq)
Ag	0.4722	0.5948	0.0793	0.0663(4)
P(1)	0.5788(2)	0.7040(2)	0.2754(2)	0.0505(9)
P(2)	0.3371(2)	0.4059(2)	-0.0686(2)	0.0497(9)
N(1)	0.521(1)	0.7095(8)	0.0059(7)	0.076(6)
C(1)	0.511(1)	0.7496(9)	-0.041(1)	0.064(7)
C(2)	0.488(1)	0.789(1)	-0.112(1)	0.088(7)
C(3)	0.5044(7)	0.7516(6)	0.3715(7)	0.055(4)
C(4)	0.5538(8)	0.8217(9)	0.4735(8)	0.078(5)
C(5)	0.494(1)	0.852(1)	0.5493(9)	0.116(6)
C(6)	0.3839(8)	0.7986(8)	0.5054(9)	0.121(4)
C(7)	0.3376(9)	0.727(1)	0.401(1)	0.078(6)
C(8)	0.3975(8)	0.7057(8)	0.334(1)	0.055(5)
C(9)	0.6230(8)	0.6093(7)	0.3036(7)	0.059(4)
C(10)	0.718(1)	0.6419(8)	0.3760(8)	0.062(5
C(11)	0.739(1)	0.555(1)	0.3901(9)	0.116(6)
C(12)	0.673(1)	0.4484(9)	0.3345(9)	0.109(6)
C(13)	0.583(1)	0.4170(9)	0.261(1)	0.101(6)
C(14)	0.5560(9)	0.4956(8)	0.247(1)	0.095(5)
C(15)	0.7009(6)	0.8212(6)	0.3210(6)	0.044(3)
C(16)	0.2396(7)	0.3615(6)	-0.0128(7)	0.047(4)
C(17)	0.266(1)	0.415(1)	0.099(1)	0.060(7)
C(18)	0.193(1)	0.379(2)	0.142(1)	0.100(9)
C(19)	0.099(1)	0.295(1)	0.083(1)	0.100(8)
C(20)	0.0767(9)	0.248(1)	-0.021(1)	0.080(6)
C(21)	0.1440(8)	0.2779(8)	-0.0715(7)	0.050(5)
C(22)	0.3868(8)	0.2904(7)	-0.1212(7)	0.069(4)
C(23)	0.3261(8)	0.1921(8)	-0.2082(8)	0.078(4)
C(24)	0.4615(8)	0.1180(7)	-0.1774(8)	0.075(4)
C(25)	0.363(1)	0.0958(9)	-0.2452(9)	0.099(6)
C(26)	0.5198(9)	0.2191(9)	-0.0924(9)	0.094(5)
C(27)	0.4802(7)	0.3014(8)	-0.0656(7)	0.079(4)
C(28)	0.2585(7)	0.3983(6)	-0.1843(6)	0.035(3)
C(29)	0.6896(6)	0.9139(7)	0.3023(6)	0.040(3)
C(30)	0.7912(8)	1.1046(7)	0.3348(6)	0.032(4)
C(32)	0.7223(8)	1.1492(7)	0.4059(6)	0.039(4)
C(33)	0.6177(7)	1.0600(7)	0.3689(6)	0.034(4)
O(1)	0.6332(4)	0.9680(5)	0.3725(4)	0.040(2)
O(2)	0.8932(6)	1.1832(5)	0.3750(5)	0.042(3)
C(34)	0.917(1)	1.239(1)	0.318(1)	0.070(6)
O(3)	0.7142(8)	1.2461(5)	0.4101(6)	0.053(4)
C(35)	0.733(1)	1.334(1)	0.5059(9)	0.065(6)
O(4)	0.5642(4)	1.0220(4)	0.2625(4)	0.038(2)
C(36)	0.4699(6)	1.0443(6)	0.2439(6)	0.022(3)

C(37)	0.3747(7)	0.9496(6)	0.2244(7)	0.033(4)	
O(5)	0.2786(4)	0.9564(5)	0.1814(4)	0.032(3)	
C(38)	0.2697(6)	0.9553(6)	0.0861(6)	0.027(3)	
C(39)	0.3573(7)	1.0592(6)	0.1094(6)	0.032(3)	
C(40)	0.4649(7)	1.0582(6)	0.1493(6)	0.021(3)	
C(41)	0.3641(9)	0.9424(7)	0.3211(7)	0.044(4)	
O(6)	0.3667(5)	1.0504(5)	0.4023(4)	0.045(3)	
C(42)	0.325(1)	1.043(1)	0.4797(8)	0.063(6)	
O(7)	0.3539(5)	1.0682(5)	0.0198(5)	0.043(3)	
C(43)	0.2965(8)	1.1337(7)	0.0121(7)	0.061(4)	
O(8)	0.5449(5)	1.1586(5)	0.1790(5)	0.036(3)	
C(44)	0.6119(9)	1.1430(9)	0.1115(8)	0.069(5)	
O(9)	0.2815(4)	0.8602(4)	0.0059(4)	0.028(2)	
C(45)	0.1865(6)	0.7668(6)	-0.0687(6)	0.021(3)	
C(46)	0.1965(8)	0.6653(8)	-0.0643(6)	0.034(4)	
O(10)	0.1200(5)	0.5631(4)	-0.1530(4)	0.028(3)	
C(47)	0.1254(6)	0.5474(6)	-0.2514(5)	0.018(3)	
C(48)	0.0958(6)	0.6365(6)	-0.2622(6)	0.029(3)	
C(49)	0.1747(6)	0.7530(6)	-0.1744(6)	0.025(3)	
C(50)	0.175(2)	0.6690(9)	0.0362(8)	0.059(7)	
O(11)	0.1087(9)	0.6637(9)	0.0569(9)	0.041(3)	*
C(51)	0.105(2)	0.661(2)	0.148(2)	0.052(6)	*
O(11A)	0.1775(8)	0.5986(9)	0.0493(8)	0.036(3)	*
C(51A)	0.127(1)	0.589(1)	0.125(1)	0.037(4)	*
O(12)	0.0939(4)	0.6270(4)	-0.3614(4)	0.031(2)	
C(52)	0.0097(8)	0.5297(8)	-0.4489(7)	0.040(4)	
O(13)	0.1419(5)	0.8374(4)	-0.1748(5)	0.041(2)	
C(53)	0.1874(9)	0.8823(7)	-0.2312(8)	0.063(4)	
O(14)	0.2254(4)	0.5530(4)	-0.2643(4)	0.021(2)	
C(54)	0.2461(6)	0.4516(6)	-0.3223(6)	0.026(3)	
C(55)	0.3181(6)	0.4389(6)	-0.2430(6)	0.026(3)	
O(15)	0.3662(4)	0.3586(4)	-0.2959(5)	0.038(2)	
C(56)	0.4239(6)	0.3825(6)	-0.3588(7)	0.031(3)	
C(57)	0.3474(6)	0.3732(6)	-0.4494(7)	0.026(3)	
C(58)	0.2935(6)	0.4580(6)	-0.4046(6)	0.024(3)	
O(16)	0.3974(5)	0.3951(4)	-0.5174(5)	0.033(3)	
C(59)	0.422(1)	0.306(1)	-0.589(1)	0.063(6)	
O(17)	0.2121(4)	0.4409(4)	-0.4872(4)	0.034(2)	
C(60)	0.2380(8)	0.5180(8)	-0.5216(6)	0.069(4)	
O(18)	0.5011(4)	0.4883(4)	-0.2983(5)	0.028(2)	
C(61)	0.6081(6)	0.4962(6)	-0.2980(6)	0.021(3)	
C(62)	0.6610(6)	0.4874(7)	-0.2060(6)	0.021(3)	
O(19)	0.7733(4)	0.5204(4)	-0.1895(4)	0.026(2)	
C(63)	0.8210(6)	0.6316(8)	-0.1639(6)	0.024(4)	
C(64)	0.7827(7)	0.6435(8)	-0.2546(7)	0.034(4)	
C(65)	0.6620(7)	0.6057(7)	-0.2896(6)	0.032(4)	
C(66)	0.6238(6)	0.3745(7)	-0.2209(6)	0.034(3)	
O(20)	0.6355(5)	0.2947(5)	-0.3179(4)	0.042(3)	

C(67)	0.6058(9)	0.1870(8)	-0.3362(8)	0.046(5)
O(21)	0.8281(6)	0.7500(6)	-0.2337(5)	0.042(3)
C(68)	0.8797(8)	0.7623(8)	-0.3016(8)	0.065(4)
O(22)	0.6330(6)	0.5910(6)	-0.3923(6)	0.065(3)
C(69)	0.5763(9)	0.653(1)	-0.4025(9)	0.068(5)
O(23)	0.8042(4)	0.7093(4)	-0.0724(4)	0.021(2)
C(70)	0.8809(6)	0.7578(7)	0.0271(7)	0.036(4)
C(71)	0.8267(8)	0.7318(7)	0.1000(7)	0.036(4)
O(24)	0.8918(5)	0.7995(5)	0.2077(4)	0.026(3)
C(72)	0.9237(6)	0.9166(7)	0.2479(6)	0.026(4)
C(73)	0.9948(7)	0.9442(8)	0.1868(7)	0.036(4)
C(74)	0.9329(6)	0.8818(7)	0.0724(7)	0.025(4)
C(75)	0.811(1)	0.6128(8	0.0714(7)	0.043(5)
O(25)	0.7498(7)	0.5794(6)	0.1214(6)	0.079(4)
C(76)	0.760(1)	0.482(1)	0.118(1)	0.101(6)
O(26)	1.0355(5)	1.0586(6)	0.2254(5)	0.035(3)
C(77)	1.1203(9)	1.123(1)	0.3201(9)	0.041(6)
O(27)	0.9988(4)	0.8923(5)	0.0101(5)	0.037(3)
C(78)	0.9969(8)	0.9724(9)	-0.0153(8)	0.048(5)
O(28)	0.8366(4)	0.9486(4)	0.2356(4)	0.029(2)
B	0.992(3)	1.020(2)	0.599(1)	0.07(1)
F(1)	0.885(1)	0.928(1)	0.561(1)	0.16(1)
F(2)	0.995(1)	1.012(1)	0.5203(7)	0.161(7)
F(3)	1.038(2)	0.996(1)	0.660(1)	0.23(1)
F(4)	0.978(2)	1.114(1)	0.676(1)	0.20(1)
C(79)	0.790(1)	1.007(2)	0.770(2)	0.13(1)
C(80)	0.703(2)	0.986(1)	0.812(1)	0.097(9)
N(2)	0.636(2)	0.976(2)	0.844(2)	0.25(1)
C(81)	0.923(1)	0.367(1)	0.822(1)	0.147(8)
C(82)	0.8664(9)	0.321(1)	0.871(1)	0.071(6)
N(3)	0.821(1)	0.285(1)	0.908(1)	0.137(7)
C(83)	1.011(2)	0.764(2)	0.408(2)	0.18(1)
C(84)	1.033(1)	0.657(1)	0.361(1)	0.111(6)
N(4)	1.051(1)	0.584(1)	0.332(1)	0.163(6)
O(29)	0.9934(8)	1.2643(7)	0.5878(7)	0.074(5)

III.5. Catalytic properties of L3 and L4

Diphosphines **L3** and **L4** were assessed in oct-1-ene hydroformylation and hydrogenation of dimethylitaconate.

III.5.1. Hydroformylation of oct-1-ene

Oct-1-ene was first hydroformylated with **17a** in toluene at 80°C and 20 bar CO/H_2 pressure (Table 13, entry 1). The observed l/b selectivity is comparable to that of $Rh(PPh_3)_3Cl/NEt_3$. However, the activity of the catalyst is about 20 times lower than that of the reference compound, reflecting the steric encumbrance of the cavity. By performing the catalytic run in the presence of **17a** and 5 equiv. of **L3**, the TOF drops to 13 mol aldehyde · mol^{-1} Rh · h^{-1}. This probably corresponds to a higher number of coordinated phosphine ligands.

The hydroformylation experiments were also carried out by forming the catalyst *in situ*, starting from $Rh(acac)(CO)_2$. In this case the aldehyde selectivity is weaker than that obtained with the pre-formed complex (n/iso = 2.2 *vs.* 2.8). Possibly, under those conditions, the catalytically active species is not of monomeric nature, but we have no evidence for this. Similar selectivities were observed when testing the $Rh(acac)(CO)_2$/**L4** system.

Table 13. Hydroformylation of oct-1-ene

entry	Ligand/ complex	L/Rh ratio	S/Rh ratio	% conv.[f] (2h)	Aldehyde selectivity (%)	Isom. (%)	l/b ratio	TOF[h]
1[a]	**17a**[b]	-	600	90	37	33	2.8	95
2[a]	**L3/17a**	5[c]	600	11	52	0	2.0	13
3[d]	**L3**	5	640	40	92	8	2.2	130
4[d]	**L3**	10	640	16	94	6	2.1	55
5[e]	**L4**	5	600	26	22[g]	5	2.1	13

Conditions: T = 80°C; $P_{H2} = P_{CO}$ = 10 bar (initial pressure);

[a] $7{,}20\times10^{-3}$ mmol (12 mg) of **17a** in toluene (15 mL),

[b] no free ligand was used

[c] L/**17a** ratio = 4,

[d] 1×10^{-3} mmol (0.3 mg) of $[Rh(acac)(CO)_2]$ in toluene (1 mL),

[e] 6.62×10^{-3} mmol (1.7 mg) of $[Rh(acac)(CO)_2]$ in toluene (15 mL),

[f] The conversion was determined after 2 hours reaction time.

[g] Under the present conditions aldolisation reactions possibly occurred

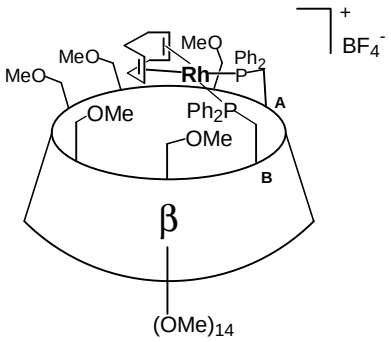
[h] mol aldehyde · mol^{-1} Rh · h^{-1}

III.5.2. Hydrogenation of dimethylitaconate

The catalysts were prepared in situ, starting from $[Rh(COD)_2]BF_4$. Both ligands turned out to be fairly active (Table 14), complete conversion being achieved after 24 h reaction time. Unfortunately, the observed ees are very low, suggesting that upon complexation the metal centre is not located close to the cavity. Indeed, molecular models clearly show that diphosphines **L3** and **L4** cannot bind a rhodium centre in a *cis* fashion. Hence, oligomers are probably formed during catalysis thus moving the metal away from the chiral cavity.

Recently, Jia *et al*. reported on the synthesis of a related chelating diphosphine ligand which is based on an A,B- difunctionalised *β*-CD derivative.[31] The cationic rhodium(I) complex **23**, obtained from this ligand, displays ees as high as 92% in the hydrogenation of itaconic acid (**24**). Very favourable interactions between the coordinated substrate and the CD cavity must account for this remarkable result which,

in stark contrast with those obtained with **L3** and **L4**, confirms the need to operate with a chelating ligand.



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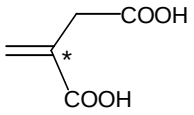

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Table 14. Hydrogenation of dimethylitaconate

entry	ligand	S/Rh ratio	% conv. (24h)[a]	ee	TOF[b]
1	**L3**	500	100	0	20
2	**L4**	500	100	<10	20

Conditions: T = 50°C; P_{H2} = 1 bar, diphosphine/Rh = 1; 2.71×10^{-2} mmol (11 mg) of $[Rh(COD)_2]BF_4$ in MeOH (15 mL),

[a]The conversion was determined after 24 hours reaction time.

[b] mol product · mol^{-1} Rh · h^{-1}

III.5.3. Experimental procedures

Hydroformylation studies were performed in a glass-lined stainless steel autoclave (100 mL) a magnetic stirring bar. The autoclave was successively charged with toluene solutions of the diphosphine ligand and $[Rh(acac)(CO)_2]$ (total volume 15 mL), then with the internal standard (decane). The autoclave was flushed several times with CO/H_2 (1:1, v/v), then pressurised to 20 bar, and finally heated to 80°C for one hour. After depressurising and cooling down to room temperature, the substrate (oct-1-ene) was added. The autoclave was again pressurised and heated to reaction temperature. Samples were taken at different reaction times and analysed by GC. Experiments using

17a or an **17a**/**L3** mixture: the complex (as well as the free ligand) was dissolved in toluene (15 mL) and transferred to the autoclave, whereupon the internal standard was added. The former was flushed several times with CO/H_2 (1:1, v/v), whereupon oct-1-ene was added. The autoclave was pressurised to 20 bar and heated to 80°C. Samples were taken at different reaction times and analysed by GC.

Hydrogenation experiments were carried out in a Schlenk tube under ambient pressure and room temperature. The diphosphine ligand was dissolved in 15 mL of MeOH. After addition of $[Rh(COD)_2]BF_4$, the solution was saturated with H_2 for 10 min., whereupon the substrate (dimethylitaconate) was added. Then the reaction mixture was heated to 50°C. Samples were taken at different reaction times and analysed by GC. Enantiomeric excess was determined by ^1H NMR using tris[3-heptafluoropropylhydroxymethylene)-(+)-camphorato] europium (III) ((+)-$Eu(hfc)_3$) as an optically active shift reagent. A $CDCl_3$ solution of the organic substrate was prepared in an NMR tube and small amounts of the shift reagent were gradually added until a clean splitting of the peaks was achieved (*ca.* 5 % of shift reagent).

III.6. References

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[49] Complex **20a** crystallised with a water molecule located outside the cavity. The latter is hydrogen-bonded to the BF_4^- ion and a MeO-3 oxygen atom. Similar noncovalent aggregates are known to withstand the conditions used for this ESI-MS experiment.

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

[51] This includes H-1, H-2, H-4, H-6, MeO-3 and MeO-6 protons. Molecular models show that coordination of MeCN molecules outside the cavity would result in strong steric interactions with some of the MeO-6 and H-6 protons.

[52] Owing to C_2 symmetry, the B and C glucose units are equivalent to the E and F units, respectively.

[53] calculated using the formula $\Delta G^* = RT_c(22.96+\ln T_c/\delta\nu)$ [J·mol $^{-1}$].

[54] The whole variable-temperature NMR study required the use of two distinct solvents, CD_2Cl_2 (-60–20°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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[60] Unlike the MeO-2 groups, the MeO-3 protons are known to point towards the cavity interior.

[61] The 2D ROESY spectrum shows NOEs between the coordinated acetonitrile protons and three H-5 (A,C,E) protons, three H-3 (B,C,D) protons as well as some MeO-3 groups. No correlation with the aromatic protons, nor with the primary OMe groups were detected.

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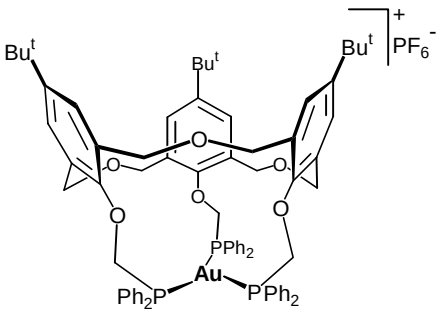
Chapter IV. A cavity-shaped, chiral triphosphine with C_3-symmetry

IV. A cavity-shaped, chiral triphosphine with C_3-symmetry

IV.1. Introduction

An interesting feature of α-cyclodextrin is that appropriate functionalisation may not only lead to C_2-symmetrical ligands, but can also give access to C_3-symmetrical ones. Triphosphines built on a macrocyclic platform and possessing a threefold axis remain very scarce. An example of such a tridentate ligand was recently described by Dieleman *et al.*, who managed to graft three phosphine moieties onto an hexahomotrioxacalix[3]arene receptor.[1] The three coordinating sidearms of this cavity were found to be able to bind simultaneously a single transition metal centre and to position it along the C_3 axis, producing for example complexes **25** and **26**. This ligand, however, is not chiral (the ligand and the complexes have C_{3v} symmetry). In the following, we describe the synthesis, coordination behaviour, and catalytic properties of a C_3-symmetrical triphosphine built on a chiral platform, namely an α-CD. Triphosphines having a threefold axis have already been reported, but none of the known examples incorporates a cavity-shaped macrocycle.[2-5]



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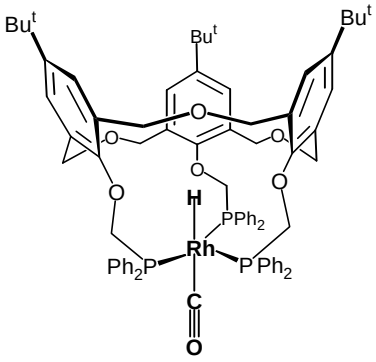

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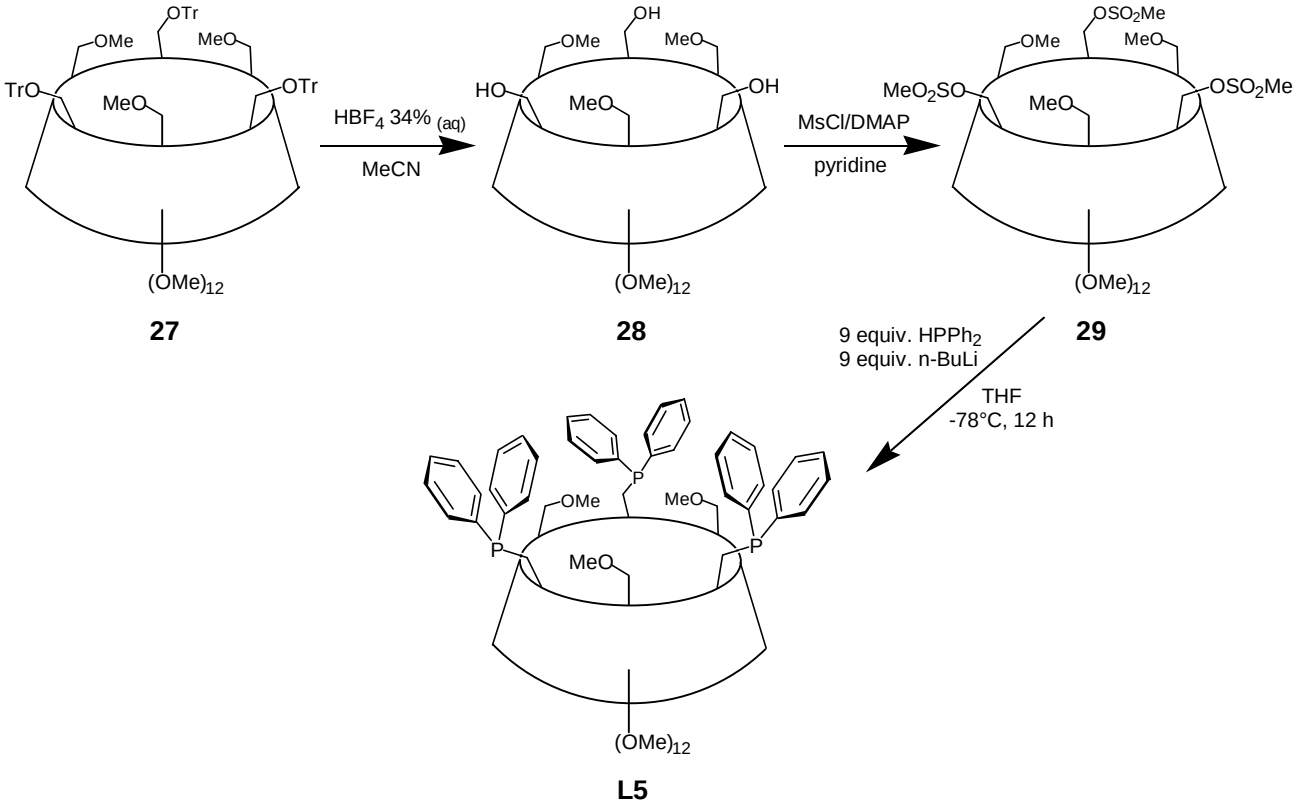
IV.2. Results and Discussion

IV.2.1. Ligand synthesis and chelating properties

Triphosphine **L5** was obtained in three steps from the known tris-tritylated CD **27**[6,7] according to Scheme 1 (Note that precursor **27** can only be obtained in *ca.* 10% overall yield from natural α-CD). First, the trityl groups were cleaved using aqueous HBF_4 (34%) to afford intermediate **28**. After mesylation and subsequent reaction with PPh_2Li in THF, **L5** was obtained in 87% yield. Triphosphine **L5** was characterised by elemental analysis and NMR (see experimental part). The ^{31}P NMR spectrum shows a singlet at -23.6 ppm. The presence of 5 methyl signals and 2 signals for the anomeric protons in the ^{1}H NMR spectrum is fully consistent with a C_3-symmetrical species (Figure 1).



27 **28** **29** **L5**

Scheme 1. Synthesis of the C_3-symmetrical triphosphine **L5**.

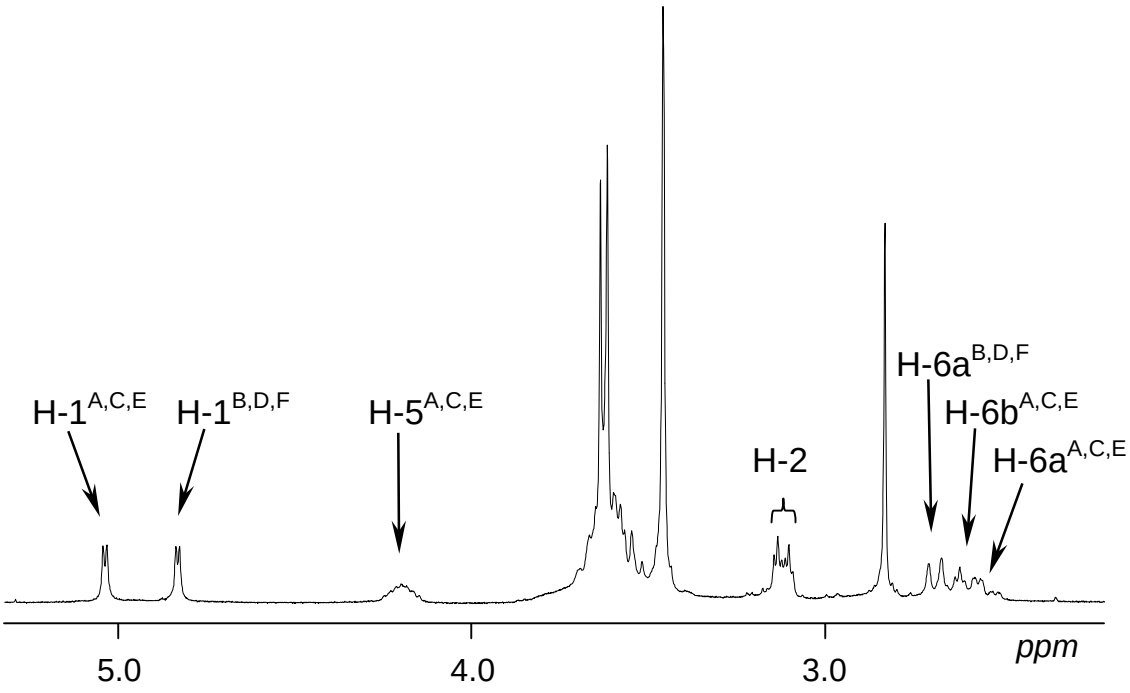
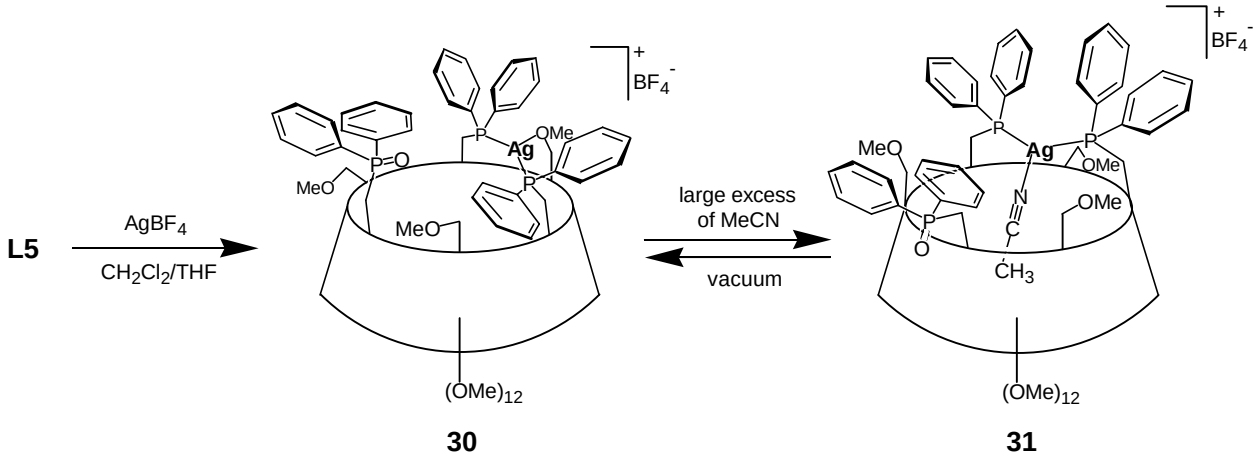


Figure 1. ^{1}H NMR spectrum of **L5** recorded at 300 MHz in $CDCl_3$

Our attempts to synthesise complexes analogous to **25** (starting from $[Au(THT)(THF)]BF_4$) or **26** (using $Rh(acac)(CO)_2$-H_2/CO) failed, the corresponding reactions leading to inseparable product mixtures. On the other hand, reaction of **L5** with $AgBF_4$ afforded a single product, namely **30** (Scheme 2). Oxidation of one of the three phosphorus atoms was confirmed by FAB mass spectrometry. The ^{31}P NMR spectrum (Figure 2) displays a phosphoryl signal at 28.9 ppm (singlet) along with an ABX system (X = ^{107}Ag and ^{109}Ag; δ_A = 4.8, δ_B = 9.4 ppm, $^{107}J_{Ag,A}$ = 507 Hz, $^{109}J_{Ag,A}$ = 585 Hz and $^{107}J_{Ag,B}$ = 514 Hz, $^{109}J_{Ag,B}$ = 593 Hz, $^{2}J_{A,B}$ = 148 Hz) corresponding to two coordinated P(III) centres. The formation of complex **30** is reproducible, but we do not know at which stage oxidation occurred. The present results suggest that a structure in which the silver atom is dicoordinate and one phosphorus unit remains unbonded is less strained than a silver complex in which all three phosphorus atoms are metal-bonded. This feature would explain the easy oxidation of one of the three phosphine ligands during the reaction with Ag^+.

In order to verify whether the phosphoryl group is coordinated, we added a large excess of CD_3CN (*ca.* 60 equiv.) to a solution of **30** in $CDCl_3$. As with the previously described related complex **21b** (chapter III), coordination of an acetonitrile molecule



Scheme 2. Synthesis of the Ag(I)-complex **30** and addition of acetonitrile

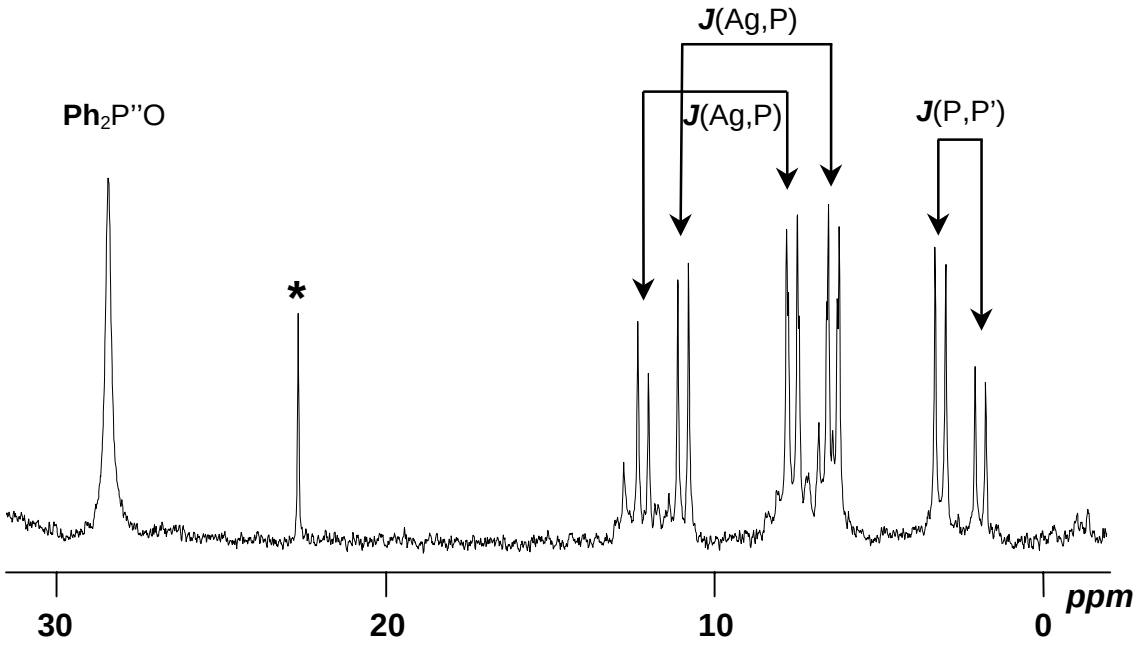


Figure 2. ^{31}P NMR spectrum of **30** recorded at 121.5 MHz in $CDCl_3$. The peak marked with an asterisk corresponds to residual $Ph_2P(O)H$

occurred, producing complex **31**. The ^{31}P NMR spectrum exhibits a sharp ABX system (X = ^{107}Ag and ^{109}Ag; δ_A = 4.2, δ_B = 7.3 ppm, $^{107}J_{Ag,A}$ = 482 Hz, $^{109}J_{Ag,A}$ = 557 Hz and $^{107}J_{Ag,B}$ = 480 Hz, $^{109}J_{Ag,B}$ = 554 Hz, $^{2}J_{A,B}$ = 138 Hz). Interestingly, the phosphoryl signal did not undergo any significant shift upon addition of acetonitrile (δ = 28.3 *vs.* 28.9 ppm in **30**), which is in keeping with an uncoordinated phosphoryl unit in **30**. As in complex **21b**, coordination of the OMe^B group may explain the large excess of acetonitrile required to produce complex **31**.

IV.2.2. Catalytic properties of L5

IV.2.2.1. Hydroformylation of oct-1-ene

Ligand **L5** was assessed in the hydroformylation of oct-1-ene (T = 80°C; P_{H2} = P_{CO} = 10 bar; 6.62×10^{-3} mmol (1.7 mg) of [Rh(acac)$(CO)_2$] in toluene (15 mL); S/Rh = 600). The aldehyde production turned out to be relatively low (TOF = 10 mol aldehyde · mol^{-1} Rh · h^{-1}), like that of ligand **L4** (see chapter III), while the selectivity (l/b = 2.0) lies in the range of the selectivities obtained with the previously described ligands (chapters II and III). The low activity is likely to arise from a too crowded metal centre.

IV.3. Conclusion

In this study, we have described the synthesis of a new C_3-symmetrical triphosphine, in fact the first one built on a chiral molecular cavity. Our preliminary complexation studies suggest that the P···P separations in **L5** are too large to allow simultaneous binding of the three P(III) centres about a single metal atom. Further work is in progress, aiming at lengthening the phosphine arms. We are also currently trying to synthesise a non-oxidised version of complex **30**. It may be anticipated that in such a species the silver atom will jump from one (*P*,*P*) chelating unit to the neighbouring one, thus moving along the macrocyclic core.

IV.4. Experimental section

IV.4.1. General procedures

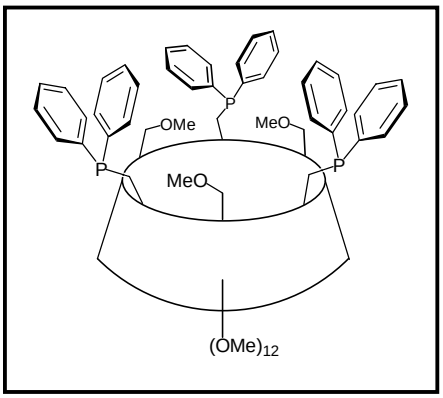
All commercial reagents were used as supplied. All manipulations involving phosphines were performed in Schlenk-type flasks under argon. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under argon over molecular sieves (4 Å).

Routine ^{1}H, $^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectra were recorded with an FT Avance 300 Bruker instrument at 25°C (^{1}H: 300.1 MHz, ^{31}P: 121.5 MHz, ^{13}C: 75.5 MHz). ^{1}H NMR spectral data were referenced to residual protiated solvents (δ 7.26 for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuterated solvents (δ 77.0 for $CDCl_3$), and the ^{31}P NMR data are given relative to external H_3PO_4. The mass spectrum was recorded on a ZAB HF VG Analytical spectrometer using *m*-nitrobenzyl alcohol as matrix. 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. Diphenylphosphine was synthesised according to literature procedure.

The hydroformylation experiments were performed in a stainless steel autoclave (100 mL) containing a glass beaker and a magnetic stirring bar. The beaker was charged with a toluene solution containing both the triphosphine ligand and $[Rh(CO)_2(acac)]$ (total volume 15 mL), then with the internal standard (decane). The autoclave was flushed several times with CO/H_2 (1:1, v/v), then pressurised to 20 bar, and finally heated to 80°C for one hour. After depressurising and cooling the autoclave down to room temperature, the substrate (oct-1-ene) was added, and the mixture was again pressurised and heated to reaction temperature. Samples were taken at different reaction times and analysed by GC.

IV.4.2. Synthesis

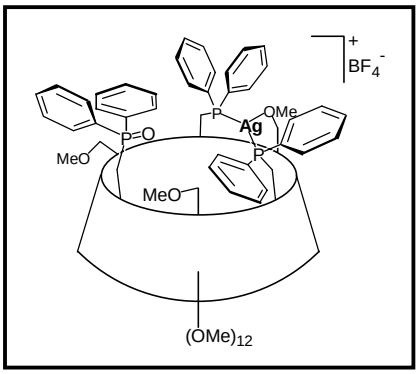
$6^A,6^C,6^E$-tris-(Diphenylphosphinyl)-$6^A,6^C,6^E$-trideoxy-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^D,6^F$-pentadeca-*O*-methyl-$\alpha$-cyclodextrin (L5)



A solution of *n*-BuLi in hexane (1.6 M, 2.0 mL, 3.18 mmol) was added, at –78°C, to a solution of Ph_2PH (0.591 g, 3.18 mmol) in THF (15 mL). The solution was allowed to warm to room temperature and stirred for additional 10 min., whereupon it was cooled down again to –78°C, prior to the addition of powdered **29** (0.500 g, 0.353 mmol). 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 in toluene (15 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, which allows removal of residual Ph_2PH. This operation was repeated 4 times to afford **L4** as a white powder (0.510 g, 87 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.23; Mp 102-105°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (assignment by COSY) = 2.55 (ddd, $^2J_{H\text{-}6b,H\text{-}6a}$ = 14.6 Hz, $^3J_{H\text{-}5,H\text{-}6a}$ = 6.0 Hz, $^2J_{P,H\text{-}6a}$ = 2.0 Hz, 3H; H-6a^{A,C,E}), 2.65 (dt, $^2J_{H\text{-}6b,H\text{-}6a}$ = 14.6 Hz, $^3J_{H\text{-}5,H\text{-}6a}$ = 4.0 Hz, $^2J_{P,H\text{-}6a}$ = 4.0 Hz, 3H; H-6b^{A,C,E}), 2.69 and 3.62 (br AB, $^2J_{AB}$ = 10.8 Hz, 6H; H-6^{B,D,F}), 2.83 (s, 9H; CH_3O-6), 3.12 (dd, $^3J_{H\text{-}3,H\text{-}2}$ = 9.4 Hz, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 3H; H-2^{A,C,E}), 3.14 (dd, $^3J_{H\text{-}3,H\text{-}2}$ = 9.5 Hz, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 3H; H-2^{B,D,F}), 3.46 (s, 18H; CH_3O-2), 3.54 (dd, 3H; H-3^{B,D,F}), 3.57–3.64 (2 overlapping dd, 6H; H-3^{A,C,E}, H-4^{A,C,E}), 3.62 (s, 9H; CH_3O-3), 3.62 (dd, 3H; H-5^{B,D,F}), 3.64 (s, 9H; CH_3O-3), 3.66 (dd, 3H; H-4^{B,D,F}), 4.20 (m, 3H; H-5^{A,C,E}), 4.84 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 2.9 Hz, 3H; H-1^{B,D,F}), 5.04 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.3

Hz, 3H; H-1^{A,C,E}), 7.22-7.28 (18H; H$_{meta}$, H$_{para}$), 7.37-7.42 (12H, H$_{ortho}$); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 31.60 (d, $J_{C,P}$ = 14.9 Hz; C-6 ^{A,C,E}), 57.73 and 57.91 (CH_3O-2), 58.48 (CH_3O-6), 61.60 and 61.83 (CH_3O-3), 69.94 (d, $J_{C,P}$ = 4.3 Hz; C-6^{B,D,F}), 70.74 (d, $^{3}J_{C,P}$ = 11.1 Hz; C-4^{A,C,E}, tent. assignment), 71.31 (C-5^{B,D,F}), 80.98, 81.08, 81.39, 81.97 and 82.47 (C-2, C-3, C-4^{B,D,F}), 69.94 (d, $^{2}J_{C,P}$ = 10.5 Hz; C-5^{A,C,E}), 99.23 and 100.28 (C-1), 128.17 (d, $^{3}J_{C,P}$ = 6.8 Hz; C$_{meta}$), 128.21 (d, $^{3}J_{C,P}$ = 6.8 Hz; C$_{meta}$), 128.12 (s, C$_{para}$), 128.36 (s; C$_{para}$), 132.88 (d, $^{2}J_{C,P}$ = 18.6 Hz; C$_{ortho}$), 133.16 (d, $^{2}J_{C,P}$ = 19.8 Hz; C$_{ortho}$), 139.86 (d, $J_{C,P}$ = 11.2 Hz; C$_{ipso}$), 140.47 (d, $J_{C,P}$ = 13.0 Hz; C$_{ipso}$); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = -23.6 (s); elemental analysis (%): calcd for $C_{87}H_{117}O_{27}P_3 \bullet 0.1\ CHCl_3$ (1687.78 + 11.92): C 61.55, H 6.94; found: C 61.34, H 6.77.

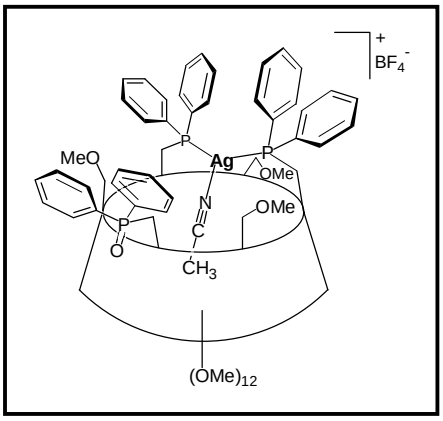
{6^{A},6^{C}-bis-(Diphenylphosphinyl)-6^{E}-(diphenyl)phosphinoyl-6^{A},6^{C},6^{E}-trideoxy-2^{A}, 2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{F}-pentadeca-*O*-methyl-α-cyclodextrin}silver(I) tetrafluoroborate (30)



A solution of $AgBF_4$ (0.010 g, 0.51 mmol) in THF/CH_2Cl_2 (50 mL, 1 : 4, v/v) was added to a solution of **L5** (0.090 g, 0.53 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 **30** as a white precipitate which was filtered off (0.080 g, 80 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.18; Mp 185°C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08 (s, 3H; CH_3O-6), 2.55 (d, ^{3}J = 2.6 Hz, $^{2}J_{H\text{-}6b\text{-}H\text{-}6a}$ = 9.6 Hz, 1H; H-6a, tent. assignment), 2.79 (s, 3H; CH_3O-6), 3.15 (s, 3H; CH_3O-6), 3.36 (s, 3H; OCH_3), 3.41 (s, 3H; OCH_3), 3.45 (s, 3H; OCH_3), 3.46 (s, 6H; OCH_3), 3.47 (s, 3H; OCH_3), 3.59 (s, 3H; OCH_3), 3.60 (s, 6H; OCH_3), 3.64 (s, 3H; OCH_3), 3.65 (s, 3H; OCH_3), 3.74 (s, 3H; OCH_3), 2.65-4.97 (35H; H-2, H-3, H-4, H-5, H-6a, H-6b), 4.56 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.8

Hz, 1H; H-1), 4.68 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.4 Hz, 1H; H-1), 4.82 (br d, 1H; H-1), 4.95 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.2 Hz, 1H; H-1), 5.10 (2d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.4 Hz, 2H; H-1), 6.89 (br t, J = 7.4 Hz, 2H; arom. H), 7.18-7.74 (24H; arom. H), 7.94 (br m, J = 7.4, 2H; H_{ortho}), 8.18 (br m, J = 7.8, 2H; H_{ortho}); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ (the phosphoryl function has been assigned to glucose unit E) = 30.60 (d, $J_{C,P}$ = 17.4 Hz; C-$6^{A \text{ or } C}$), 31.39 (d, $J_{C,P}$ = 70.7 Hz; C-6^{E}), 32.19 (d, $J_{C,P}$ = 19.9 Hz; C-$6^{C \text{ or } A}$), 57.31, 57.60 and 57.75 (CH_3O-6), 58.09, 58.16, 58.26, 58.33, 58.77 and 58.94 (CH_3O-2), 60.97, 61.19, 61.48, 62.03, 62.08 and 62.35 (CH_3O-3), 67.60 (d, $J_{C,P}$ = 8.1 Hz; C-5^{E}, tent. assignment), 69.54, 70.19 and 70.51 (C-$6^{B,D,F}$), 70.13, 70.26 and 71.18 (C-$5^{B,D,F}$), 79.61, 79.87, 79.98, 80.71 [×2], 80.76 [×2], 80.86 [×3], 81.37, 81.93, 82.32, 82.42, 82.65, 83.00, 83.08 and 85.10 (C-2, C-3, C-4), 89.61 (d, $J_{C,P}$ = 9.9 Hz; C-$5^{A \text{ or } C}$), 91.09 (d, $J_{C,P}$ = 13.7 Hz; C-$5^{C \text{ or } A}$), 98.17, 98.61, 99.07, 99.74, 101.07 and 101.27 (C-1), 128.05-135.13 (arom. C); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 4.8 and 9.4 (ABX, $^{107}J_{Ag,P}$ = 507 Hz, $^{109}J_{Ag,P}$ = 585 Hz and $^{107}J_{Ag,P'}$ = 514 Hz, $^{109}J_{Ag,P'}$ = 593 Hz, $^{2}J_{P,P'}$ = 148 Hz, P and P'), 28.9 (br s, P(O)); elemental analysis (%): calcd for $C_{87}H_{117}AgBF_4O_{28}P_3 \bullet CH_2Cl_2$ (1898.44 + 84.93): C 53.15, H 5.99; found: C 53.29, H 6.05; MS (FAB): *m/z* (%): 1795.6 (30) [M-BF_4-O]$^{+}$, 1811.6 (72) [M-BF_4]$^{+}$, 1827.6 (42) [M-BF_4+O]$^{+}$.

Acetonitrile-{6^{A},6^{C}-bis-(Diphenylphosphinyl)-6^{E}-(diphenyl)phosphinoyl-6^{A},6^{C},6^{E}-trideoxy-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^{F}-pentadeca-*O*-methyl-α-cyclodextrin}silver(I) tetrafluoroborate (31)



Addition of a large excess of MeCN (ca. 60 equiv.) to a solution of **30** (see below) in $CDCl_3$ afforded **31** quantitatively. Solvent evaporation regenerated **30**. ^{1}H NMR (300

MHz, $CDCl_3/CD_3CN$): δ = 2.19 (s, 3H; CH_3O-6), 2.79 (s, 3H; CH_3O-6), 3.32 (s, 3H; CH_3O-6), 3.39 (s, 3H; OCH_3), 3.41 (s, 6H; OCH_3), 3.43 (s, 3H; OCH_3), 3.44 (s, 6H; OCH_3), 3.50 (s, 3H; OCH_3), 3.52 (s, 6H; OCH_3), 3.55 (s, 3H; OCH_3), 3.56 (s, 3H; OCH_3), 3.58 (s, 3H; OCH_3), 2.28-4.60 (36H; H-2, H-3, H-4, H-5, H-6), 4.60 (br d, $^3J_{H\text{-}2,H\text{-}1}$ = 2.0 Hz, 1H; H-1), 4.62 (br d, $^3J_{H\text{-}2,H\text{-}1}$ = 2.6 Hz, 1H; H-1), 4.66 (br d, $^3J_{H\text{-}2,H\text{-}1}$ = 2.1 Hz; H-1), 4.99 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.0 Hz, 1H; H-1), 5.07 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 2.8 Hz, 1H; H-1), 5.19 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.0 Hz, 1H; H-1), 7.13 (br t, J = 7.2 Hz, 2H; arom. H), 7.25-7.68 (24H; arom. H), 7.73 (br m, J = 7.9, 2H; H_{ortho}), 7.83 (br m, J = 7.2, 2H; H_{ortho}); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ (the phosphoryl function has been assigned to glucose unit E) = 29.58 (d, $J_{C,P}$ = 16.8 Hz; C-$6^{A \text{ or } C}$), 30.12 (d, $J_{C,P}$ = 64.5 Hz; C-6^{E}), 30.58 (d, $J_{C,P}$ = 16.8 Hz; C-$6^{C \text{ or } A}$), 57.18, 57.77 and 57.83 (CH_3O-6), 57.83, 58.12, 58.17, 58.26, 58.70 and 59.01 (CH_3O-2), 60.00, 60.18, 60.80 and 61.30 [×3] (CH_3O-3), 68.65 (d, $J_{C,P}$ = 6.8 Hz; C-5^{E}, tent. assignment), 69.44, 69.96 and 70.15 (C-$6^{B,D,F}$), 71.17 [×2] and 71.94 (C-$5^{B,D,F}$), 79.38, 80.07, 80.21, 80.33 [×3], 80.46, 80.84 [×6], 81.05, 81.46, 81.61, 82.04 and 82.77 (C-2, C-3, C-4), 88.54 (d, $J_{C,P}$ = 11.8 Hz; C-$5^{A \text{ or } C}$), 88.98 (d, $J_{C,P}$ = 11.8 Hz; C-$5^{C \text{ or } A}$), 97.29, 97.72, 98.71 [×2], 100.28 and 100.38 (C-1), 128.16-134.05 (arom. C); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 4.2 and 7.3 (ABX, $^{107}J_{Ag,P}$ = 482 Hz, $^{109}J_{Ag,P}$ = 557 Hz and $^{107}J_{Ag,P'}$ = 480 Hz, $^{109}J_{Ag,P'}$ = 554 Hz, $^2J_{P,P'}$ = 138 Hz, P and P'), 28.3 (s, P(O)).

IV.5. References

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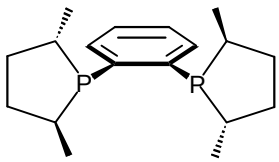
Chapter V. Phosphorus-bridged CDs as new optically active cyclic phosphines

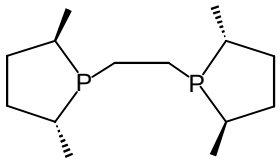
V. Phosphorus-bridged CDs as new optically active cyclic phosphines

V.1. Introduction

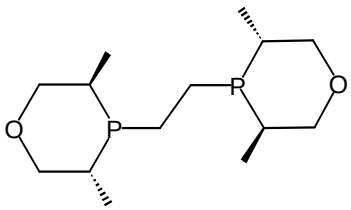
Recent efforts in homogeneous asymmetric catalysis have focussed on the design and synthesis of chiral phosphines in which the phosphorus centres are incorporated in a rigid cycle. The most significant progress in this area has been achieved by Burk *et al.* with the bisphospholane-based (5-membered rings) Du-PHOS and BPE ligands.[1-3] With ees higher than 99% when used in the economically relevant rhodium-catalysed hydrogenation of prochiral enamides, these ligands opened a new way to the production of enantiomerically pure unnatural amino acids.[2,4-6] Recently, Helmchen *et al.* described the synthesis of mono- and bis(oxaphosphinane)-based ligands (6-membered rings). Their use in the hydrogenation of prochiral substrates such as itaconic acid or enamides again produced high enantioselectivities (up to 97.5% ee).[7] Marinetti *et al.* have reported on the efficient application of monodentate menthyl-substituted



(*S*,*S*)-Me-DuPHOS

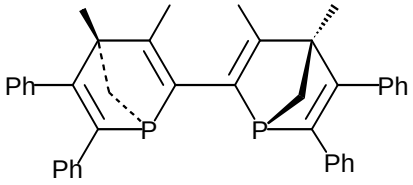


(*R*,*R*)-Me-BPE

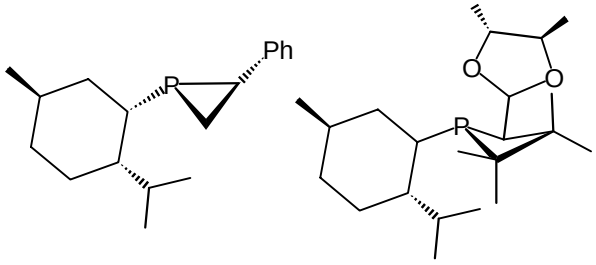


(*R*,*R*)-bis(oxaphosphinano)ethane

phosphetanes (4-membered rings)[8] in palladium-catalysed allylic substitution[9] and hydrosilylation reactions.[10] The synthesis of the sterically strained phosphiranes (3-membered rings) has also been reported.[11] A diphosphine in which each phosphorus atom is part of two cycles is Mathey's BIPNOR.[12,13] A challenge so far not met is the capping of a chiral cavity with a "PPh" unit. It is anticipated that such a structure will bring a P-coordinated metal centre close to the cavity and thus favour entrapment of coordinated substrates inside the receptor. In this chapter, we present the synthesis

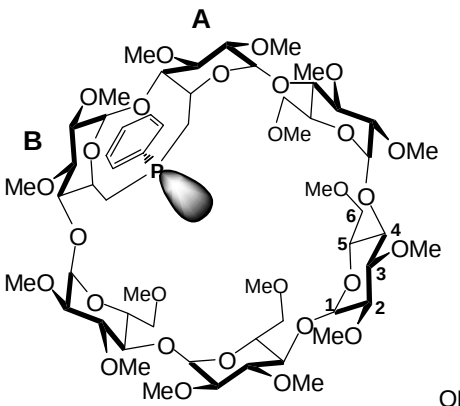


(*R*,*R*)-(+)-BIPNOR

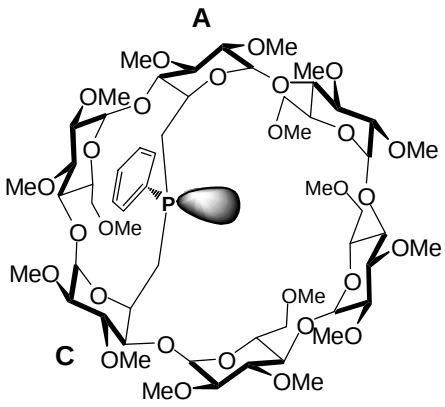


menthyl-substituted phosphirane (left) and phosphetane (right) ligands

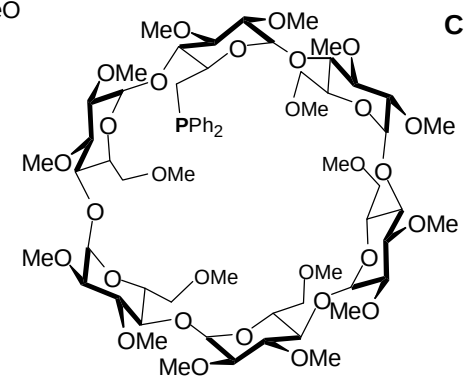
as well as the coordination properties of the two first CD-based cyclic phosphines, whose chiral phosphorus atoms are part of 9- and 14-membered rings, respectively. In order to compare the reactivity of the new ligands with that of a non-cyclic and flexible analogue, the coordination properties of the monophosphine **L8** were also studied. In the following, the letters "**a**" and "**b**" refer to A,B- and A,C-substituted derivatives, respectively.



L6



L7

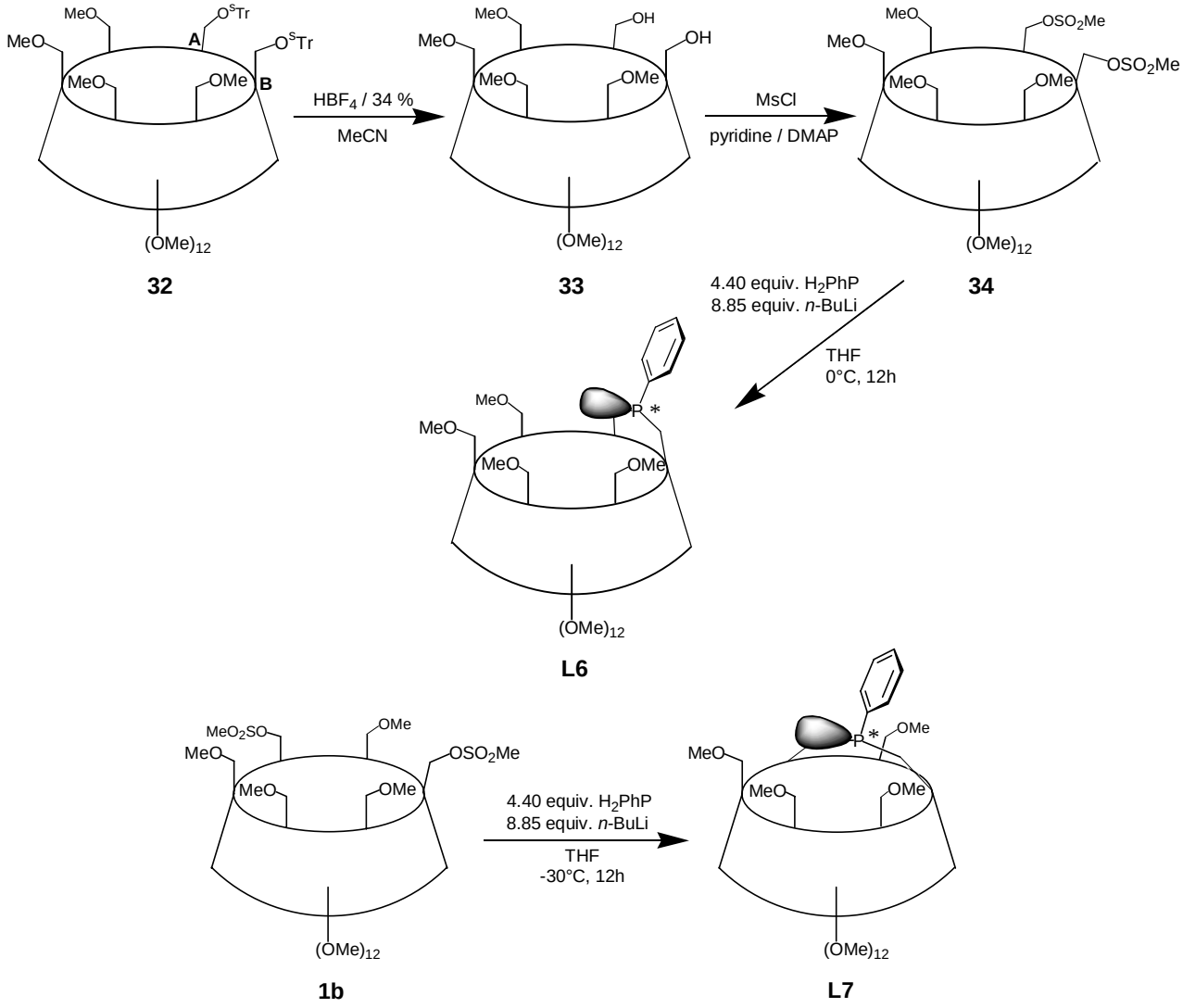


L8

V.2. Results and Discussion

V.2.1. Synthesis and coordination properties of two cyclic monophosphines derived from α-CD

Ligand **L6** was synthesised from the previously described tris(*p-tert*-butylphenyl)methyl AB-disubstituted CD derivative **32**, whose protecting groups were cleaved upon treatment with HBF_4 in MeCN, affording diol **33** (Scheme 1). Reaction of the latter with MsCl led to the formation of dimesylate **34**. Double nucleophilic substitution with the lithiated dianion $PhPLi_2$ at 0°C gave **L6**. This reaction proceeds



Scheme 1. Synthesis of two cyclic phosphines based on an α-CD-macrocycle

with a remarkable yield (*ca.* 65 %) and is highly stereoselective, as a single diastereoisomer is formed. Clearly, the pre-organisation of the functionalised C-6 positions of units A and B favour cyclisation over oligomerisation, even in the absence of high-dilution conditions. The resulting ligand **L6** is characterised by a singlet at -16.2 ppm in ^{31}P NMR spectroscopy. The ^{1}H NMR spectrum shows no dispersion of the anomeric protons ($\Delta\delta$ = 0.08 ppm), which suggests that the CD macrocycle underwent no significant distortion upon capping (Figure 1). Cyclisation did not proceed as selectively when the two leaving groups were positioned further away from each other as in the AC-substituted dimesylate **1b**, the reaction leading in this case to significant amounts of side products. Nevertheless, a reasonable yield of the capping ligand **L7** could be obtained (*ca.* 60 %), provided the reaction was carried out at -30°C. The ^{31}P NMR spectrum of **L7** displays a singlet at -21.1 ppm. Unlike **L6**, the ^{1}H NMR spectrum of **L7** reveals an unprecedented dispersion of the anomeric protons ($\Delta\delta_{max}$ = 1.09 ppm), likely caused by the deformation of the macrocyclic structure (Figure 1), which is brought about by the presence of the very short PPh cap. This cavity deformation is consistent with the fact that the AC-disubstituted dimesylate is more prone to form oligomeric material than its AB analogue.

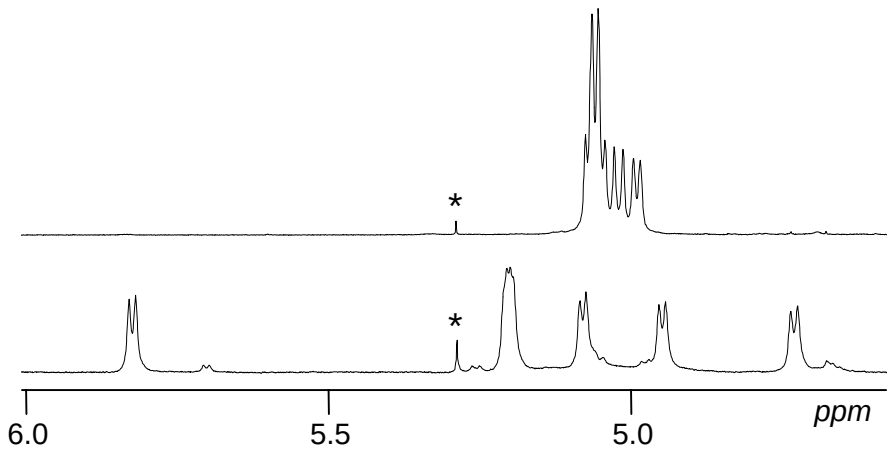
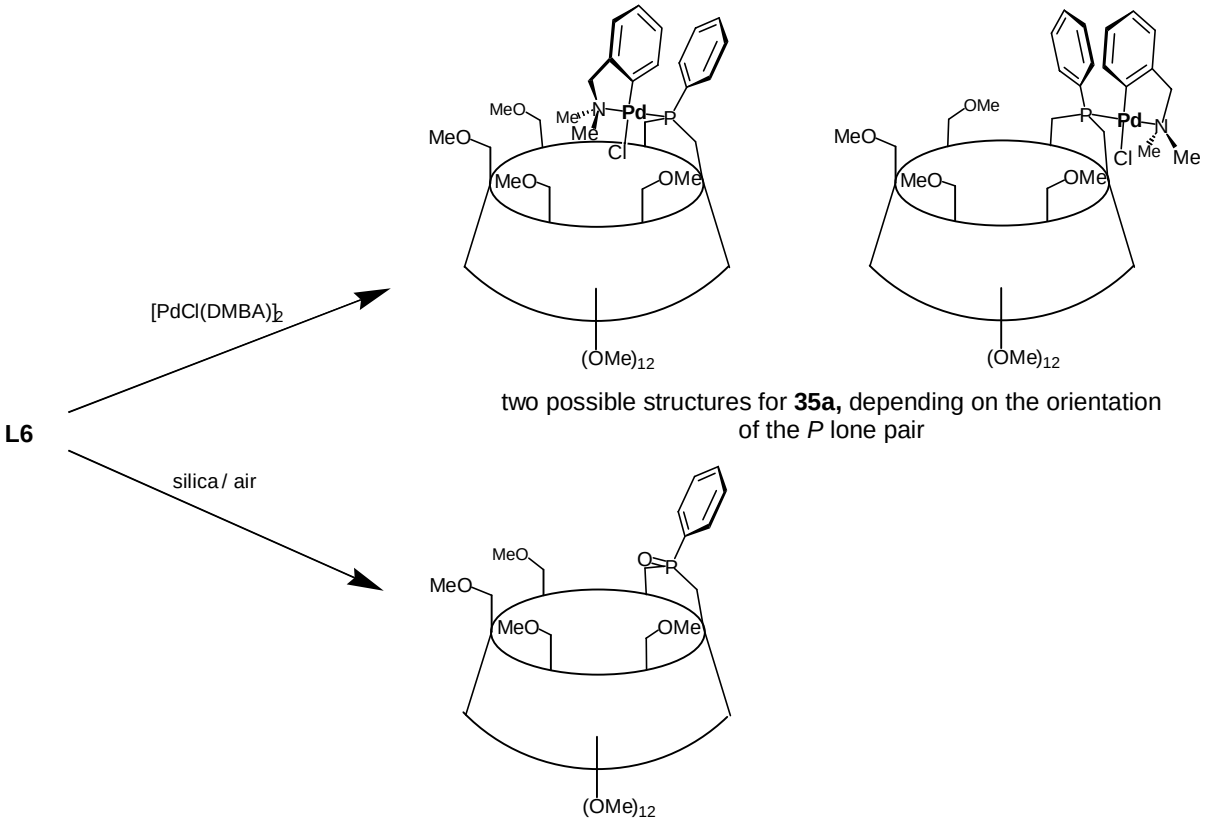


Figure 1. Anomeric regions of the ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **L6** (top) and **L7** (bottom). The asterisk denotes residual CH_2Cl_2.

An answer to the question whether in each ligand the phosphorus lone pair points towards the CD axis or away from it was provided by complexes **35a** and **35b**, which were obtained when respectively **L6** and **L7** were reacted with 0.5 equivalent



two possible structures for **35a,** depending on the orientation of the *P* lone pair

36a

of [(*o*-$C_6H_4CH_2NMe_2$)PdCl]$_2$. The ^{31}P NMR spectra of **35a** and **35b** display a singlet at 17.4 and 7.8 ppm, respectively. For both compounds the expected structure was confirmed by the presence of intense peaks in their FAB-MS spectra corresponding to the $[M\text{-}Cl]^+$ ions (*m/z* 1510.8 for **35a** and 1510.5 for **35b**). Phosphorus coordination was inferred from the presence of ^4J(P-NCH) coupling constants in the ^{1}H NMR spectra (^4J(P-NCH) = 1.4 and 2.6 Hz in **35a** and <1.0 Hz and 1.7 Hz in **35b**, Figures 2 and 4). The 2D ROESY spectrum of **35a** revealed a spatial proximity between the NMe_2 groups and three primary methoxy groups of the CD macrocycle as well as the H-6^D, H-6^E and H-6^F protons (Figure 3). Conversely, no NOEs were detected between CD protons and aromatic benzyl protons. These findings indicate that the C,N metallacycle group lies above the cavity and its plane parallels more or less the CD axis. Furthermore, the fact that the H-5^A and H-5^B protons in **35a** are significantly low-field shifted relative to their counterparts in free **L6** ($\Delta\delta$ = 0.65 and >0.5 ppm, respectively, Figure 2) is consistent with the encapsulation of the chloride ligand (see chapter III). All these observations are

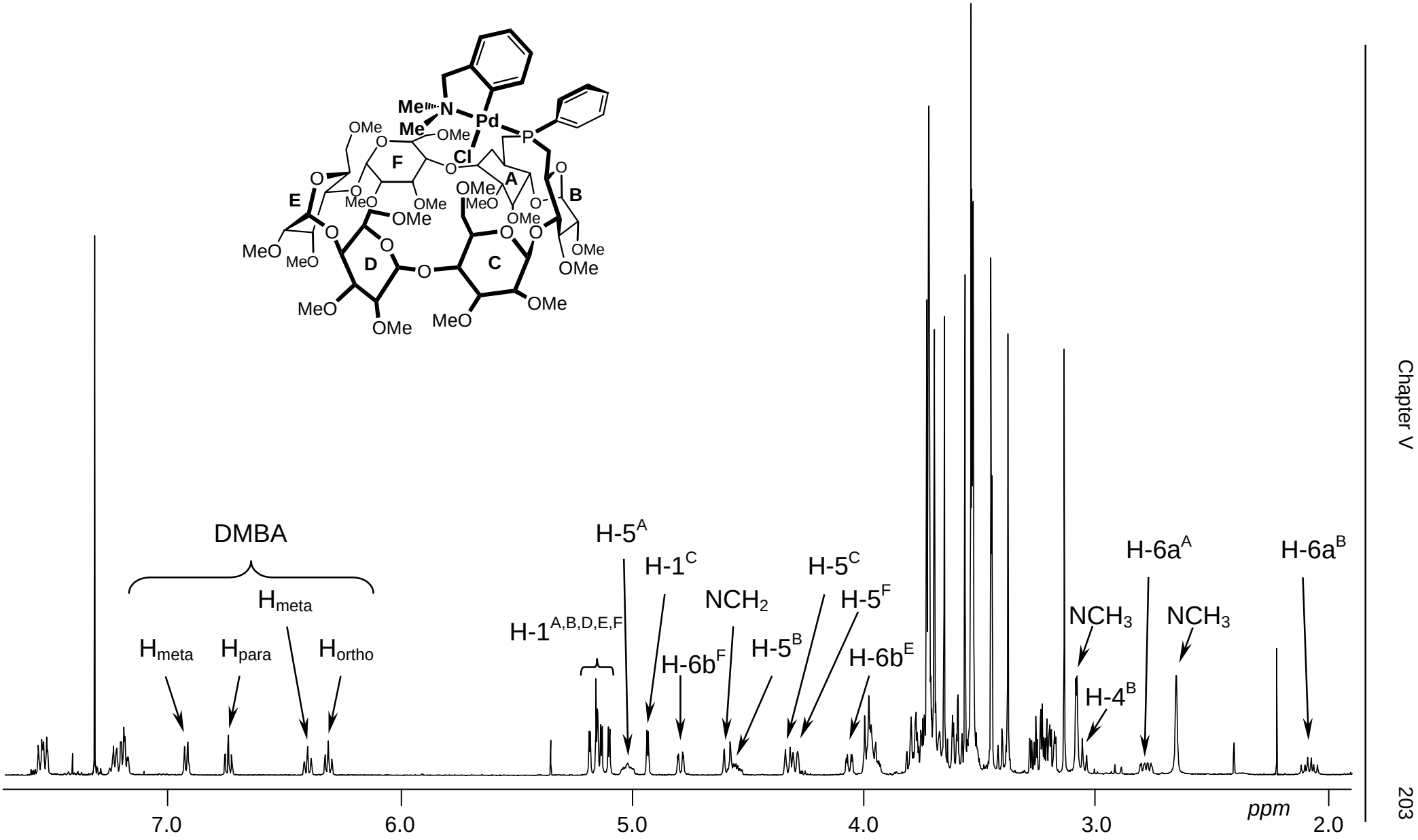


Figure 2. ^{1}H NMR spectrum of **35a** recorded at 500 MHz in $CDCl_3$, showing the dispersion of several of the H-5 and H-6 protons

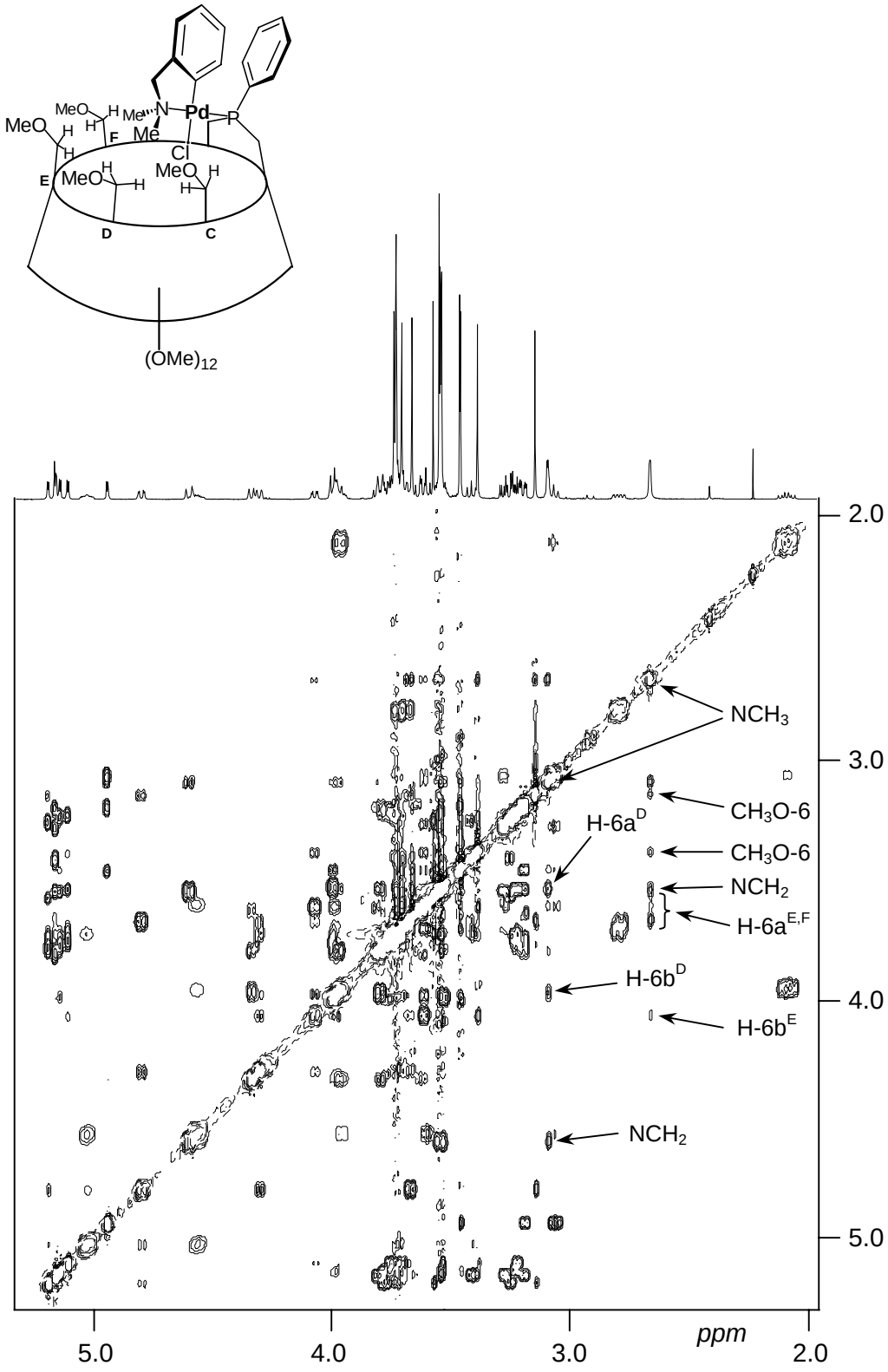
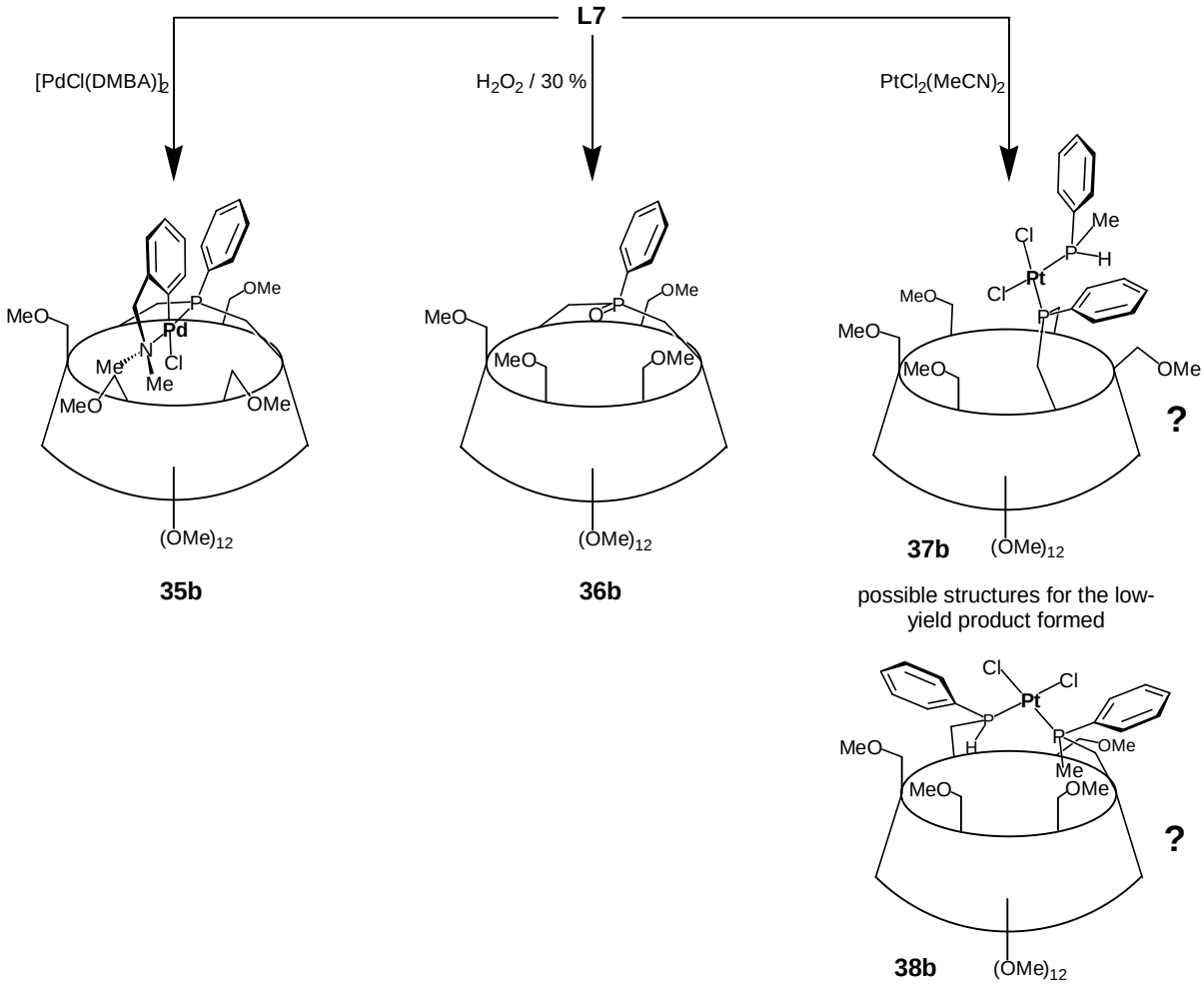


Figure 3. Portion of the 2D ROESY spectrum of **35a** recorded at 500 MHz in $CDCl_3$

in agreement with a phosphorus lone pair in **L6** pointing towards the CD axis. Similarly, the 2D ROESY spectrum for **35b** contains cross-peaks arising from NOEs between the NMe_2 groups and two primary methoxy groups of the CD platform as well as the H-6^D, H-6^E and H-6^F protons (Figure 5). The absence of any significant H-5 proton deshielding upon complexation suggests that in this case the chloride lies above the cavity, probably as a result of the considerable narrowing of the cavity brought about by the very short bridging PPh fragment.



The proximity of the CD torus is likely to provide the phosphorus atom of these dialkylphosphines with a remarkable degree of protection against oxidation. Indeed, leaving chloroform solutions of both compounds in the presence of air for a week produced only small amounts of phosphine oxides (*ca.* 10 %). Complete oxidation of

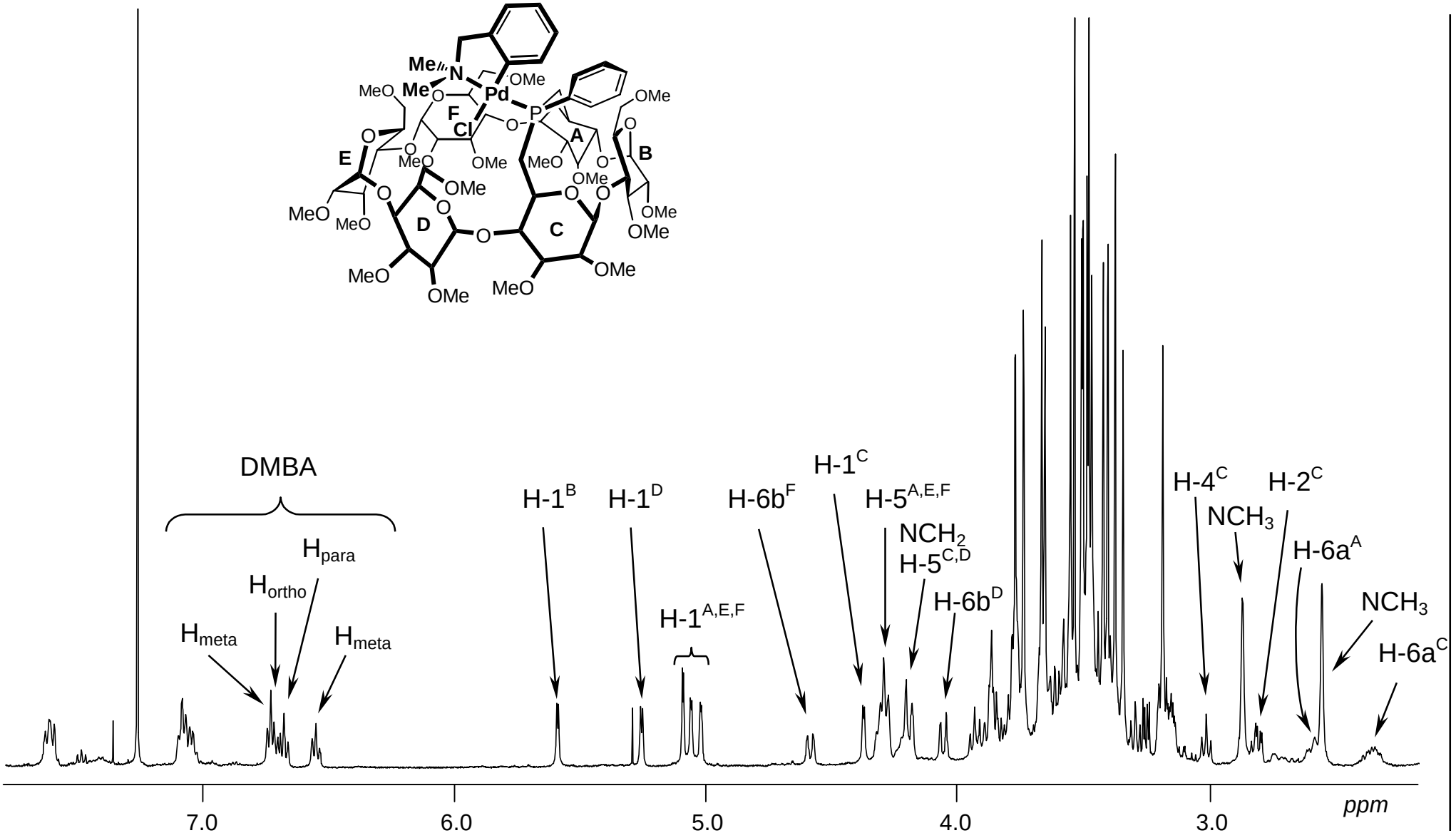


Figure 4. ^{1}H NMR spectrum of **35b** recorded at 500 MHz in $CDCl_3$, showing the extensive dispersion of the anomeric protons as a result of strong interglycosidic torsion and possibly deformation of the chair conformation of some glucose units

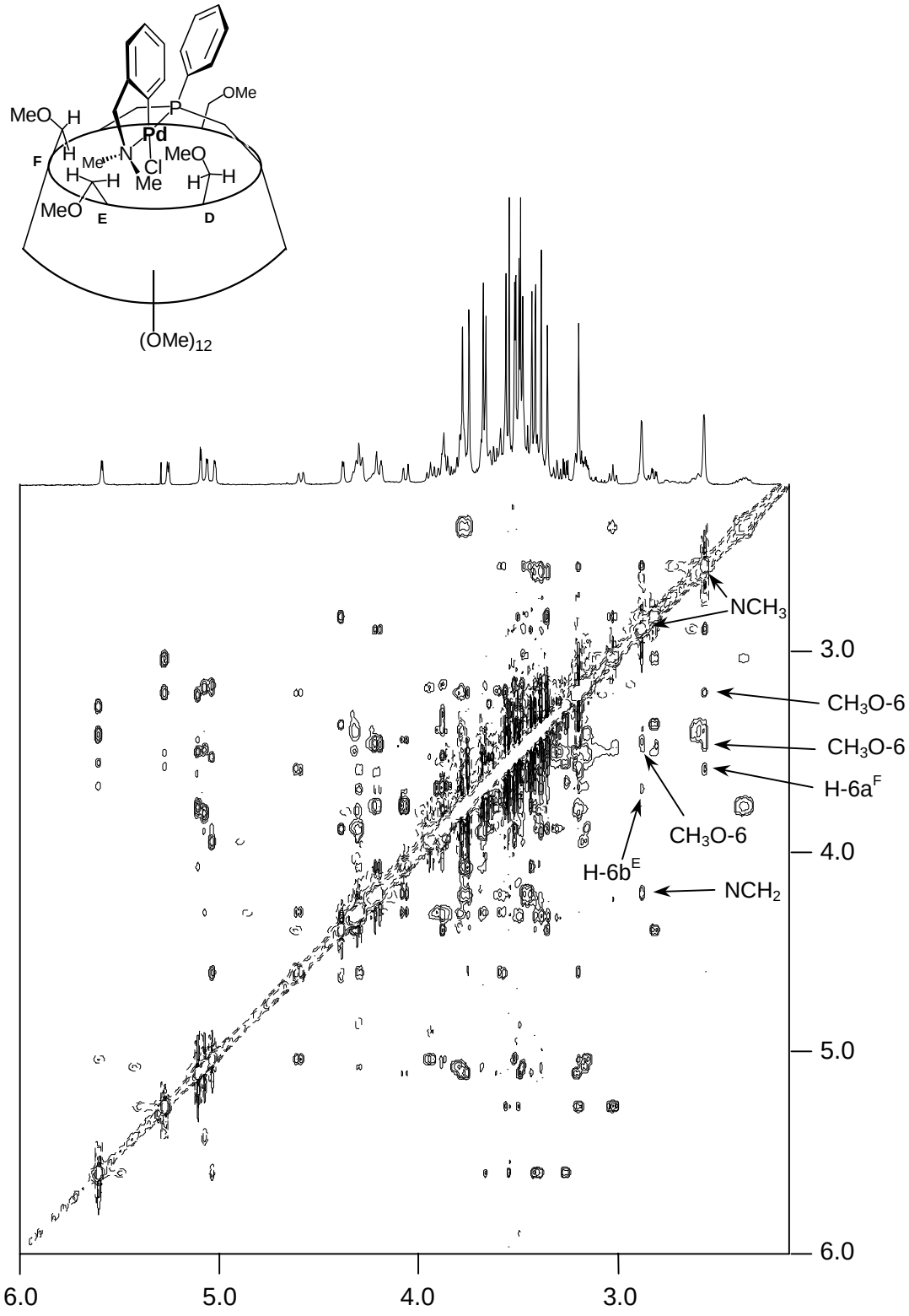


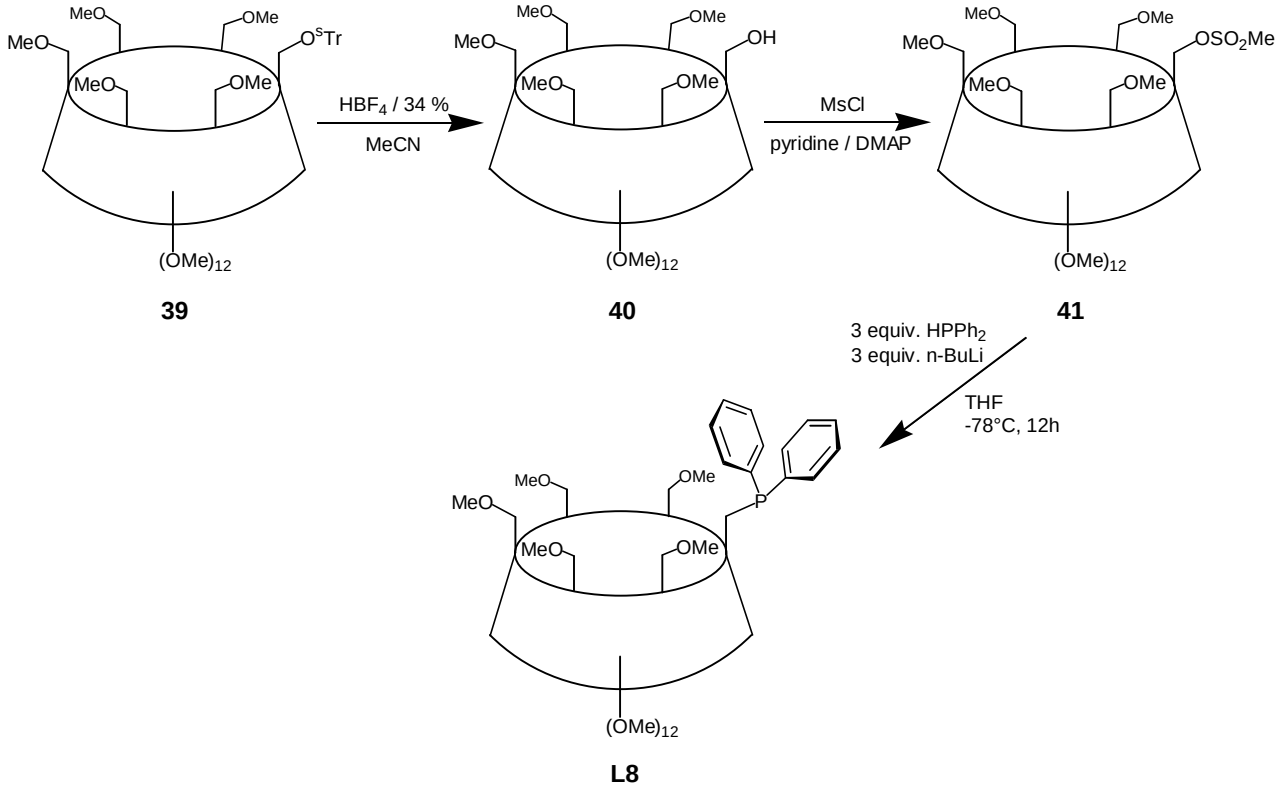
Figure 5. Portion of the 2D ROESY spectrum of **35b** recorded at 500 MHz in $CDCl_3$

L6, which affords **36a** (δ = 34.6 ppm in ^{31}P NMR), required treatment of a CH_2Cl_2 solution of the phosphine with SiO_2. Oxidation of **L7** was only possible with H_2O_2, resulting in the phosphine oxide **36b** (δ = 35.3 ppm in ^{31}P NMR).

In order to test the ability of a transition metal centre to bind two of these bulky phosphines, we reacted 2 equivalent of **L7** with 1 equivalent of $[PtCl_2(MeCN)_2]$. Unfortunately, because the coordinating centre is poorly accessible, most of **L7** was recovered unmodified after 24 h. Purification of the remaining solid by column chromatography afforded a small amount (3.5 % yield) of a Pt(II)-complex bearing two *cis*-arranged phosphorus atoms which resonate as an AB system centred at -37.5 and -25.3 ppm in ^{31}P NMR spectroscopy. Confirmation of the *cis*-stereochemistry was provided by the values of the *J*(PtP) and *J*(PtP') constants[14-17] (3360 and 3375 Hz) as well as the *J*(PP') coupling constant (16.7 Hz), which all lie in the range of those reported in the literature for *cis*-$PtCl_2P_2$ complexes. From the FAB-MS spectrum, it became apparent that the present species does not comprise two molecules of **L7**, as the major peak at *m/z* 1624.0 is consistent with a *cis* complex such as **37b** or **38b**. This species most likely results from the cleavage of the CD bridge. Our findings indicate that for steric reasons, it is not possible to coordinate two phosphines of type **L7** on a single $PtCl_2$ moiety.

V.2.2. Synthesis and coordination behaviour of a CD ligand bearing a single PPh_2 group

The flexible monodentate phosphine ligand **L8** was prepared in order to compare its coordination and catalytic properties with those of the two rigidly capped phosphines **L6** and **L7**. Cleavage of the protecting group of the known tris(*p-tert*-butylphenyl)methyl monosubstituted CD derivative **39** with HBF_4 afforded alcool **40**, which was converted into mesylate **41** upon reaction with MsCl (Scheme 2). After treatment of the latter with an excess of PPh_2Li at -78°C, monophosphine **L8** was obtained in high yield. As expected, the ^{31}P NMR spectrum shows a singlet at -20.4 ppm. Unlike the cyclic phosphines **L6** and **L7**, **L8** oxidises readily when dissolved in an aerated chloroform solution to afford **42** after one day. The ^{31}P NMR spectrum of the latter displays a typical phosphoryl signal at 28.5 ppm.

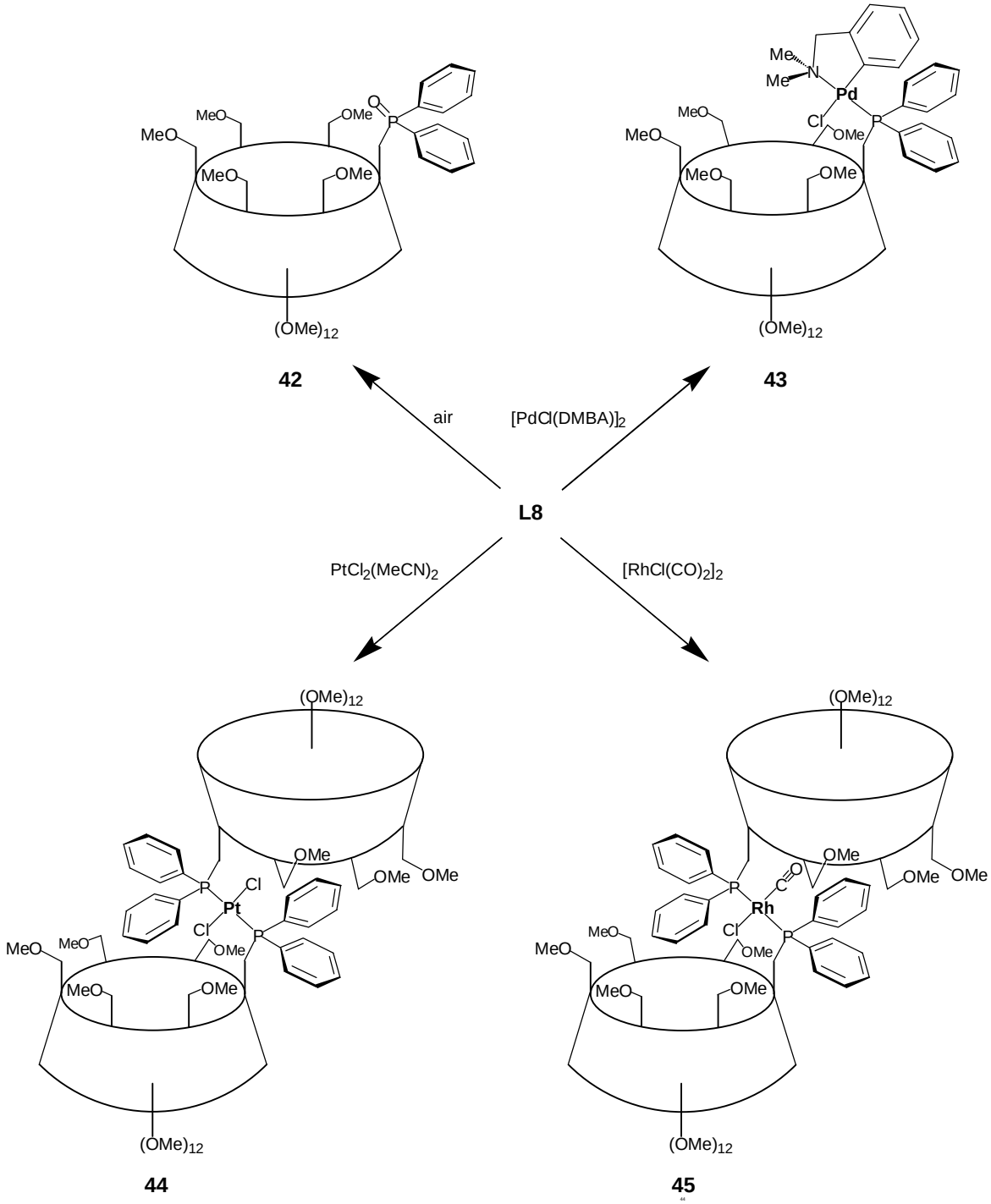


Scheme 2. Synthesis of a flexibly phosphine-substituted α-CD

Complex **43**, which gives rise to a singlet at 25.3 ppm in ^{31}P NMR spectroscopy, was obtained by reacting **L8** with 0.5 equivalent of [*o*-$C_6H_4CH_2NMe_2$)PdCl]$_2$. Coordination of the phosphorus atom is again inferred from the ^4J(P-NCH) coupling constants in the ^{1}H NMR spectrum (<1.0 and 2.0 Hz). Consistent with the rather flexible nature of the pending phosphine ligands of **L8**, no significant shielding or deshielding effects were observed in **43**.

In addition, coordination of two **L8** ligands to the same metal centre was readily achieved by reacting 2 equivalents of **L8** with [$PtCl_2(MeCN)_2$]. The formation of **44**, which may be viewed as an assembly of two cavitands linked by a $PtCl_2$ unit, was confirmed by the presence of a strong peak in the FAB-MS spectrum corresponding to the $[M–Cl+H]^+$ ion (*m/z* 2989.1). The *J*(PtP) coupling constant value of 2614 Hz is consistent with a *trans*-stereochemistry. Clearly, the steric bulk of **L8** prevents the formation of a *cis*-$PtCl_2$(**L8**)$_2$ complex.

The reaction of [$RhCl(CO)_2]_2$ with **L8** afforded the relatively unstable bis(phosphine) complex **45**, which is characterised by a strong carbonyl absorption band



at 1972 cm^{-1}. The phosphorus atoms appear as a doublet centred at 14.2 ppm (J(RhP) = 126 Hz) in the ^{31}P NMR spectrum, in keeping with phosphine units that rotate freely about the Rh–P axis. Unlike the *trans*-$RhCl(CO)P_2$ complexes **16a** and **16b**, which are stable under N_2, about half of complex **45** decomposed after 3 days.

V.2.3. Catalytic properties of L6-L8

V.2.3.1 Hydroformylation of oct-1-ene

Both cyclic phosphines **L6** and **L7** exhibited no activity in the hydroformylation of oct-1-ene (Table 1, entries 1 and 2). As mentioned previously, coordination of two CD ligands to the same metal centre seems rather unlikely and therefore, under typical hydroformylation conditions, probably only monophosphine species were formed. Steric crowding in the resulting complexes may explain the system lack of activity, together with the pronounced electron donor character of dialkylphosphines.

On the other hand, **L8** (entry 3) showed catalytic activity in the hydroformylation of oct-1-ene. The TOF and the aldehyde regioselectivity were similar to that of the related chelating diphosphine **L3** (chapter III). The fact that the observed activity is *ca.* 15 times lower than that of PPh_3/Rh catalysts is consistent with the steric bulk of the phosphine.

Table 1. Hydroformylation of oct-1-ene

entry	ligand	L/Rh ratio	S/Rh ratio	% conv.[a] (2h)	l/b ratio	TOF[b]
1	**L6**	5	600	-	-	-
2	**L7**	5	600	-	-	-
3	**L8**	5	600	84	2.3	120

Conditions: T = 80°C; $6.62 \cdot 10^{-3}$ mmol (1.7 mg) of $[Rh(acac)(CO)_2]$ in toluene (15 mL); $P_{H2} = P_{CO}$ = 10 bar

[a] The conversion was determined after 2 h reaction time.

[b] mol aldehyde · mol^{-1} Rh · h^{-1}

V.2.3.2. Hydrogenation of dimethylitaconate

Both **L6** and **L7** exhibited moderate activity in the rhodium-catalysed hydrogenation of dimethylitaconate during the first 2 hours of reaction (table 2 , entries 1 and 2), whereupon both systems rapidly turned almost inactive (only 11 and 28% of olefin were hydrogenated between 2 h and 3 days of reaction using **L6** and **L7**,

respectively). Unfortunately, no enantioselectivity was observed with these systems. Thus **L6** and **L7** behave as most chiral monodentate ligands.

L8 turned out to be practically inactive in hydrogenation (entry 3). Furthermore the catalyst decomposed completely after 3 days of reaction.

Table 2. Hydrogenation of dimethylitaconate

entry	ligand	S/Rh ratio	% conv. (2h)[a]	% ee	TOF[b]
1	**L6**[c]	200	16	4.2 (*S*)	16
2	**L7**[d]	200	25	6.4 (*R*)	25
3	**L8**[c]	500	1.3 [e]	n.d.[f]	3.3

Conditions: T = 25°C; CH_2Cl_2 (15 mL), P_{H2} = 1 bar

[a] The conversion was determined after 2 h reaction time.

[b] mol product · mol^{-1} Rh · h^{-1} after 2 h

[c] ligand/Rh = 2; $1.96 \cdot 10^{-2}$ mmol of $[Rh(COD)_2]BF_4$

[d] ligand/Rh = 2; $2.20 \cdot 10^{-2}$ mmol of $[Rh(COD)_2]BF_4$

[e] The catalyst started to decompose after *ca.* 36 h

[f] not determined

V.3. Conclusion

We have successfully synthesised the first cyclic phosphines based on a CD receptor, by capping the cavity with the very short “PPh” unit. The remarkable stereospecificity observed during the phosphination steps allowed us to prepare phosphino-cavitands in which the phosphorus lone pair is oriented towards the CD axis. Our preliminary complexation studies indicate that both phosphines are only suited for the formation of monophosphine complexes. Further work with these ligands is aimed at designing chiral catalysts which require coordination of a *single* phosphine, as *e.g.* in the hydrovinylation of olefins, or allylic alkylations. Changing the size of the cyclodextrin may result in increased selectivity control.

V.4. Experimental Section

V.4.1. General procedures

All commercial reagents were used as supplied. All manipulations involving phosphines were performed in Schlenk-type flasks under argon. Solvents were dried by conventional methods and distilled immediately prior to use. Column chromatography was performed on silica gel 60 (particle size 40-63 μm, 230-240 mesh). $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under argon over molecular sieves (4 Å). Routine ^{1}H, $^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectra were recorded with an FT Bruker Avance 300 (^{1}H: 300.1 MHz, ^{31}P: 121.5 MHz, ^{13}C: 75.5 MHz) instrument at 25°C while 500 MHz-spectra were recorded on an Avance 500 (^{1}H: 500.1 MHz) Bruker instrument. ^{1}H NMR spectral data were referenced to residual protiated solvents (δ 7.26 for $CDCl_3$ and δ 7.16 for C_6D_6), ^{13}C chemical shifts are reported relative to deuterated solvents (δ 77.00 for $CDCl_3$ and δ 128.30 for C_6D_6), and the ^{31}P NMR data are given relative to external H_3PO_4. All mass spectra were recorded on a ZAB HF VG Analytical spectrometer using *m*-nitrobenzyl alcohol as matrix. The IR spectrum was 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. Complexes $[(o\text{-}C_6H_4CH_2NMe_2)PdCl]_2$[18] and $[PtCl_2(MeCN)_2]$[19] were synthesised according to literature procedures.

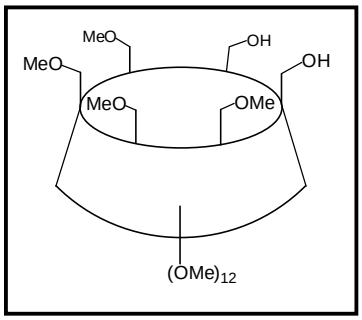
Hydroformylation studies were performed in a stainless steel autoclave (100 mL) containing a glass beaker and a magnetic stirring bar. The beaker was charged with toluene solutions of both the phosphine ligands and $[Rh(acac)(CO)_2]$ (total volume 15 mL), followed by the internal standard (decane). The autoclave was flushed several times with CO/H_2 (1:1, v/v), then pressurised to 20 bar, and finally heated to 80 °C for one hour. After depressurising and cooling down to room temperature, the substrate (oct-1-ene) was added, and the mixture was again pressurised and heated to reaction temperature. Samples were taken at different reaction times and analysed by GC.

Hydrogenation experiments were carried out in a Schlenk tube under ambient pressure and room temperature. The phosphine ligands were dissolved in 15 mL of

CH_2Cl_2. After addition of $[Rh(COD)_2]BF_4$, the solution was saturated with H_2 for 10 min., whereupon the substrate (dimethylitaconate) was added. The reaction was followed by GC. Enantiomeric excess was determined by GC using a Cyclodextrin/OV1701 column.

V.4.2. Synthesis of ligands and complexes

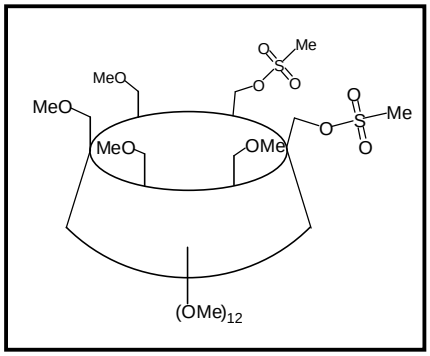
2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F-Hexadeca-*O*-methyl-α-cyclodextrin (33)



Tetrafluoroboric acid (34%, 1.4 mL) was added to a solution of **32** (1.340 g, 0.664 mmol) in MeCN (50 mL). The solution was stirred for 20 min. at room temperature whereupon Et_3N (3 mL) was added. Addition of water (200 mL) caused ^{s}TrOH to precipitate. The latter was filtered and the filtrate extracted with CH_2Cl_2 (4 x 100 mL). The organic extract was washed with saturated aqueous $NaHCO_3$ (2 x 100 mL) before being dried ($MgSO_4$), and evaporated to dryness, affording **33** as a colourless solid (0.770 g, 97 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.10; Mp 113-115°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (br s, 1H; $OH^{A\ or\ B}$) , 2.61 (br s, 1H; $OH^{B\ or\ A}$), 3.38 (s, 3H; CH_3O-6) 3.39 (s, 9H; CH_3O-6), 3.47 (s, 3H; CH_3O-2), 3.48 (s, 9H; CH_3O-2), 3.49 (s, 3H; CH_3O-2), 3.50 (s, 3H; CH_3O-2), 3.63 (s, 6H; CH_3O-3), 3.64 (s, 9H; CH_3O-3), 3.65 (s, 3H, CH_3O-3), 3.12-4.03 (36H; H-2, H-3, H-4, H-5, H-6), 5.02 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.3 Hz, 1H; H-1), 5.03-5.06 (4 overlapping d, 4H; H-1), 5.08 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.3 Hz, 1H; H-1); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 57.64, 57.69 [×3], 57.75 and 57.77 (CH_3O-2), 58.75, 58.76 [×2] and 58.89 (CH_3O-6), 61.47, 61.50, 61.52 [×2] and 61.56 [×2] (CH_3O-3), 61.76 and 62.19 (C-$6^{A,B}$), 70.95, 70.99 [×2] and 71.07 (C-$5^{C,D,E,F}$), 71.29, 71.32 and

71.37 [×2] (C-$6^{C,D,E,F}$), 72,37 and 72.73 (C-$5^{A,B}$), 81.08 [×3], 81.13 [×3], 81.77, 81.82 [×2], 81.92 [×4], 81.98, 82.07 [×2], 82.19 and 82.51 (C-2, C-3, C-4), 99.36, 99.51, 99.59, 99.66, 99.69 and 99.73 (C-1); elemental analysis (%) calcd for $C_{52}H_{92}O_{30}$•0.2 CH_2Cl_2 (1197.27 + 16.99): C 51.63, H 7.67; found: C 51.56, H 7.80.

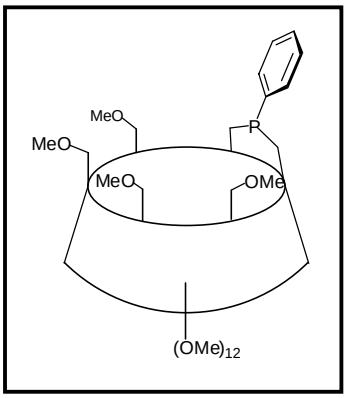
6^{A},6^{B}-Di-*O*-methylsulfonyl-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (34)



Methylsulfonyl chloride (0.184 g, 1.61 mmol) was added to a solution of **33** (0.770 g, 0.643 mmol) and DMAP (0.127 g, 1.04 mmol) in anhydrous pyridine (10 mL). The reaction mixture was stirred overnight at room temperature whereupon brine (50 mL) was added. The solution was then extracted with EtOAc (4 x 50 mL), and the organic phase washed respectively with HCl 2M (2 x 50 mL), NaOH 2M (2 x 50 mL), before being dried ($MgSO_4$) and filtered. Removal of the solvent *in vacuo* afforded pure **34** as a colorless solid (0.780 g, 90 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.25; Mp 105-106°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.05 (s, 3H; OSO_2CH_3), 3.06 (s, 3H; OSO_2CH_3), 3.38 (s, 6H, CH_3O-6), 3.39 (s, 3H; CH_3O-6), 3.40 (s, 3H; CH_3O-6), 3.47 (s, 6H; CH_3O-2), 3.49 (s, 3H; CH_3O-2), 3.50 (s, 9H; CH_3O-2), 3.62 (s, 3H; CH_3O-3), 3.63 (s, 6H; CH_3O-3), 3.65 (s, 3H; CH_3O-3), 3.66 (s, 6H; CH_3O-3), 3.12-4.15 (32H; H-2, H-3, H-4, H-5, H-$6^{C,D,E,F}$), 4.34 (dd, $^3J_{H\text{-}5,H\text{-}6a}$ = 7.0 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.8 Hz, 1H; H-$6a^{A\text{ or }B}$), 4.60 (br d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.8 Hz, 1H; H-$6b^{A\text{ or }B}$), 4.76 (br d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.8 Hz, 1H; H-$6b^{A\text{ or }B}$), 4.77 (dd, $^3J_{H\text{-}5,H\text{-}6a}$ = 4.2 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.8 Hz, 1H; H-$6a^{A\text{ or }B}$), 5.00 (2d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.1 Hz, 1H; H-1), 5.04-5.08 (4 overlapping d, 4H; H-1); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 37.27 and 37.57 (OSO_2CH_3), 57.53, 57.58, 57.69, 57.76, 57.98 and 58.25 (CH_3O-2) 58.85 [×2], 58.90 and 58.95 (CH_3O-6), 61.51, 61.57, 61.66 [×2], 61.73

and 61.76 (CH_3O-3), 69.72, 70.32, 70.80, 70.86, 70.96 and 71.37 (C-5), 69.77, 70.39, 71.01, 71.15, 71.43 and 71.53 (C-6), 80.85, 80.92 [×3], 81.13 [×2], 81.60, 81.73, 81.85, 81.94 [×3], 82.00, 82.16, 82.25 [×2] and 82.66 [×2] (C-2, C-3, C-4), 99.10, 99.27, 99.69, 100.00, 100.27 and 100.32 (C-1); elemental analysis (%) calcd for $C_{54}H_{96}O_{34}S_2$•0.7 $CHCl_3$ (1353.45 + 83.56): C 45.72, H 6.78, S 4.46; found: C 45.59, H 6.82, S 4.39.

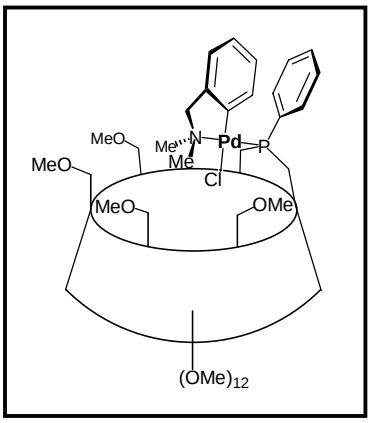
[6^{A},6^{B}]Phenylphosphino-6^{A},6^{B}-dideoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (L6)



A solution of *n*-BuLi in hexane (1.6 M, 2.5 mL, 4.00 mmol) was added to a solution of $PhPH_2$ (0.200 g, 1.82 mmol) in THF (14 mL) at room temperature. The resulting yellow suspension was stirred for 1 h, whereupon an aliquot of the latter (8 mL, 1.04 mmol) was added dropwise using a syringe to a solution of **34** (0.320 g, 0.236 mmol) in THF (20 mL) at 0°C, which turned gradually dark red. After stirring overnight at room temperature, THF was evaporated. The yellow residue was treated in benzene (20 mL) and the resulting suspension filtered over celite. The solvent was evaporated and excess $PhPH_2$ was eliminated *in vacuo* under moderate heating, yielding **L6** as a white solid. (0.190 g, 64 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.78 (br d, $^2J_{H\text{-}6b,H\text{-}6a}$ = 16.4 Hz, 1H; H-6a$^{A\text{ or }B}$), 1.81 (m, 1H; H-6a$^{B\text{ or }A}$), 3.22 (s, 3H; CH_3O-6), 3.29 (s, 3H; CH_3O-6), 3.36 (s, 3H; CH_3O-6), 3.38 (s, 3H; CH_3O-6), 3.48 (s, 6H; CH_3O-2), 3.49 (s, 3H; CH_3O-2), 3.50 (s, 3H; CH_3O-2), 3.51 (s, 3H; CH_3O-2), 3.52 (s, 3H; CH_3O-2), 3.62 (s, 3H; CH_3O-3), 3.64 (s, 3H; CH_3O-3), 3.65 (s, 6H; CH_3O-3), 3.66 (s, 3H; CH_3O-3), 3.69 (s, 3H; CH_3O-3), 2.78-4.09 (33H; H-2, H-3, H-4, H-5$^{A\text{ or }B,C,D,E,F}$, H-6a^{C,D,E,F}, H-6b), 4.33 (m, 1H; H-5$^{B\text{ or }A}$), 4.99 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.3

Hz, 1H; H-1), 5.02 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 4.4 Hz, 1H; H-1), 5.04 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.2 Hz, 1H; H-1), 5.06 (2d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.1 Hz, 2H; H-1), 5.07 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.2 Hz, 1H; H-1), 7.29-7.35 (3H; H_{meta}, H_{para}), 7.43-7.49 (m, 2H; H_{ortho}); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 26.72 (d, $J_{C,P}$ = 16.8 Hz; C-$6^{A \text{ or } B}$), 34.28 (d, $J_{C,P}$ = 19.9 Hz; C-$6^{B \text{ or } A}$), 57.50, 57.70, 57.83, 57.88 and 57.98 [×2] (CH_3O-2), 58.75, 58.87 and 58.92 [×2] (CH_3O-6), 61.58, 61.66 [×2], 61.88, 61.90 and 62.02 (CH_3O-3), 70.88, 71.02, 71.24 and 71.35 (C-$6^{C,D,E,F}$), 70.83 [×2], 70.94 and 71.09 (C-$5^{C,D,E,F}$), 72.52 (C-$4^{A \text{ or } B}$), 73.02 (C-$4^{B \text{ or } A}$), 81.27, 81.32, 81.35, 81.45, 81.51, 81.54, 81.73, 81.80, 81.92, 82.01, 82.19 [×2], 82.22, 82.24, 82.35 and 83.43 (C-2, C-3, C-$4^{C,D,E,F}$), 87.35 (br d, $^{2}J_{C,P}$ = 3.7 Hz; C-$5^{A \text{ or } B}$), 88.77 (d, $^{2}J_{C,P}$ = 3.7 Hz; C-$5^{B \text{ or } A}$), 97.59 (br), 99.36, 99.65, 99.68, 99.89 and 100.26 (C-1), 128.32 (d, $^{3}J_{C,P}$ = 6.8 Hz; C_{meta}), 128.47 (d, $^{4}J_{C,P}$ = 1.9 Hz; C_{para}), 131.37 (d, $^{2}J_{C,P}$ = 18.6 Hz; C_{ortho}), 140.64 (d, $J_{C,P}$ = 10.5, Hz; C_{ipso}); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = -16.2 (s); elemental analysis (%) calcd for $C_{58}H_{95}O_{28}P$ (1271.33): C 54.80, H 7.53; found: C 54.82, H 7.37.

_P_-([6^{A},6^{B}]Phenylphosphino-6^{A},6^{B}-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^{C},6^{D},6^{E},6^{F}-hexadeca-_O_-methyl-α-cyclodextrin)-[chloro(_o_-dimethylaminobenzyl) palladium(II)] (35a)

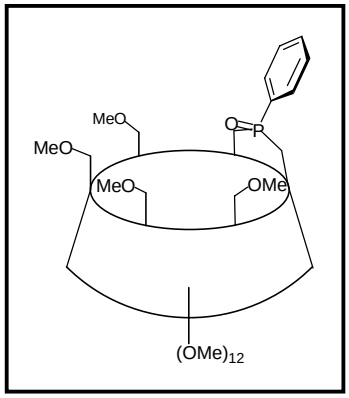


To a solution of **L6** (0.040 g, 0.0315 mmol) in CH_2Cl_2 (10 mL) was added a solution of [(_o_-$C_6H_4CH_2NMe_2$)PdCl]$_2$ (0.009 g, 0.0163 mmol) in CH_2Cl_2 (5 mL). After 15 min. the reaction mixture was concentrated to 2 mL and pentane (150 mL) was added to precipitate side products, which were then filtered off over celite. Evaporation of pentane afforded **35a** as a yellow powder (36 mg, 74 %). R_f (CH_2Cl_2/MeOH, 94 : 6,

v/v) = 0.25; Mp 162°C dec. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ (assignment by COSY, ROESY and TOCSY) = 2.03 (dt, $^{2}J_{H\text{-}6b,H\text{-}6a}$ = 13.4 Hz, $^{3}J_{H\text{-}5,H\text{-}6a}$ = 13.4 Hz, $^{2}J_{P,H\text{-}6a}$ = 7.8 Hz 1H; H-6a^{B}), 2.60 (d, $^{4}J_{P,H}$ = 1.4 Hz, 3H; NCH_3), 2.73 (ddd, $^{2}J_{H\text{-}6b,H\text{-}6a}$ = 15.0 Hz, $^{3}J_{H\text{-}5,H\text{-}6a}$ = 2.0 Hz, $^{2}J_{P,H\text{-}6a}$ = 7.8 Hz, 1H; H-6a^{A}), 3.00 (t, $^{3}J_{H\text{-}5,H\text{-}4}$ = 9.4 Hz, $^{3}J_{H\text{-}3,H\text{-}4}$ = 9.4 Hz; H-4^{B}), 3.03 (d, $^{4}J_{P,H}$ = 2.6 Hz, 3H; NCH_3), 3.08 (s, 3H; CH_3O-6), 3.12-3.23 (6 overlapping dd, 6H; H-2), 3.32 (s, 3H; CH_3O-6), 3.35 (t, $^{3}J_{H\text{-}5,H\text{-}4}$ = 8.7 Hz, $^{3}J_{H\text{-}3,H\text{-}4}$ = 8.7 Hz; H-4^{A}), 3.39 (s, 3H; CH_3O-6), 3.40 (s, 3H; CH_3O-6), 3.46-3.50 (2 overlapping signals, 2H; H-6a^{D} and NCH_2), 3.47 (s, 6H; CH_3O-2), 3.48 (s, 3H; CH_3O-2), 3.48 (s, 3H; CH_3O-2), 3.49 (s, 6H; CH_3O-2), 3.51 (s, 3H; CH_3O-2), 3.52-3.59 (6 overlapping signals, 6H; H-3^{A,B,C}, H-6a^{E,F}, H-6b^{A}), 3.60 (s, 3H; CH_3O-3), 3.62-3.76 (7 overlapping signals, 7H; H-4^{C,D,E,F}, H-3^{D,E,F}), 3.64 (s, 3H; CH_3O-3), 3.66 (s, 3H; CH_3O-3), 3.66 (s, 3H; CH_3O-3), 3.67 (s, 3H; CH_3O-3), 3.68 (s, 3H; CH_3O-3), 3.88-3.94 (5 overlapping signals, 5H; H-6a^{C}, H-6b^{B,D}, H-5^{D,E}), 4.01 (dd, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 10.1 Hz, $^{3}J_{H\text{-}6a,H\text{-}5}$ = 2.9 Hz, 1H; H-6b^{E}), 4.24 (br d, ^{3}J = 9.6 Hz, 1H; H-5^{F}), 4.27 (br d, ^{3}J = 9.8 Hz, 1H; H-5^{C}), 4.50 (m, 1H; H-5^{B}), 4.54 (d, ^{2}J = 12.8 Hz, 1H; NCH_2), 4.74 (dd, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 11.0 Hz, $^{3}J_{H\text{-}6a,H\text{-}5}$ = 2.3 Hz, 1H; H-6b^{F}), 4.88 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 1H; H-1^{C}), 4.97 (m, 1H; H-5^{A}), 5.05 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 1H; H-1^{F}), 5.08 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.2 Hz, 2H; H-1^{E}), 5.10 (2d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 2H; H-1^{B,D}), 5.13 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.9 Hz, 1H; H-1^{A}), 6.25 (br t, J = 7.0 Hz, 1H; H_{ortho} of DMBA), 6.34 (br t, J = 7.4 Hz, 1H; H_{meta} of DMBA), 6.68 (dt, J = 7.4 and 0.8 Hz, 1H; H_{para} of DMBA), 6.87 (br d, J = 7.2 Hz, 1H; H_{meta} of DMBA), 7.11-7.18 (3H; H_{meta}, H_{para}), 7.46-7.50 (m, 2H; H_{ortho}), H-6b^{C} not assigned; $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 35.28 (d, $J_{C,P}$= 20.5 Hz; C-6$^{A\text{ or }B}$), 36.07 (d, $J_{C,P}$ = 27.3 Hz; C-6$^{B\text{ or }A}$), 49.62 (br d; NCH_3), 51.68 (br d; NCH_3), 57.20, 57.46, 57.55, 57.58 and 57.81 [×2] (CH_3O-2), 58.73, 59.07, 59.12 and 59.19 (CH_3O-6), 61.47, 61.73, 61.85 [×2], 62.03 and 62.38 (CH_3O-3), 66.20 (d, $^{3}J_{C,P}$ = 8.1 Hz; C-4$^{A\text{ or }B}$), 68.13 (d, $^{3}J_{C,P}$ = 2.2 Hz; C-4$^{B\text{ or }A}$), 70.47, 70.91, 71.04 and 71.21 (C-5^{C,D,E,F}), 71.46, 71.80, 72.00 and 72.21 (C-6^{C,D,E,F}), 73.33 (NCH_2), 80.07, 80.69, 80.83, 80.92, 81.04, 81.44, 81.61, 81.68, 82.07 [×2], 82.13, 82.32, 82.43 [×2], 82.53 and 83.56 (C-2, C-3, C-4^{C,D,E,F}), 88.77 (d, $^{2}J_{C,P}$ = 8.1 Hz; C-5$^{A\text{ or }B}$), 91.38 (d, $^{2}J_{C,P}$ = 3.7 Hz; C-5$^{B\text{ or }A}$), 97.45, 99.94, 99.99, 100.42 [×2] and 101.40 (C-1), 122.34 (C_{meta} of DMBA), 123.50 (C_{para} of DMBA), 125.38 (d, $^{3}J_{C,P}$ = 5.6 Hz; C_{meta} of DMBA), 127.77 (d, $^{3}J_{C,P}$ = 10.6 Hz; C_{meta}), 129.61 (C_{para}), 132.17 (d, $^{2}J_{C,P}$ = 11.2 Hz; C_{ortho}), 135.67 (d, $^{2}J_{C,P}$ = 10.5 Hz; C_{ortho} of DMBA), 136.92 (d, $J_{C,P}$ = 51.5 Hz; C_{ipso}),

146.39 (d, $J_{C,P}$ = 2.3 Hz; C_{quat} of DMBA), 153.91 (C_{quat} of DMBA); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 17.4 (s); elemental analysis (%) calcd for $C_{67}H_{107}ClNO_{28}PPd$ (1547.39): C 52.00, H 6.97; found: C 51.67, H 6.94; MS (FAB): *m/z* (%): 1546.8 (1) $[M+H]^+$, 1510.8 (8) $[M-Cl]^+$.

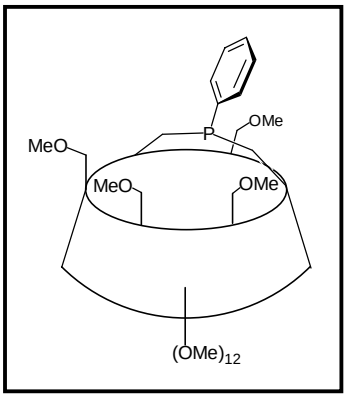
[6^{A},6^{B}]Phenyloxophosphino-6^{A},6^{B}-dideoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C}, 6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (36a)



A solution of **L6** (0.020 g, 0.0157 mmol) in CH_2Cl_2/MeOH (0.50 mL, 94 : 6, v/v) was passed down a silica gel column (eluent: CH_2Cl_2/MeOH, 94 : 6, v/v), affording **36a** quantitatively (0.020 g) as a microcristalline powder. R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.20; Mp > 230°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.15 (s, 3H; CH_3O-6), 3.18 (s, 3H; CH_3O-6), 3.41 (s, 3H; CH_3O-6), 3.42 (s, 3H; CH_3O-6), 3.46 (s, 3H; CH_3O-2), 3.47 (s, 3H; CH_3O-2), 3.48 (s, 3H; CH_3O-2), 3.49 (s, 3H; CH_3O-2), 3.50 (s, 3H; CH_3O-2), 3.53 (s, 3H; CH_3O-2), 3.60 (s, 3H; CH_3O-3), 3.65 (s, 3H; CH_3O-3), 3.66 (s, 6H; CH_3O-3), 3.67 (s, 3H; CH_3O-3), 3.68 (s, 3H; CH_3O-3), 1.93-4.05 (34H; H-2, H-3, H-4, H-5^{C,D,E,F}, H-6), 4.46 (m, ^{3}J = 11.6 Hz, 1H; H-5$^{A\text{ or }B}$), 4.73 (m, 1H; H-5$^{B\text{ or }A}$), 4.97 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.1 Hz, 1H; H-1), 4.98 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.1 Hz, 1H; H-1), 5.03 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.9 Hz, 1H; H-1), 5.04 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.7 Hz, 1H; H-1), 5.05 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.6 Hz, 1H; H-1), 5.07 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.5 Hz, 1H; H-1), 7.44-7.53 (H_{meta} and H_{para}), 7.64-7.71 (m, 2H; H_{ortho}); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 33.04 (d, $J_{C,P}$ = 67.6 Hz; C-6$^{A\text{ or }B}$), 38.00 (d, $J_{C,P}$ = 65.1 Hz; C-6$^{B\text{ or }A}$), 57.56, 57.64, 57.75, 57.81 [×2] and 57.96 (CH_3O-2), 58.70, 58.73, 58.95 and 58.97 (CH_3O-6), 61.56, 61.71, 61.79, 61.89, 62.03 and 62.21 (CH_3O-3), 62.98 (d, $^{3}J_{C,P}$ = 4.3 Hz; C-4$^{A\text{ or }B}$), 65.77 (s, C-4$^{B\text{ or }A}$), 70.84 and 70.94 [×3] (C-

$5^{C,D,E,F}$), 70.71, 71.24 and 71.38 [×2] (C-$6^{C,D,E,F}$), 81.15, 81.17, 81.28 [×2], 81.33, 81.61, 81.88, 81.90, 81.99, 82.19, 82.24, 82.30, 82.33 [×2], 82.56 and 83.48 (C-2, C-3, C-$4^{C,D,E,F}$), 87.00 (d, $^{2}J_{C,P}$ = 11.2 Hz; C-$5^{A\text{ or }B}$), 88.88 (d, $^{2}J_{C,P}$ = 3.7 Hz; C-$5^{B\text{ or }A}$), 97.95, 99.54, 99.70, 99.78, 100.11 and 100.50 (C-1), 128.60 (d, $^{2}J_{C,P}$ = 11.2 Hz; C_{ortho}), 129.36 (d, $^{3}J_{C,P}$ = 9.3 Hz; C_{meta}), 131.64 (d, $^{4}J_{C,P}$ = 1.9 Hz; C_{para}), 135.47 (d, $J_{C,P}$ = 96.1 Hz; C_{ipso}); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 34.6 (s); elemental analysis (%) calcd for $C_{58}H_{95}O_{29}P\bullet 0.2\ CHCl_3$ (1287.33 + 23.88): C 53.31, H 7.32; found: C 53.10, H 7.63.

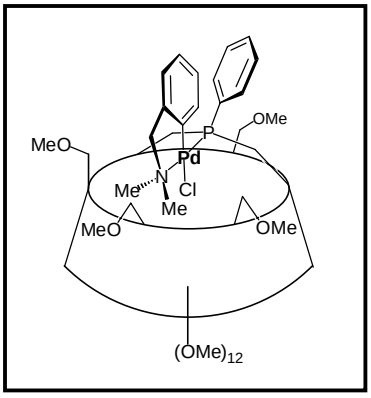
[6^{A},6^{C}]Phenylphosphino-6^{A},6^{C}-dideoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (L7)



A solution of *n*-BuLi in hexane (1.6 M, 2.9 mL, 4.56 mmol) was added to a solution of $PhPH_2$ (0.250 g, 2.27 mmol) in THF (15 mL) at room temperature. The resulting yellow suspension was stirred for 1 h, whereupon an aliquot of the latter (13 mL, 1.97 mmol) was added dropwise, using a syringe, to a solution of **1b** (0.600 g, 0.443 mmol) in THF (80 mL) at -30°C, which turned gradually dark red. After stirring overnight at room temperature, the solution was concentrated to *ca.* 10 mL and dry MeOH was added (5 mL). Evaporation to dryness afforded a pale yellow residue which was taken up in benzene (20 mL). The resulting suspension was filtered over celite to eliminate lithium salts and the solvent was evaporated. The residue was then suspended in hexane and sonicated to dissolve the target compound prior to filtration over celite and evaporation of the solvent. This procedure was repeated one more time and excess $PhPH_2$ was eliminated *in vacuo* under moderate heating, yielding **L7** as a white powder. (0.335 g, 60 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.26; Mp 175°C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ (assignment by COSY) = 1.64 (dt, $^{2}J_{H\text{-}6b,H\text{-}6a}$ = 14.7 Hz, $^{3}J_{H\text{-}5,H\text{-}6a}$ =

$^{2}J_{P,H\text{-}6a}$ = 6.0 Hz, 1H; H-6a$^{A\ or\ C}$), 2.05 (m, 1H; H-6a$^{C\ or\ A}$), 2.23 (br dd, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 14.7 Hz, $^{2}J_{P,H\text{-}6b}$ = 18.6 Hz, 1H; H-6b$^{A\ or\ C}$), 2.49 (br d, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 13.5 Hz, 1H, H-6b$^{C\ or\ A}$), 2.54 and 3.20 (AB, $^{2}J_{A,B}$ = 11.3 Hz, 2H, H-6), 2.87 (s, 3H; CH_3O-6), 3.36 (s, 3H; OCH_3), 3.38 (s, 3H; OCH_3), 3.39 (s, 3H; OCH_3), 3.41 (s, 3H; OCH_3), 3.43 (s, 6H; OCH_3), 3.51 (s, 3H; OCH_3), 3.52 (s, 6H; OCH_3), 3.54 (s, 3H; OCH_3), 3.55 (s, 3H; OCH_3), 3.64 (s, 3H; OCH_3), 3.69 (s, 3H; OCH_3), 3.71 (s, 3H; OCH_3), 3.73 (s, 3H; OCH_3), 3.90 (br dd, $^{3}J_{H\text{-}6a,H\text{-}5}$ = 6.0 Hz, 1H, H-5$^{A\ or\ C}$), 4.09 (t, $^{3}J_{H\text{-}3,H\text{-}4}$ = $^{3}J_{H\text{-}5,H\text{-}4}$ = 5.2 Hz, 1H, H-4), 3.07-4.14 (26H; H-2, H-3, H-4, H-5, H-6), 4.33 (br q, $^{3}J_{H\text{-}6a,H\text{-}5}$ = $^{3}J_{H\text{-}4,H\text{-}5}$ = $^{3}J_{P,H\text{-}5}$ = 10.0 Hz, 1H; H-5$^{C\ or\ A}$), 4.41 (dd, $^{3}J_{H\text{-}6,H\text{-}5}$ = 10.2 Hz, $^{3}J_{H\text{-}4,H\text{-}5}$ = 5.2 Hz, 1H; H-5), 4.73 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 1H; H-1), 4.94 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 1H; H-1), 5.07 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.2 Hz, 1H; H-1), 5.19 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.6 Hz, 1H; H-1), 5.20 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.4 Hz, 1H; H-1), 5.82 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 1H; H-1), 7.27-7.35 (3H; H_{meta}, H_{para}), 7.46-7.51 (m, 2H; H_{ortho}); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 25.37 (d, $J_{C,P}$ = 18.6 Hz; C-6$^{A\ or\ C}$), 33.02 (d, $J_{C,P}$ = 13.7 Hz; C-6$^{C\ or\ A}$), 57.40, 57.90 [×2], 57.92, 58.47 and 58.98 (CH_3O-2), 59.02, 59.11, 59.22 and 59.26 (CH_3O-6), 59.69, 59.99, 60.65, 61.63, 61.74 and 62.14 (CH_3O-3), 67.75 (d, $^{2}J_{C,P}$ = 8.1 Hz; C-5$^{A\ or\ C}$), 70.66, 71.01, 71.40 and 71.67 (C-5^{C,D,E,F}), 70.87, 71.40, 72.02 and 75.48 (C-6^{C,D,E,F}), 72.41 and 72.71 (C-4^{A,C}, tent. assignment), 75.59 (d, $^{2}J_{C,P}$ = 10.6 Hz; C-5$^{C\ or\ A}$), 78.96, 79.04, 80.40, 80.49, 81.47, 81.50, 81.69, 82.31, 81.47 [×2], 82.57, 82.89, 82.92, 83.38, 83.47 and 83.67 (C-2, C-3, C-4^{C,D,E,F}), 92.58, 95.14, 95.95, 98.58, 99.22 and 100.06 (C-1), 127.97 (d, $^{3}J_{C,P}$ = 6.2 Hz; C_{meta}), 128.11 (s; C_{para}), 131.56 (d, $^{2}J_{C,P}$ = 18.0 Hz; C_{ortho}), 140.80 (d, $J_{C,P}$ = 15.5, Hz; C_{ipso}); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = -21.1 (s); elemental analysis (%) calcd for $C_{58}H_{95}O_{28}P\bullet 0.2\ CHCl_3$ (1271.33 + 16.99): C 54.26, H 7.46 found: C 54.03, H 7.24.

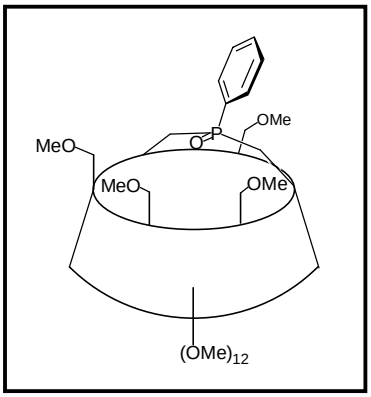
_P_-([6^{A},6^{C}]Phenylphosphino-6^{A},6^{C}-dideoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin)-[chloro(*o*-dimethylaminobenzyl) palladium(II)] (35b)



To a solution of **L7** (0.100 g, 0.0786 mmol) in CH_2Cl_2 (10 mL) was added a solution of [(*o*-$C_6H_4CH_2NMe_2$)PdCl]$_2$ (0.022 g, 0.04 mmol) in CH_2Cl_2 (5 mL). After 1 h the reaction mixture was concentrated to 2 mL and pentane (150 mL) was added to precipitate side products, which were then filtered off over celite. Evaporation of pentane afforded a yellow powder which was subjected to column chromatogaphy, affording pure **35b** (23 mg, 19 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.24; Mp 126°C dec. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ (assignment by COSY, ROESY and TOCSY) = 2.35 (m, 1H; H-6a^{C}), 2.56 (br d, 3H; NCH_3), 2.57 (m, 1H; H-6a^{A}), 2.81 (dd, $^3J_{H\text{-}3,H\text{-}2}$ = 9.3 Hz, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, 1H, H-2^{C}), 2.87 (d, $^4J_{P,H}$ = 1.7 Hz, 3H; NCH_3), 3.02 (t, $^3J_{H\text{-}5,H\text{-}4}$ = $^3J_{H\text{-}3,H\text{-}4}$ = 9.1 Hz; H-4^{C}), 3.19 (s, 3H; CH_3O-6), 3.14-3.21 (5 overlapping dd, 5H; H-2^{A,D,E,F} and H-6a^{E}), 3.26 (dd, $^3J_{H\text{-}3,H\text{-}2}$ = 8.6 Hz, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz; H-2^{B}), 3.30 (dd, ^3J = 10.0 Hz, ^3J = 7.5 Hz; H-4^{A}), 3.32 (m, 1H; H-6b^{A}), 3.35 (s, 3H; CH_3O-6), 3.38 (s, 3H; CH_3O-6), 3.41 (s, 3H; CH_3O-6), 3.43 (s, 3H; CH_3O-6), 3.44 (dd, 1H, H-3^{C}), 3.47 (s, 3H; CH_3O-2), 3.48 (s, 3H; CH_3O-2), 3.49 (s, 3H; CH_3O-2), 3.50 (s, 3H; CH_3O-2), 3.51 (s, 3H; CH_3O-2), 3.52-3.66 (4 overlapping signals, 4H; H-3^{B,D}, H-5^{B}, H-6a^{F}), 3.54 (s, 3H; CH_3O-2), 3.56 (s, 3H; CH_3O-3), 3.66 (s, 3H; CH_3O-3), 3.67 (s, 3H; CH_3O-3), 3.68 (2 overlapping signals, 2H; H-6a^{D}, H-6b^{E}), 3.72-3.83 (3 overlapping signals, 3H; H-3^{E}, H-4^{D} and H-6b^{C}), 3.74 (s, 3H; CH_3O-3), 3.78 (s, 3H; CH_3O-3), 3.80-3.90 (4 overlapping signals, 4H; H-3^{A,F}, H-4^{B,E}), 3.94 (t, $^3J_{H\text{-}5,H\text{-}4}$ = $^3J_{H\text{-}3,H\text{-}4}$ = 9.2 Hz; H-4^{F}), 4.06 (d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.5 Hz, 1H; H-6b^{D}), 4.18-4.25 (4 overlapping signals, 4H; H-5^{C,D}, NCH_2), 4.28-4.33 (4 overlapping signals, 4H; H-5^{A,E,F}, H-6b^{B}), 4.38 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.1

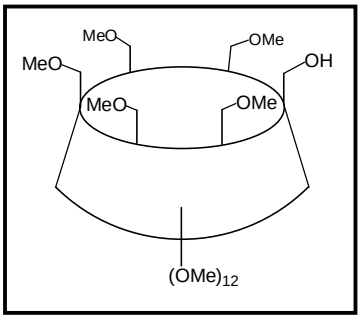
Hz, 1H; H-1^{C}), 4.59 (br d, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 11.5 Hz, 1H; H-6b^{F}), 5.02 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.6 Hz, 1H; H-1^{A}), 5.06 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.7 Hz, 2H; H-1^{F}), 5.10 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 2.4 Hz, 2H; H-1^{E}), 5.26 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 4.1 Hz, 1H; H-1^{D}), 5.59 (d, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 1H; H-1^{B}), 6.55 (br t, J = 7.2 Hz, 1H; H$_{meta}$ of DMBA), 6.67-6.75 (3 overlapping signals, 3H; H$_{ortho}$, H$_{meta}$, H$_{para}$ of DMBA), 7.03-7.10 (3H; H$_{meta}$, H$_{para}$), 7.59-7.63 (m, 2H; H$_{ortho}$), H-6a^{B} not assigned; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 24.26 (d, $J_{C,P}$= 24.8 Hz; C-6$^{A\text{ or }B}$), 31.30 (d, $J_{C,P}$ = 24.2 Hz; C-6$^{B\text{ or }A}$), 49.09 (br d; NCH_3), 51.73 (br d $^{3}J_{C,P}$ = 2.5 Hz; NCH_3), 56.97, 57.15, 57.32, 58.38, 58.52, 58.88, 58.93, 58.99 and 59.23 [×2] (CH_3O-2, CH_3O-6), 60.29, 60.74, 60.88, 61.25, 61.46 and 61.86 (CH_3O-3), 67.30 (d, $^{3}J_{C,P}$ = 10.5 Hz; C-4$^{A\text{ or }C}$), 67.77 (s; C-4$^{C\text{ or }A}$), 70.42, 70.72, 71.82 and 72.62 (C-5^{B,D,E,F}), 72.21, 72.41, 73.01 and 73.37 (C-6^{B,D,E,F}), 74.40 (NCH_2), 75.22 (d, $^{2}J_{C,P}$ = 16.1 Hz; C-5$^{A\text{ or }C}$), 75.43 (d, $^{2}J_{C,P}$ = 11.8 Hz; C-5$^{C\text{ or }A}$), 76.90, 77.76, 79.10, 80.18, 81.22 [×2], 81.65, 81.78, 81.90, 81.93, 82.52, 82.64, 82.76, 82.84, 84.27 and 84.59 (C-2, C-3, C-4^{B,D,E,F}), 91.60, 95.64, 97.76, 98.95 [×2] and 100.51 (C-1), 121.73 (C$_{meta}$ of DMBA), 122.96 (C$_{para}$ of DMBA), 125.25 (d, $^{3}J_{C,P}$ = 5.0 Hz; C$_{meta}$ of DMBA), 126.73 (d, $^{3}J_{C,P}$ = 10.5 Hz; C$_{meta}$), 127.90 (d, $^{4}J_{C,P}$ = 1.2 Hz C$_{para}$), 131.20 (d, $^{2}J_{C,P}$ = 11.1 Hz; C$_{ortho}$), 135.36 (d, $^{2}J_{C,P}$ = 9.9 Hz; C$_{ortho}$ of DMBA), 139.72 (d, $J_{C,P}$ = 52.1 Hz; C$_{ipso}$), 146.37 (d, $J_{C,P}$ = 2.3 Hz; C$_{quat}$ of DMBA), 154.34 (C$_{quat}$ of DMBA); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 7.8 (s); elemental analysis (%) calcd for $C_{67}H_{107}ClNO_{28}PPd$ (1547.39): C 52.00, H 6.97; found: C 52.15, H 7.08; MS (FAB): *m/z* (%): 1546.5 (1.3) [*M*+H]$^{+}$, 1510.5 (6.5) [*M*–Cl]$^{+}$.

[6^{A},6^{C}]Phenyloxophosphino-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 (36b)



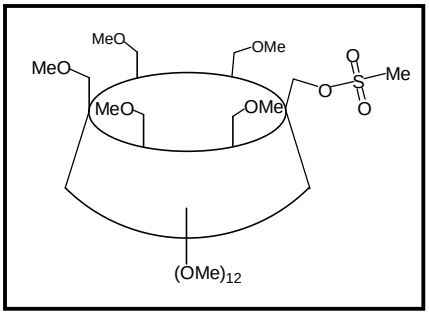
To a solution of **L7** (0.050 g, 0.039 mmol) in CH_2Cl_2 (5 mL) was added $H_2O_{2\,(aq)}$ (30 % m/m, 8 μL, 0.078 mmol). The mixture was stirred for 2 h at r.t. whereupon it was washed twice with water and dried ($MgSO_4$). Evaporation of CH_2Cl_2 afforded **36b** quantitavely (0.050 g) as a microcristalline powder. R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.20; Mp 220°C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ (assignment by COSY) = 1.60 (m, 1H; H-6a$^{A\text{ or }C}$), 2.02 (br dd, $^2J_{H\text{-}6b,H\text{-}6a}$ = 14.9 Hz, $^3J_{H\text{-}5,H\text{-}6a}$ = 12.3 Hz, 1H; H-6a$^{C\text{ or }A}$), 2.44 (br dd, $^2J_{H\text{-}6b,H\text{-}6a}$ = 18.5 Hz, $^3J_{H\text{-}5,H\text{-}6a}$ = 16.2 Hz, 1H; H-6b$^{A\text{ or }C}$), 2.71 and 2.96 (AB, $^2J_{A,B}$ = 11.4 Hz, 2H; H-6), 2.87 (s, 3H; CH_3O-6), 3.03 (br dd, $^2J_{H\text{-}6b,H\text{-}6a}$ = 14.9 Hz, 1H, H-6b$^{C\text{ or }A}$), 3.06-3.17 (7H, H-2, H-4), 3.32 (s, 3H; OCH_3), 3.38 (s, 3H; OCH_3), 3.39 (s, 3H; OCH_3), 3.43 (s, 3H; OCH_3), 3.44 (s, 3H; OCH_3), 3.46 (s, 3H; OCH_3), 3.49 (s, 6H; OCH_3), 3.51 (s, 3H; OCH_3), 3.52 (s, 3H; OCH_3), 3.54 (s, 3H; OCH_3), 3.66 (s, 6H; OCH_3), 3.67 (s, 3H; OCH_3), 3.69 (s, 3H; OCH_3), 4.37 (m, 1H; H-5$^{A\text{ or }C}$), 3.31-4.50 (21H; H-3, H-4, H-5^{B,D,E,F}, H-6), 4.66 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.2 Hz, 1H; H-1), 4.68 (br q, $^2J_{H\text{-}6a,H\text{-}5}$ = $^3J_{H\text{-}4,H\text{-}5}$ = 12.3 Hz, 1H; H-5$^{C\text{ or }A}$), 4.97 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.3 Hz, 1H; H-1), 5.05 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.7 Hz, 1H; H-1), 5.06 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.3 Hz, 1H; H-1), 5.25 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.6 Hz, 1H; H-1), 5.69 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 2.9 Hz, 1H; H-1), 7.43-7.52 (3H; H$_{meta}$, H$_{para}$), 7.59-7.66 (m, 2H; H$_{ortho}$); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 26.20 (d, $J_{C,P}$ = 68.9 Hz; C-6$^{A\text{ or }C}$), 37.29 (d, $J_{C,P}$ = 69.5 Hz; C-6$^{C\text{ or }A}$), 57.23, 57.64, 58.01, 58.27, 58.46 and 58.76 (CH_3O-2), 58.88, 58.99, 59.17 and 59.26 (CH_3O-6), 59.46, 60.36, 61.06, 61.49, 61.69 and 61.80 (CH_3O-3), 65.41 (d, $^3J_{C,P}$ = 1.9 Hz; C-4$^{A\text{ or }C}$, tent. assignment), 66.23 (d, $^2J_{C,P}$ = 6.2 Hz; C-5$^{A\text{ or }C}$), 69.54, 70.46, 71.14 and 72.75 (C-5^{C,D,E,F}), 71.66, 71.87, 72.45 and 75.92 (C-6^{C,D,E,F}), 75.71 (d, $^2J_{C,P}$ = 11.2 Hz; C-5$^{C\text{ or }A}$), 78.44, 78.73, 80.72 [×2], 80.91, 81.12, 81.28, 82.04, 82.05, 82.25, 82.52, 82.89, 83.12, 83.22, 83.44, 83.52 and 83.66 (C-2, C-3, C-4$^{C\text{ or }A,B,D,E,F}$), 92.73, 95.36, 95.68, 98.99, 99.91 and 100.05 (C-1), 128.10 (d, $^2J_{C,P}$ = 11.8 Hz; C$_{ortho}$), 130.20 (d, $^3J_{C,P}$ = 9.3 Hz; C$_{meta}$), 131.13 (d, $^4J_{C,P}$ = 2.5 Hz; C$_{para}$), 135.57 (d, $J_{C,P}$ = 96.2 Hz; C$_{ipso}$); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 35.3 (s); elemental analysis (%) calcd for $C_{58}H_{95}O_{29}P$ (1287.33): C 54.11, H 7.44; found: C 54.43, H 7.91.

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^{D},6^{E},6^{F}-Heptadeca-*O*-methyl-α-cyclodextrin (40)



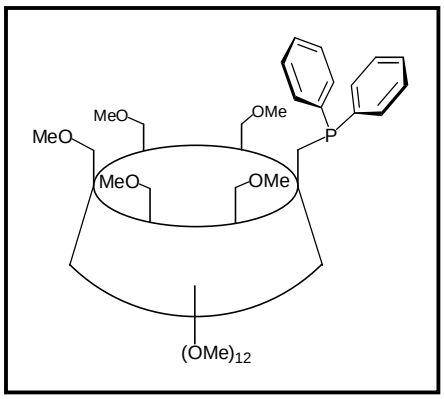
Tetrafluoroboric acid (34%, 6.6 mL) was added to a suspension of **39** (7.36 g, 4.54 mmol) in MeCN (120 mL). The solution was stirred for 20 min. at room temperature whereupon Et_3N (15 mL) was added. Addition of water (400 mL) caused ^{s}TrOH to precipitate. The latter was filtered and the filtrate extracted with CH_2Cl_2 (5 x 150 mL). The organic extract was washed with saturated aqueous $NaHCO_3$ (2 x 150 mL) before being dried ($MgSO_4$), and evaporated to dryness, affording **40** as a colourless solid (5.450 g, 99 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.15; Mp 179-181°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (t, 1H; OH), 3.13-3.18 (6 overlapping dd, 6H, H-2), 3.38 (s, 3H; CH_3O-6) 3.39 (s, 12H; CH_3O-6), 3.48 (s, 3H; CH_3O-2), 3.48 (s, 3H; CH_3O-2), 3.49 (s, 6H; CH_3O-2), 3.49 (s, 3H; CH_3O-2), 3.50 (s, 3H; CH_3O-2), 3.63 (s, 9H; CH_3O-3), 3.64 (s, 9H; CH_3O-3), 3.48-3.97 (30H; H-3, H-4, H-5, H-6), 5.02 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.3 Hz, 1H; H-1), 5.03-5.06 (4 overlapping d, 4H; H-1), 5.07 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.6 Hz, 1H; H-1); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 57.73 [×4], 57.80 and 57.88 (CH_3O-2), 58.85 [×3], 58.93 and 59.01 (CH_3O-6), 61.58 and 61.67 [×5] (CH_3O-3), 62.28 (C-6^{A}), 71.31 [×5] (C-$6^{B,C,D,E,F}$), 71.06 [×3], 71.13, 71.21 and 72.42 (C-5), 81.16 [×6], 81.92, 82.02, 82.10 [×3], 82.15 [×2], 82.21 [×3], 82.29 and 82.39 (C-2, C-3, C-4), 99.63, 99.82, 99.91 [×3] and 99.96 (C-1); elemental analysis (%) calcd for $C_{53}H_{94}O_{30}$•0.3 $CHCl_3$ (1211,30 + 35.81): C 51.33, H 7.62; found: C 51.36, H 7.70.

6^{A}-*O*-Methylsulfonyl-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{D},6^{E},6^{F}-heptadeca-*O*-methyl-α-cyclodextrin (41)



Methylsulfonyl chloride (0.854 g, 7.46 mmol) was added to a solution of **40** (4.62 g, 3.73 mmol) and DMAP (0.592 g, 4.85 mmol) in anhydrous pyridine (40 mL). The reaction mixture was stirred overnight at room temperature whereupon brine (50 mL) was added. The solution was then extracted with EtOAc (4 x 50 mL), and the organic phase washed respectively with HCl 2M (2 x 50 mL), NaOH 2M (2 x 50 mL), before being dried ($MgSO_4$) and filtered. Removal of the solvent *in vacuo* afforded pure **41** as a colorless solid (4.75 g, 99 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.20; Mp 108-109°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.06 (s, 3H; OSO_2CH_3), 3.12-3.19 (6 overlapping dd, 6H, H-2), 3.39 (s; 6H, CH_3O-6), 3.39 (s, 3H; CH_3O-6), 3.40 (s, 3H; CH_3O-6), 3.41 (s, 3H; CH_3O-6), 3.48 (s, 6H; CH_3O-2), 3.48 (s, 3H; CH_3O-2), 3.49 (s, 3H; CH_3O-2), 3.49 (s, 3H; CH_3O-2), 3.50 (s, 3H; CH_3O-2), 3.62 (s, 3H; CH_3O-3), 3.62 (s, 3H; CH_3O-3), 3.63 (s, 3H; CH_3O-3), 3.64 (s, 3H; CH_3O-3), 3.65 (s, 6H; CH_3O-3), 3.35-4.05 (28H; H-3, H-4, H-5, H-$6^{B,C,D,E,F}$), 4.46 (dd, $^3J_{H\text{-}5,H\text{-}6a}$ = 5.6 Hz, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.4 Hz, 1H; H-$6a^{A}$), 4.66 (br d, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.2 Hz, 1H; H-$6b^{A}$), 5.00 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.6 Hz, 1H; H-1), 5.01 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.7 Hz, 1H; H-1), 5.04 (2d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.5 Hz, 2H; H-1), 5.06 (2d, $^3J_{H\text{-}2,H\text{-}1}$ = 4.2 Hz, 2H; H-1); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 37.22 (OSO_2CH_3), 57.58, 57.67 [×4] and 58.14 (CH_3O-2) 58.83 [×4] and 58.99 (CH_3O-6), 61.57 [×3], 61.68 [×2] and 61.72 (CH_3O-3), 69.84, 70.99 [×4] and 71.35 (C-5), 69.91, 71.10 [×2], 71.21, 71.39 and 71.65 (C-6), 80.90, 80.98 [×3], 81.13 [×2], 81.73, 81.84, 81.91, 81.99 [×3], 82.14 [×3], 82.33, 82.51 and 82.74 (C-2, C-3, C-4), 98.95, 99.85, 99.89, 100.00, 100.17, and 100.23 (C-1); elemental analysis (%) calcd for $C_{54}H_{96}O_{32}S$•0.5 $CHCl_3$ (1289.39 + 59.69): C 48.52, H 7.21, S 2.38; found: C 48.34, H 7.29, S 2.39.

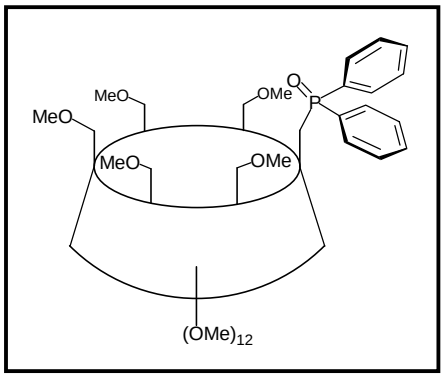
6^{A}-Diphenylphosphinyl-6^{A}-deoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{D},6^{E},6^{F}-heptadeca-*O*-methyl-α-cyclodextrin (L8)



A solution of *n*-BuLi in hexane (1.6 M, 1.5 mL, 2.33 mmol) was added, at –78°C, to a solution of Ph_2PH (0.433 g, 2.33 mmol) in THF (15 mL). The solution was allowed to warm to room temperature and stirred for additional 10 min., whereupon it was cooled down again to –78°C, prior to the addition of powdered **41** (1.000 g, 0.778 mmol). After stirring the solution overnight at room temperature, THF was evaporated. Excess lithium salt was eliminated with MeOH (10 mL). After evaporation, the residue was treated with toluene (15 mL) and the resulting suspension filtered over 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, which allows removal of residual Ph_2PH. This operation was repeated 4 times to afford **L8** as a white solid (0.900 g, 84 %). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.30; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 2.55-2.65 (overlapping AB, $^{2}J_{A,B}$ = 10.7 Hz, 2H; H-6^{A}), 2.98 (s, 3H; CH_3O-6), 3.10-3.20 (6 overlapping dd, 6H; H-2), 3.11 (s, 3H; CH_3O-6), 3.38 (s, 3H; CH_3O-6), 3.43 (s, 3H; CH_3O-6), 3.45 (s, 3H; CH_3O-6), 3.46 (s, 6H; CH_3O-2), 3.48 (s, 6H; CH_3O-2), 3.49 (s, 6H; CH_3O-2), 3.61 (s, 3H; CH_3O-3), 3.62 (s, 3H; CH_3O-3), 3.63 (s, 3H; CH_3O-3), 3.64 (s, 3H; CH_3O-3), 3.65 (s, 3H; CH_3O-3), 3.67 (s, 3H; CH_3O-3), 3.26-4.01 (27H; H-3, H-4, H-5^{B,C,D,E,F} and H-6^{B,C,D,E,F}), 4.22 (m, ^{3}J = 8.7 Hz, 1H; H-5^{A}), 4.88 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, 1H; H-1), 5.00 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 1H; H-1), 5.01 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1), 5.05 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, 1H; H-1), 5.06 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1), 5.08 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 1H; H-1), 7.25-7.31 (6H; H_{meta}, H_{para}), 7.37-7.47 (4H; H_{ortho}); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 31.75 (d, $J_{C,P}$ = 14.3 Hz; C-6^{A}),

57.69 [×3], 57.83, 57.93 and 58.12 (CH_3O-2), 58.56, 58.64, 58.98 and 59.02 [×2] (CH_3O-6), 61.55, 61.65, 61.72 and 61.83 [×2] (CH_3O-3), 69.66, 71.07 [×2] and 71.49 [×2] (C-$6^{B,C,D,E,F}$), 70.91, 70.99, 71.16, 71.28 [×2] and 71.40 (C-$5^{B,C,D,E,F}$, C-4^{A}), 81.08 [×2], 81.24 [×4], 81.44, 81.84 [×2], 82.01, 82.10 [×2], 82.15, 82.28, 82.45 [×2] and 82.62 (C-2, C-3, C-$4^{B,C,D,E,F}$), 88.24 (d, $^2J_{C,P}$ = 9.9 Hz; C-5^{A}), 98.88, 99.94, 100.01 [×2], 100.35 and 100.49 (C-1), 128.13 (d, $^3J_{C,P}$ = 6.8 Hz; C_{meta}), 128.35 (d, $^3J_{C,P}$ = 7.5 Hz; C_{meta}), 130.62 (s; C_{para}), 130.78 (s; C_{para}), 132.35 (d, $^2J_{C,P}$ = 18.0 Hz; C_{ortho}), 133.33 (d, $^2J_{C,P}$ = 20.5 Hz; C_{ortho}), 139.72 (d, $J_{C,P}$ = 11.8 Hz; C_{ipso}), 140.78 (d, $J_{C,P}$ = 12.4 Hz; C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = -20.4 (s); elemental analysis (%) calcd for $C_{65}H_{103}O_{29}P$ (1379.47): C 56.60, H 7.53; found: C 56.90, H 7.47.

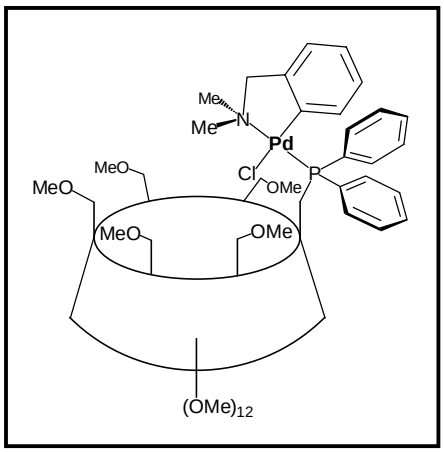
6^{A}-(Diphenyl)phosphinoyl-6^{A}-deoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{D},6^{E}, 6^{F}-heptadeca-*O*-methyl-α-cyclodextrin (42)



A solution of **L8** (0.020 g, 0.0157 mmol) in CH_2Cl_2 was passed down a silica gel column (eluent: CH_2Cl_2/MeOH, 94 : 6, v/v), affording **42** quantitatively (0.020 g). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.15; Mp 88-89°C. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 2.76-2.91 (overlapping AB, $^2J_{A,B}$ = 10.1 Hz, 2H; H-6^{A}), 2.94 (s, 3H; OCH_3), 3.08 (s, 3H; OCH_3), 3.42 (s, 6H; OCH_3), 3.44 (s, 3H; OCH_3), 3.45 (s, 3H; OCH_3), 3.46 (s, 3H; OCH_3), 3.47 (s, 3H; OCH_3), 3.48 (s, 6H; OCH_3), 3.48 (s, 3H; OCH_3), 3.61 (s, 3H; CH_3O-3), 3.62 (s, 3H; CH_3O-3), 3.63 (s, 3H; CH_3O-3), 3.63 (s, 3H; CH_3O-3), 3.64 (s, 6H; CH_3O-3), 3.64 (s, 3H; CH_3O-3), 3.01-3.97 (34H; H-2, H-3, H-4, H-$5^{B,C,D,E,F}$, H-$6^{B,C,D,E,F}$), 4.35 (m, 1H; H-5^{A}), 4.72 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1), 5.01 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, 1H; H-1), 5.04 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.5 Hz, 1H; H-1), 5.06 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, 1H; H-1), 5.07 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, 1H; H-1), 5.23 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.5 Hz, 1H; H-1), 7.40-7.47

(6H; H_{meta}, H_{para}), 7.65-7.79 (4H; H_{ortho}); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 30.12 (d, $J_{C,P}$ = 66.4 Hz; C-6^A), 57.72, 57.74 [×2], 57.82, 58.00 and 58.02 (CH_3O-2), 58.64, 58.72, 59.02, 59.04 and 59.10 (CH_3O-6), 61.60, 61.65, 61.79, 61.82 [×2] and 61.87 (CH_3O-3), 68.63 (d, $^3J_{C,P}$ = 6.8 Hz; C-4^A), 70.49, 71.07, 71.24, 71.37 and 71.49 (C-$6^{B,C,D,E,F}$), 70.98, 71.01, 71.13, 71.21 and 71.27 (C-$5^{B,C,D,E,F}$), 80.97, 81.02 [×3], 81.27 [×3], 81.36, 82.01, 82.06 [×3], 82.12, 82.15, 82.20, 82.40 and 82.50 (C-2, C-3, C-$4^{B,C,D,E,F}$), 86.90 (d, $^2J_{C,P}$ = 8.1 Hz; C-5^A), 99.09, 99.92, 99.99, 100.13 [×2] and 100.28 (C-1), 128.36 (d, $^2J_{C,P}$ = 11.8 Hz; C_{ortho}), 128.38 (d, $^2J_{C,P}$ = 11.8 Hz; C_{ortho}), 130.56 (d, $^3J_{C,P}$ = 9.3 Hz; C_{meta}), 130.79 (d, $^3J_{C,P}$ = 9.9 Hz; C_{meta}), 131.20 (d, $^4J_{C,P}$ = 1.9 Hz; C_{para}), 131.37 (d, $^4J_{C,P}$ = 3.1 Hz; C_{para}), 135.34 (d, $J_{C,P}$ = 99.9 Hz; C_{ipso}), 135.63 (d, $J_{C,P}$ = 99.9 Hz; C_{ipso}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 28.5 (s); elemental analysis (%) calcd for $C_{65}H_{103}O_{30}P$ (1395.47): C 55.95, H 7.44; found: C 56.55, H 7.36.

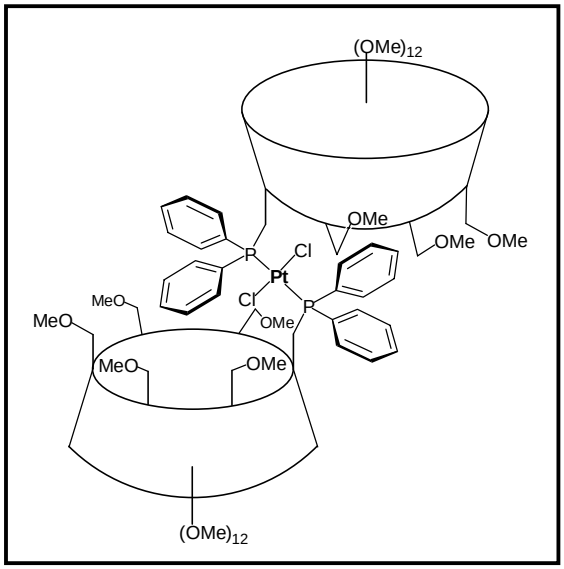
_P_-(6^A-Diphenylphosphinyl-6^A-deoxy-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^B,6^C,6^D,6^E,6^F-heptadeca-_O_-methyl-α-cyclodextrin)-[chloro(_o_-dimethylaminobenzyl) palladium(II)] (43)



To a solution of **L8** (0.100 g, 0.0725 mmol) in CH_2Cl_2 (10 mL) was added a solution of [(_o_-$C_6H_4CH_2NMe_2$)PdCl]$_2$ (0.020 g, 0.0363 mmol) in CH_2Cl_2 (5 mL). After 15 min. the reaction mixture was concentrated to 2 mL and pentane (150 mL) was added to precipitate side products, which were then filtered off over celite. Evaporation of pentane yielded a yellow residue, which was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 94 : 6, v/v) to afford pure **43** (36 mg, 55 %). R_f (CH_2Cl_2/MeOH,

94 : 6, v/v) = 0.30; Mp 139-140°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.74 (br d, 3H; NCH_3), 2.90 (m, 1H; H-6a^{A}), 2.92 (d, $^{4}J_{P,H}$ = 2.0 Hz, 3H; NCH_3), 3.11-3.19 (6 overlapping dd, 6H; H-2), 3.12 (s, 3H; OCH_3), 3.29 (s, 3H; OCH_3), 3.37 (s, 6H; OCH_3), 3.40 (s, 3H; OCH_3), 3.41 (s, 3H; OCH_3), 3.42 (s, 3H; OCH_3), 3.46 (s, 3H; OCH_3), 3.47 (s, 3H; OCH_3), 3.48 (s, 3H; OCH_3), 3.48 (s, 3H; OCH_3), 3.51 (s, 3H; OCH_3), 3.57 (s, 3H; OCH_3), 3.59 (s, 3H; OCH_3), 3.62 (s, 3H; OCH_3), 3.63 (s, 3H; OCH_3), 3.63 (s, 3H; OCH_3), 3.36-4.41 (31H, H-3, H-4, H-5, H-6a^{B,C,D,E,F}, H-6b, NCH_2), 4.82 (d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, 1H; H-1), 5.04-5.07 (4 overlapping d, 4H; H-1), 5.53 (br d, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.0 Hz, 1H; H-1), 6.32-6.42 (m, 2H; H_{ortho}, H_{meta} of DMBA), 6.79 (dt, J = 7.3 and 1.2 Hz, 1H; H_{para} of DMBA), 6.87 (br d, J = 6.9 Hz, 1H; H_{meta} of DMBA), 7.25-7.30 (6H; H_{meta}, H_{para}), 7.78-7.92 (4H; H_{ortho}); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 28.38 (d, $J_{C,P}$= 31.0 Hz; C-6^{A}), 50.00 (d, $^{3}J_{C,P}$ = 1.4 Hz; NCH_3), 51.44 (d, $^{3}J_{C,P}$ = 3.1 Hz; NCH_3), 57.24, 57.68, 57.79, 57.83, 57.89 and 58,07 (CH_3O-2), 58.91 [×2], 59.00, 59.08 and 59.29 (CH_3O-6), 61.33, 61.45, 61.61, 61.71 [×2] and 61.75 (CH_3O-3), 70.65 (d, $^{2}J_{C,P}$ = 3.9 Hz; C-5^{A}), 70.92, 71.05 [×2], 71.10 and 71.27 (C-5^{B,C,D,E,F}), 71.30, 71.38, 71.44 [×2] and 71.71 (C-6^{B,C,D,E,F}), 73.00 (NCH_2), 80.56, 80.60, 80.89, 81.04, 81.21, 81.27 [×2], 81.39, 81.61, 81.73, 82.01 [×2], 82.09, 82.16, 82.27 [×2], 82.65 and 83.72 (C-2, C-3 and C-4), 97.61, 99.29, 99.33, 99.73, 99.92 and 100.10 (C-1), 122.07 (s, C_{meta} of DMBA), 123.81 (s, C_{para} of DMBA), 124.65 (d, $^{3}J_{C,P}$ = 5.0 Hz; C_{meta} of DMBA), 127.80 (d, $^{3}J_{C,P}$ = 10.5 Hz; C_{meta}), 127.87 (d, $^{3}J_{C,P}$ = 10.5 Hz; C_{meta}), 129.84 (d, $^{4}J_{C,P}$ = 1.9 Hz; C_{para}), 129.92 (d, $^{4}J_{C,P}$ = 1.9 Hz; C_{para}), 132.68 [×2] (d, $J_{C,P}$ = 45.9 Hz; C_{ipso}), 133.86 (d, $^{2}J_{C,P}$ = 11.2 Hz; C_{ortho}), 134.01 (d, $^{2}J_{C,P}$ = 11.2 Hz; C_{ortho}), 137.93 (d, $^{2}J_{C,P}$ = 9.9 Hz; C_{ortho} of DMBA), 148.62 (d, $J_{C,P}$ = 2.5 Hz; C_{quat} of DMBA), 151.25 (s, C_{quat} of DMBA); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 25.3 (s); elemental analysis (%) calcd for $C_{74}H_{115}ClNO_{29}PPd$ (1655.54): C 53.69, H 7.00; found: C 53.45, H 6.85.

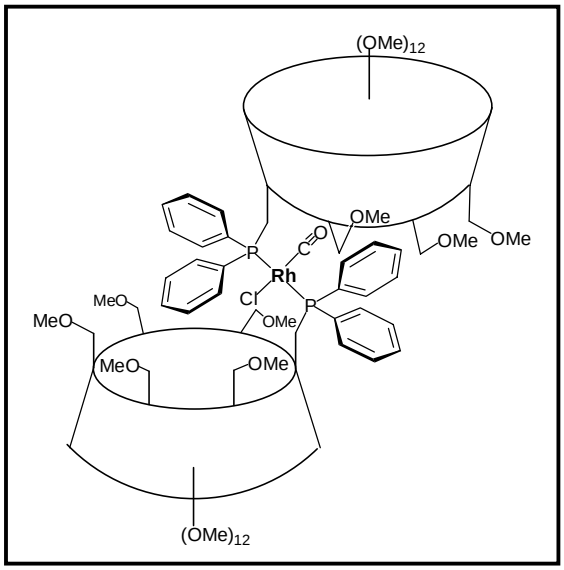
***trans*-*P*,*P'*-Dichloro-bis-(6^{A}-diphenylphosphinyl-6^{A}-deoxy-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin)platinum(II) (44)**



To a solution of CH_2Cl_2 (15 mL) containing **L8** (0.180 g, 0.131 mmol) was added a solution of CH_2Cl_2 (5 mL) containing [$PtCl_2(MeCN)_2$] (0.023 g, 0.0661 mmol). After 20 min. the solvent was evaporated to dryness. The pale yellow residue was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 94 : 6, v/v) to afford pure **44** (0.102 g, 52 % based on **L8**). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.25; Mp 152-153°C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.09 (s, 6H; OCH_3), 3.20 (s, 6H; OCH_3), 3.29 (s, 6H; OCH_3), 3.36 (s, 6H; OCH_3), 3.38 (s, 6H; OCH_3), 3.39 (s, 6H; OCH_3), 3.40 (s, 6H; OCH_3), 3.45 (s, 6H; OCH_3), 3.48 (s, 18H; OCH_3), 3.53 (s, 6H; OCH_3), 3.58 (s, 6H; OCH_3), 3.59 (s, 6H; OCH_3), 3.61 (s, 6H; OCH_3), 3.63 (s, 6H; OCH_3), 3.64 (s, 6H; OCH_3), 3.02-4.03 (70H; H-2, H-3, H-4, H-5^{B,C,D,E,F}, H-6), 4.19 (m, 2H; H-5^{A}), 4.83 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 2H; H-1), 4.90 (d, $^3J_{H\text{-}1,H\text{-}2}$ = 2.7 Hz, 2H; H-1), 5.02-5.06 (4 overlapping d, 8H; H-1), 7.34-7.39 (12H; H_{meta}, H_{para}), 7.75-7.80 (4H; H_{ortho}), 7.84-7.90 (4H; H_{ortho}); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 24.37 (virtual t, $J_{C,P} + {}^3J_{C,P'}$ = 34.8 Hz; C-6^{A}), 57.16, 57.70 [×3], 57.84 (CH_3O-6), 58.40, 58.70, 58.79, 58.81, 58.89 and 58.95 (CH_3O-2), 61.28, 61.32, 61.64 [×3] and 61.75 (CH_3O-3), 69.62 (C-4^{A}, tent. assignment), 70.64, 71.02 [×2] and 71.16 [×2] (C-5^{B,C,D,E,F}), 71.27 [×2], 71.34 [×2] and 72.06 (C-6^{B,C,D,E,F}), 80.59, 81.02, 81.20 [×5], 81.45, 81.59, 81.82, 82.15 [×2], 82.19 [×2], 82.34 and 82.41 (C-2, C-3, C-4^{B,C,D,E,F}), 89.10 (br; C-5^{A}), 98.19, 98.84, 99.49,

99.87 [×2] and 99.99 (C-1), 127.77 (br; C_{meta}), 127.83 (br; C_{meta}), 129.96 (s; C_{para}), 130.26 (s; C_{para}), 130.92 (d, $J_{C,P}$ = 9.5 Hz; C_{ipso}), 131.27 (d, $J_{C,P}$ = 10.5 Hz; C_{ipso}), 134.04 (virtual t, $^{2}J_{C,P} + {}^{4}J_{C,P'}$ = 9.9 Hz; C_{ortho}), 135.44 (virtual t, $^{2}J_{C,P} + {}^{4}J_{C,P'}$ = 10.5 Hz; C_{ortho}); $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 3.6 (s with Pt satellites, $J_{Pt,P}$ = 2614 Hz); elemental analysis (%) calcd for $C_{130}H_{206}Cl_2O_{58}P_2Pt \bullet 0.1\ CHCl_3$ (3024.92 + 11.94): C 51.45, H 6.84; found: C 51.26, H 6.65; MS (FAB): *m/z* (%): 3024.1 (4) $[M+H]^+$, 2989.1 (83) $[M–Cl+H]^+$.

***trans*-*P*,*P'*-Chloro-carbonyl-bis-(6^{A}-diphenylphosphinyl-6^{A}-deoxy-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^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin)rhodium(II) (45)**



To a solution of CH_2Cl_2 (10 mL) containing **L8** (0.100 g, 0.131 mmol) was added a solution of CH_2Cl_2 (5 mL) containing $[RhCl(CO)_2]_2$ (0.007 g, 0.0661 mmol). After 15 h the solution was concentrated to *ca.* 2 mL. Upon addition of pentane (150 mL) part of the product and ligand oxide precipitated and were filtered off over celite. Evaporation of pentane afforded **45**along with some ligand oxide. The complex was further purified by reprecipitation from CH_2Cl_2 / pentane, yielding **45** as an orange powder (0.030 g, 29 % based on **L8**). R_f (CH_2Cl_2/MeOH, 94 : 6, v/v) = 0.25; IR (KBr) ν/cm^{-1}: 1972 (C≡O). ^{1}H NMR (300 MHz, C_6D_6): δ = 2.99 (dd, $^{3}J_{H\text{-}3,H\text{-}2}$ = 9.7 Hz, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, 2H; H-2), 3.15 (s, 6H; OCH_3), 3.25 (s, 6H; OCH_3), 3.27 (s, 6H; OCH_3), 3.28 (s, 6H; OCH_3), 3.28

(s, 6H; OCH_3), 3.29 (s, 6H; OCH_3), 3.37 (s, 6H; OCH_3), 3.38 (s, 6H; OCH_3), 3.40 (s, 6H; OCH_3), 3.42 (s, 6H; OCH_3), 3.43 (s, 6H; OCH_3), 3.70 (s, 6H; OCH_3), 3.72 (s, 6H; OCH_3), 3.73 (s, 12H; OCH_3), 3.81 (s, 6H; OCH_3), 3.88 (s, 6H; OCH_3), 3.12-4.70 (68H; H-2, H-3, H-4, H-$5^{B,C,D,E,F}$, H-6), 5.04 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 2H; H-1), 5.08-5.10 (2 overlapping d, 4H; H-1), 5.14 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.2 Hz, 2H; H-1), 5.20 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 2H; H-1), 5.63 (br t, $^3J_{H\text{-}6,H\text{-}5}$ = $^3J_{H\text{-}4,H\text{-}5}$ = 7.5 Hz, 2H; H-5^A), 5.94 (d, $^3J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, 2H; H-1), 7.07-7.37 (12H; H_{meta}, H_{para}), 8.07-8.12 (m, 4H; H_{ortho}), 8.28-8.34 (m, 4H; H_{ortho}); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 14.2 (d, $J_{Rh,P}$ = 126 Hz); elemental analysis (%) calcd for $C_{131}H_{206}ClO_{59}P_2Rh \bullet 2.5\ CHCl_3$ (2925.31 + 298.44): C 49.74, H 6.52; found: C 49.54, H 6.52.

V.5. References

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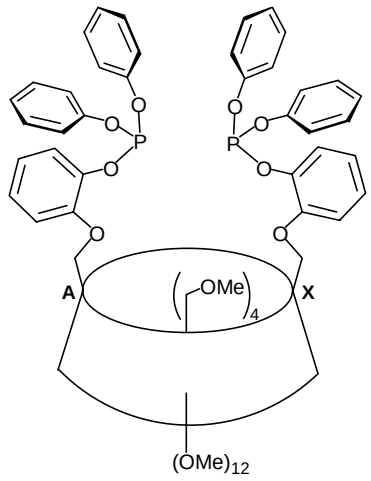
General Conclusion and Perspectives

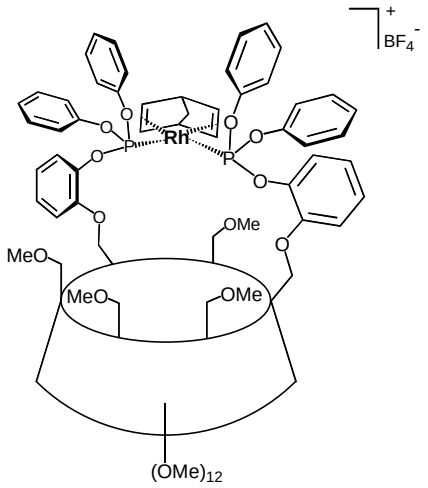
Conclusion générale

Dans cette thèse nous avons décrit la synthèse multi-étapes d'une série d'α-CD comportant jusqu'à trois ligands ″phosphane″ ancrés sur le bord primaire. Les ligands préparés ont été utilisés pour la formation de complexes chélate. La caractéristique essentielle de ces derniers concerne le positionnement du centre métallique, en aplomb de la cavité CD. Incidemment nous disposons d'un ensemble de complexes dans lesquels une cavité moléculaire est susceptible de jouer le rôle de seconde sphère de coordination.

La première partie du travail (chapitre II) fut consacrée à la préparation des deux CD **L1** et **L2**, substituées par deux fragments triarylphosphite. Leur pouvoir chélatant a été mis en évidence par la formation exclusive de métallo-macrocycles à 29 chaînons dans le cas de **L1** et 24 chaînons pour **L2** avec les cations Ag^+ et Rh^+. Ce comportement traduit un haut degré de pré-organisation de la plateforme macrocyclique qui maintient les deux sites coordinants à proximité l'un de l'autre.



L1, X=D
L2, X=C

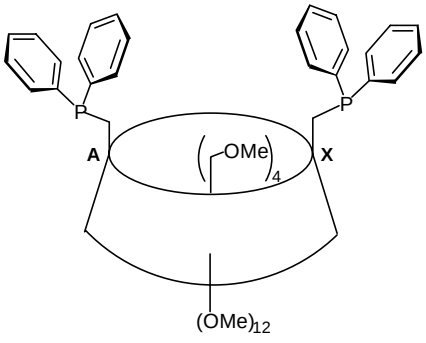


11b

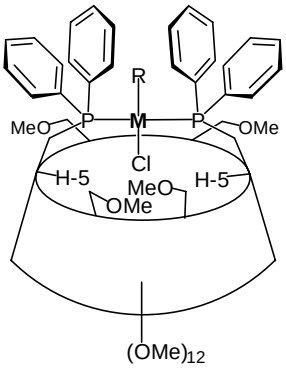
Le complexe $[Rh^I(NBD)(\mathbf{L2})]BF_4$ (**11b**) s'est avéré efficace en hydrogénation asymétrique du diméthylitaconate. Il conduit à 83.6% d'excès énantiomérique en faveur de l'isomère *R*, ce qui constitue une des valeurs les plus élevées jamais observées avec des phosphanes dérivés de CD. Ce résultat est d'autant plus remarquable que le centre catalytique se trouve éloigné des centres asymétriques de la cavité chirale. Associés à du

rhodium(I), les diphosphites **L1** et **L2** se sont également avérés efficaces en hydroformylation de l'oct-1-ène.

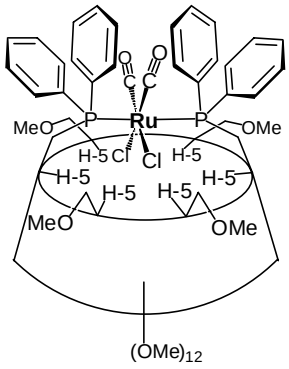
Le troisième chapitre a été consacré à l'élaboration des diphosphines chirales **L3** et **L4** qui comportent deux entités PPh_2 directement greffées sur le bord primaire (substitution A,D et A,C respectivement). De tels ligands sont parfaitement conçus pour le positionnement d'un centre métallique à l'embouchure immédiate de la cavité CD. Nous avons montré que **L3** et **L4** sont d'excellents chélatants vis-à-vis des cations Ag(I), Rh(I), Ru(II), Pt(II) et Pd(II). L'angle de chélation est toujours proche de 180°, sauf dans le cas de Ag^+ où il adopte une valeur de 143°. Les réactions de **L3** et **L4** avec les complexes chlorés [PdClMe(COD)], $[RuCl_2(CO)_2]_n$ ou $[MCl_2(PhCN)_2]$ (M = Pt, Pd) conduisent systématiquement à des complexes comportant une entité M–Cl orientée vers l'intérieur de la cavité. Une série d'études cristallographiques et en solution (RMN) ont clairement établi l'existence d'interactions faibles entre le ligand chlorure inclus et certains protons H-5, dirigés vers l'intérieur de l'espace récepteur. L'affinité de la partie interne d'une CD pour des atomes de chlore n'avait jusqu'à présent jamais été mise en évidence.



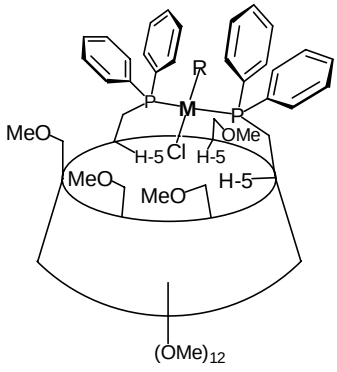
L3, X=D
L4, X=C



15a, M=Pd, R=Me
16a, M=Rh, R=CO

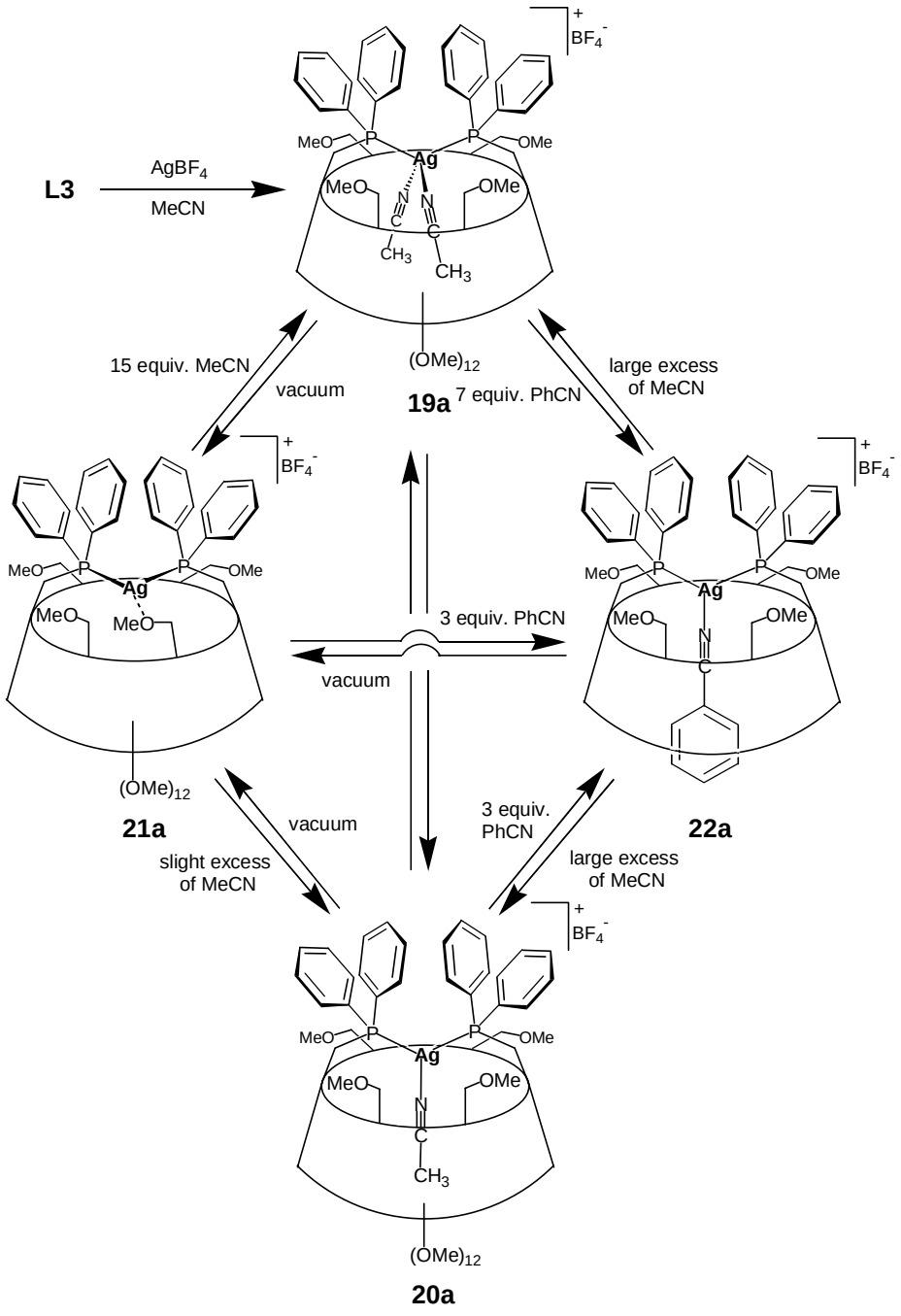


18a



15b, M=Pd, R=Me
16b, M=Rh, R=CO

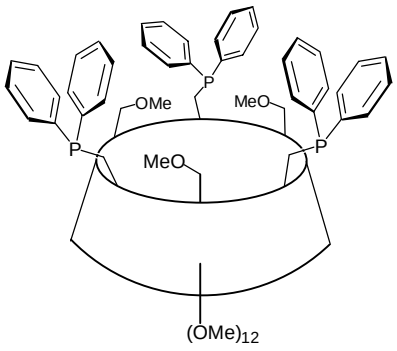
La diphosphine **L3** réagit avec $AgBF_4$ dans l'acétonitrile pour conduire à la formation de trois espèces en équilibre, **19a**-**21a**. Les complexes **20a** et **19a** contiennent respectivement un et deux coordinats acétonitrile nichés à l'intérieur de la cavité. La possibilité de former des cations de formule $[AgP_2(MeCN)_2]^+$ (P = phosphine) est ainsi démontrée pour la première fois, alors que leur existence avait déjà été postulée en 1976 par Venanzi. Visiblement, la présence d'une cavité entourant le site de complexation stabilise l'espèce dinitrile en facilitant la recoordination du second ligand acétonitrile



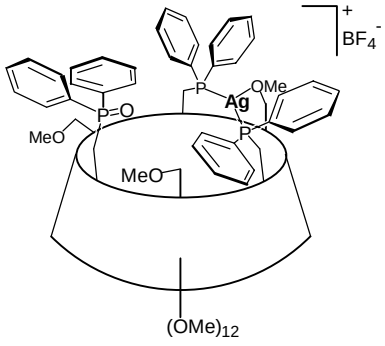
dès que celui-ci se dissocie. Cet *effet de cavité* est sans précédent en chimie de coordination. Dans le complexe **21a** on observe un rare phénomène d'hémilabilité qui implique la coordination successive de chacun des quatre groupes éther du bord primaire. Une étude par RMN à température variable a montré que l'échange des groupes méthoxy a lieu non seulement entre atomes d'oxygène diamétralement opposés, mais aussi entre atomes d'oxygène adjacents. Ainsi, le ligand **L3** constitue la première phosphine hémilabile portée par une entité macrocyclique.

Les deux diphosphines **L3** et **L4** catalysent l'hydroformylation de l'oct-1-ène ainsi que l'hydrogénation du diméthylitaconate. Cependant, les quatre groupements phényle liés aux atomes de phosphore génèrent un encombrement stérique important au-dessus de la cavité, empêchant le substrat d'accéder au centre métallique et expliquant la faible activité de ces systèmes.

L'ancrage de trois entités PPh_2 sur les positions A,C,E d'une CD fonctionnalisée a été discutée au chapitre IV. Nous avons réussi à synthétiser le premier exemple de triphosphine de symétrie C_3 basée sur une cavité moléculaire (**L5**). Nos premières études ont montré qu'en raison de la faible longueur des bras phosphorés, ce ligand est incapable d'assurer la coordination simultanée des trois atomes de phosphore à un même centre métallique. En présence de l'ion Ag^+, la triphosphine conduit au complexe **30** contenant une entité oxyde de phosphine non liée à l'argent.



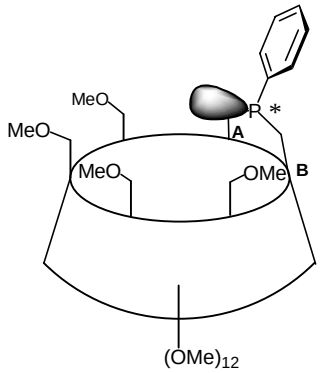
L5



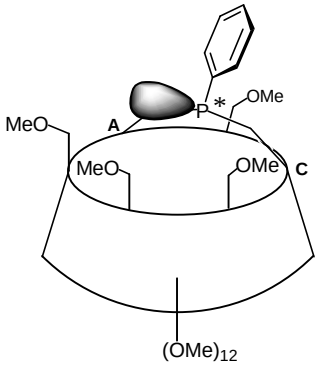
30

Dans le chapitre V, nous avons décrit le pontage stéréospécifique de deux unités glucose par une entité "PPh". Celui-ci aboutit à des monophosphines très encombrées dont l'atome de phosphore est chiral et situé sous le plan des groupements méthoxy du bord primaire. Dans les deux phosphines **L6** le **L7**, le doublet libre du phosphore est orienté vers l'axe de la cyclodextrine. L'intérêt majeur de ces ligands est de pouvoir

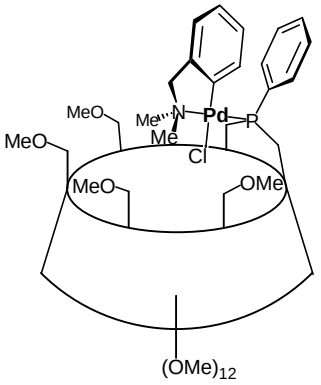
positionner de manière rigide un centre métallique à l'entrée de la cavité sans avoir à utiliser une entité chélatante.



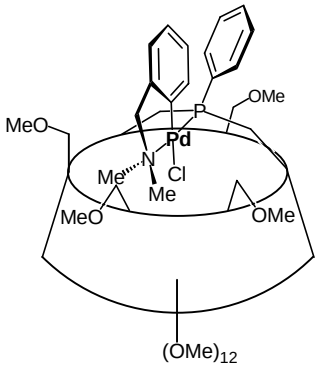
L6



L7



35a



35b

Perspectives

Les complexes présentés dans cette thèse sont tous solubles dans des solvants organiques. Une version hydrosoluble des catalyseurs étudiés permettrait de forcer le piégeage des substrats à transformer à l'intérieur de la CD et ainsi, probablement, améliorer les sélectivités de nos systèmes.

Au vu des résultats prometteurs acquis avec le diphosphite **L2** en hydrogénation asymétrique, il nous paraît intéressant d'étudier une version ″A,B″ de ce sytème qui présente également une symétrie C_1.

Les monophosphines **L6** et **L7** présentées au chapitre V se prêtent à des réactions de catalyse asymétrique fonctionnant avec des complexes monophosphine. On pourra donc envisager leur utilisation en hydrovinylation du styrène ou l'alkylation allylique.