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Synthesis and properties of TRANSDIP, a rigid chelator built upon a cyclodextrin cavity. Is TRANSDIP an authentic *trans-spanning* ligand ?

Laurent Poorters,^[a] Dominique Armspach,^{*[a]} Dominique Matt,^{*[a]} Loïc Toupet,^[b] Sylvie Choua,^[c] Philippe Turek^[c]

Dedicated to Professor Pierre Braunstein on the occasion of his 60th birthday

Abstract: The C_2 -symmetrical diphosphane **TRANSDIP** was obtained in high yield by reacting 6^A,6^B,6^D,6^E-tetramesylated, permethylated α -cyclodextrin (α -CD) with PPhLi₂ in excess. The double cascade cyclisation thus produced is regioselective as phosphinidene capping involves only adjacent glucose units. It is also stereospecific, both phosphorus lone pairs being orientated towards the CD axis. The restricted flexibility of the phosphorus atoms, which are part of 9-membered heterocyclic rings, is responsible for $J(PC)$ spin–spin couplings with the eight-bond distant CH₂OMe carbon atoms of glucose units *C* and *F*. Treatment of **TRANSDIP** with group 10-metal dihalides gave *quantitatively* square-planar chelate complexes in which a M–X bond points towards the centre of the cavitand. The favourable P...P separation and the directional control of the phosphorus lone pairs rule out the possibility of forming binuclear complexes or higher oligomers. Further, in all the complexes, the P atoms are in a *trans* arrangement. **TRANSDIP** may therefore be regarded as an authentic *trans*-spanning diphosphane. In the complex [NiCl₂•**TRANSDIP**], the cavity provides effective protection of the encapsulated M–X bond towards nucleophilic attack by MeLi. The same complex, upon activation with methylaluminoxane, efficiently dimerises ethene and propene.

Keywords: large bite angles, cavitand, diphosphane, cyclodextrin, nickel, palladium, platinum, gold, ethene dimerisation.

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Introduction

Speculations began early in the 20th century concerning the possibility of a bidentate ligand spanning opposite sites in a complex of square-planar geometry.^[1, 2] It was considered that a bidentate species with a link of sufficient length between the donor atoms might be suitable. However, nearly all efforts to build *trans*-spanned complexes led to inconclusive or negative results^[3-8] so that in the early thirties it was generally agreed that these complexes were not to be obtained simply by such means. In fact, most of the early long bidentates behaved as bridging ligands upon metal complexation, leading to coordination oligomers and polymers.^[9]

The first *trans*-spanned diphosphane complex was eventually reported in 1961 by Issleib and Hohfeld.^[10] It consists of a simple diphosphane with a pentamethene link which formed a *trans*-chelate on four-coordinate nickel(II) (Figure 1). In the following years, a multitude of ligands capable of spanning metal ions in a *trans* fashion were studied.^[11]

Figure 1. The first *trans*-spanned diphosphane complex, published by Issleib and Hohfeld in 1961.^[10]

It is noteworthy that the first *trans*-spanned diamine complex was fully characterised in 1975,^[12] although its synthesis was already reported in a Thesis published in 1946.^[13]

In 1974, Venanzi and co-workers described the **TRANSPHOS** ligand, the first *trans*-spanning diphosphane having a rigid backbone (**A**, Figure 2).^[14, 15] Built upon a benzo[*c*]phenanthrene scaffold, it was said to have a consistent preference for *trans*-coordination.^[14, 16] Since then, other diphosphines conceived as *trans*-spanning ligands were prepared, notably Ito's **ArylTRAPs** (**B**),^[17, 18] van Leeuwen's **XANTPHOS** (**C**)^[19-21] and **SPANPHOS** (**D**),^[22] Protasiewicz's *m*-terphenyl based pincer **E**^[23] and Gelman's triptycene derived bidentates **F**^[24, 25] (Figure 2). All these diphosphanes were designed to behave as chelators capable of precluding the formation of *cis* complexes. It is noteworthy that genuine

trans-spanning ligands are expected not to form bimetallic complexes or higher oligomers, in other words they should function as real chelators.

Figure 2. Some well-known *trans*-spanning diphosphanes from the literature.

While initial results were consistent with exclusive *trans*-spanning ligands, later experiments showed that *all* these diphosphanes still possess sufficient flexibility for chelate complexes with smaller bite angles to be formed. Some of them could even coordinate in a *cis* fashion. Thus, although **XANTPHOS** and its derivatives were originally designed as diphosphines having large bite angles, the P-M-P angles found in some of their complexes were as small as 98° .^[26-28] Moreover, strongly distorted square-planar geometries around the metal centre were observed in $[\text{PdCl}_2(\text{F})]$ complexes (with P-Pd-P angles of 150° and 155°), not to mention the ability of these ligands to form *P,P*-bridged dipalladium complexes.^[24] Further, treatment of **TRAP** with *trans*- $[\text{PtCl}_2(\text{MeCN})_2]$ afforded, along with the hoped-for *trans* complex, also the corresponding *cis* chelate.^[17] Likewise, about six years after their first publication dealing with **TRANSPHOS**, Venanzi's group had to admit that the latter also acts as *cis*-spanning ligand towards the PtCl_2 unit.^[29] Finally, van Leeuwen and co-workers recently published a paper entitled "**SPANPHOS**: *trans*-spanning diphosphines as *cis*-chelating ligands!", describing cationic rhodium(I)-**SPANPHOS** complexes with a *cis* configuration.^[30] Note that all of the above described diphosphines **A-F** were also shown to produce binuclear or oligomeric materials upon metal complexation.

All these setbacks demonstrate the difficulty in obtaining *genuine trans* chelators. As a consequence, even though the advantages of such diphosphines may range from the stabilisation of exotic metal geometries to unusual selectivities in various catalytic processes, their preparation still remains a challenge.

In the following, we describe the synthesis of a large diphosphane, **TRANSDIP**, leading *exclusively* to a chelate complex when reacted with a transition metal ion able to accept two two-electron donors. **TRANSDIP** is based on a α -cyclodextrin platform (α -CD). The synthetic strategy outlined hereafter allowed not only the positioning of the two coordinating atoms above the primary face of the CD macrocycle but also to control the orientation of the phosphorus lone pairs. Because of the ligand's rigidity and the appropriate phosphorus–phosphorus separation, we anticipated that this diphosphine should *selectively* result in complexes with *trans* stereochemistry when reacted with metal halides of groups IX and X. It has to be mentioned here that *trans*-chelating diphosphanes built upon a cavity (*e. g.* calixarenes,^[31, 32] and cyclodextrins^[33, 34]) have been published previously, but all these either readily form *cis*-complexes or coordination oligomers. A preliminary publication on the synthesis of **TRANSDIP** has been published previously.^[35]

Results and Discussion

Ligand synthesis: **TRANSDIP** was synthesised from the previously described tetramesylate **1**^[35] by treatment with an excess of the lithiated dianion PhPLi₂ at 18°C (Scheme 1). The resulting cyclisations produced a *single* diastereoisomer in high yield (> 95%). The formulation of the diphosphine was inferred from its FAB mass spectrum which revealed a strong peak for the $[M + H]^+$ cation (m/z 1317.4). The presence of three doublets for the H-1

Scheme 1. Synthesis of **TRANSDIP**

protons and seven singlets for the methyl groups in the ¹H NMR spectrum is consistent with a C₂-symmetrical molecule. The signals of the anomeric protons appear in a narrow range ($\Delta\delta = 0.06$ ppm), hence suggesting that the CD torus underwent no significant distortion upon capping. These findings imply that bridging of adjacent glucose units is clearly favoured over *A,C*- and *A,D*-cyclisation as well as oligomerisation, even when operating in concentrated solutions. In accord with the C₂-symmetry of the compound, the ³¹P{¹H} NMR spectrum shows a single peak at −16.8 ppm. Careful examination of the ¹³C NMR spectra (Figures 3 and 4, and SI) revealed an unexpected coupling between the phosphorus atoms and each of the symmetrically sited C-6^C and C-6^F carbon atoms. The corresponding assignments were made by HMQC (see experimental section). The couplings are likely to occur *via* through-space interactions involving the H-6^C, H-6^F hydrogen atoms and the *introverted* phosphorus lone pairs, as shown in Figure 5. Through-bond $J_{\text{P,C-6}^{\text{C,F}}}$ interactions can reasonably be ruled out in view to the fact that the C-6^{C,F} carbon atoms are separated from each phosphorus atom by 8 *single* bonds. Note that, due to overlapping signals, the corresponding $J_{\text{P,H-6}}$ couplings could not be identified. Preliminary molecular mechanics calculations (MM2) reveal that in the minimised structure the H-6^{C,F} and the P atoms lie

roughly in the same plane (Figure 5). We note that the C-6^{A,B} and C-6^{D,E} carbon atoms also experience couplings with *both* phosphorus atoms. Overall, these findings reflect the high rigidity of the two capping units.

Figure 3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **TRANS DIP** recorded in CDCl_3 at 125.8 MHz. Enlargements are found in Fig. 4 and in the supplementary information.

Figure 4. C-6^{C,F} and C-5^{C,F} signals of TRANS DIP in the $^{13}\text{C}\{^1\text{H}\}$ (top) and $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ (bottom) NMR spectra recorded in CDCl_3 at 125.8 MHz.

The calculations further show that both phosphorus lone pairs of **TRANSDIP** point towards the cavity axis (Figure 5), resulting in rather protected P(III) centres. Consistent with this structural feature, solutions of **TRANSDIP** display high stability when exposed to air. The oxidised phosphine **2** was nevertheless obtained during attempts to form nickel(II) complexes *in air* (see experimental section). Note that reaction of **TRANSDIP** with H_2O_2 resulted in a mixture of unseparable compounds. On the other hand, reaction of **TRANSDIP** with sulfur in excess gave quantitatively the di(phosphane sulfide) **3**. When the sulfuration reaction was repeated in the presence of stoichiometric amounts of sulfur, **3** was formed as the major compound, together with small amounts of a compound, which could not be separated. In view of the ^{31}P NMR spectrum of the latter, which displays an AB spectrum ($\delta_{\text{A}} = 42.2$, $\delta_{\text{B}} = -19.5$, $J(\text{PP}') = 48.7$ Hz), we assign to it the structure of monosulfide **4** (Scheme 2). In **2** as well as in **3**, the $\text{P}\cdots\text{C}-6^{\text{C (or F)}}$ couplings are lost, as revealed by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in which the corresponding C-6 signal appears as singlet. As well, the $\text{C}-6^{\text{A,D}}$ and $\text{C}-6^{\text{B,E}}$ carbon atoms give rise to well-resolved doublets in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra ($^1J_{\text{P,C-6}} = 67.0$ Hz and 67.6 Hz for **2**; $^1J_{\text{P,C-6}} = 50.8$ Hz and 52.6 Hz for **3**). These observations are a further indication of the involvement of the phosphorus lone pairs in the P-C couplings observed in **TRANSDIP**.

Figure 5. Calculated structure (MM2) of free **TRANSDIP** (right: view along the CD axis from the primary face; left, sideview).

Scheme 2. Formation of P(V) derivatives of **TRANSDIP**.

trans-Chelating properties of TRANSDIP: According to CPK models, **TRANSDIP** possesses the right geometrical features to promote the formation of *trans-P,P*-chelates upon metal complexation. Evidence of the latter was given by studying the coordination of **TRANSDIP** towards various d^8 transition metal ions prone to form square-planar metal complexes. Thus, treatment of **TRANSDIP** with a mixture of *cis* and *trans* isomers of $[\text{PtCl}_2(\text{PhCN})_2]$ afforded *quantitatively* complex **5** (Scheme 3). It should be mentioned that this reaction takes about three days in refluxing toluene to be completed and $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring showed that *neither cis nor* oligomeric compounds are formed during complexation. Complex **5** is characterised by a sharp $^{31}\text{P}\{^1\text{H}\}$ NMR signal at -6.5 ppm, flanked by Pt satellites with a $^1J_{\text{P,Pt}}$ coupling constant (2463 Hz) lying in the range expected for complexes of *trans* stereochemistry.^[36]

Scheme 3. Preparation of the chelate complexes **5** and **6**.

The palladium analogue **6**, which was *quantitatively* obtained from $[\text{PdCl}_2(\text{PhCN})_2]$ (Scheme 3), is characterised by a singlet at -0.4 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The presence in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a virtual triplet for each PCH_2 carbon atom of the *A,D* and *B,E* glucose units ($|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 20.0$ and 25.0 Hz, respectively) is in keeping with a *trans* disposition of the two phosphorus atoms.^[37] The monomeric nature of this complex was inferred from the presence of an intense signal in its mass spectrum corresponding to the $[\text{M}]^+$ ion (m/z 1494.1). In contrast to the demanding reaction conditions required for the preparation of **5** (see above), reaction between **TRANSDIP** and the palladium(II) precursor is complete within 30 min. in CH_2Cl_2 at room temperature. As for the ligand, the ^1H as well as the $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes **5** and **6** show clear evidence for twofold molecular symmetry. The location of the chlorine atoms along the CD axis could be unambiguously deduced from the ^1H NMR spectra. The latter reveal a strong deshielding (> 0.9 ppm with respect to the free ligand) of two inwardly pointing H-5 atoms, indicative of weak $\text{C-H}^5 \cdots \text{Cl}$ interactions (Figure 6). The H-5 atoms in question belong to phosphane-substituted glucose units as revealed by COSY experiments. Such interactions have already been evidenced in other CDs incorporating metal chloride entities.^[38] Moreover, the phenyl groups were found to freely rotate about the P-C(aryl) axis, as evidenced by the presence of (only) two virtual triplets for the *ortho*- and *meta*-carbon atoms in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (see experimental section). Each triplet becomes a singlet after ^{31}P decoupling.

Figure 6. ^1H NMR spectra of **TRANSDIP** (top), **5** (middle), and **6** (bottom) recorded in CDCl_3 at 300.1 MHz. The asterisks denote residual solvents (CH_2Cl_2 or toluene)

An X-ray diffraction study confirmed the *trans* disposition of the phosphorus atoms (Figure 7 and Table 1). Note that, owing to the presence of two pentane molecules in the unit cell, the refinement of this structure did not fully converge, as frequently observed for cyclodextrins. The data are, nevertheless, provide clear information about the most important structural features of the complex. The unit cell contains two distinct molecules (denoted *a* and *b*) displaying non-significant structural differences.

Figure 7. Molecular structure of complex **6**: side view (left) and bottom view (right) showing the slightly bent Cl-Pd-Cl rod (only molecule *a* is represented). Hydrogen atoms and solvent molecules are omitted for clarity (except three H-5 atoms).

Table 1. Selected bond lengths (Å) and angles (°) for 2(**6**)•2(C₅H₁₂).

Bond lengths and distances (Å)			
molecule <i>a</i>		molecule <i>b</i>	
P(1)-Pd(1)	2.394(5)	P(3)-Pd(2)	2.331(5)
P(2)-Pd(1)	2.343(5)	P(4)-Pd(2)	2.353(5)
Pd(1)-Cl(1)	2.271(5)	Pd(2)-Cl(3)	2.329(6)
Pd(1)-Cl(2)	2.337(6)	Pd(2)-Cl(4)	2.306(5)
Cl(1)-H ⁵ (5)	2.652	Cl(4)-H ⁵ (135)	2.629
Cl(1)-H ⁵ (55)	2.852	Cl(4)-H ⁵ (125)	2.747
Cl(1)-H ⁵ (45)	2.956	Cl(4)-H ⁵ (115)	2.932

Angles (°)			
molecule <i>a</i>		molecule <i>b</i>	
P(1)-Pd(1)-P(2)	174.6(2)	P(3)-Pd(2)-P(4)	171.3(2)
Cl(1)-Pd(1)-Cl(2)	162.6(3)	Cl(3)-Pd(2)-Cl(4)	163.7(2)

As expected, one of the chlorine atoms points towards the centre of the CD cavity, the other being *exo*-oriented. The shortest contacts involving the inner Cl(1) atom of molecule *a* are with the H-5 atoms H(5), H(55) and H(45) (**Figure 7**; Cl...H-5 distances: 2.652, 2.852 and 2.956 Å, respectively). Similar short separations were found in molecule *b* (**Table 1**). These are consistent with the previously established chlorophilicity of methylated α -CDs.^[34, 38] The stereochemistry of the palladium centre deviates in both molecules from an ideal square plane

coordination geometry, resulting in slightly bent Cl-Pd-Cl and P-Pd-P units, but the non linearity is more marked for the Cl-Pd-Cl rods (Cl-Pd-Cl = 162.6° and 163.7°; P-Pd-P = 174.6° and 171.3°). In fact, the observed distortion goes towards a slightly tetrahedral coordination geometry, the whole molecule being no longer C_2 -symmetric. Both P-C(aryl) bonds are inclined towards one side of the CD torus, with the *exo*-Cl atom being obviously pushed away by the phenyl rings (Cl(2)-Pd(1)-P-C(Ar) torsion angles in a: 34.7 and -29.6°). On the other hand, repulsion of the *endo*-Cl atom by the CD wall prevents the metal centre from adopting a perfect square-planar geometry. The apparent twofold symmetry observed in solution can be rationalised in terms of a fast oscillation of the Cl-Pd-Cl unit about the P-P axis, as shown in Figure 8. This motion could however not be frozen out on the NMR time scale on cooling a CD₂Cl₂ solution of the complex down to -80°C.

Figure 8. Proposed fast oscillation of the Cl-Pd-Cl unit about the P-P axis in complex 6.

The coordination properties of **TRANSDIP** were further assessed towards nickel(II) centres. Thus, the violet nickel complex **7** and the green complex **8** were *quantitatively* formed by reaction of **TRANSDIP** with [NiCl₂] and [NiBr₂], respectively (Scheme 4). In both reactions a transient red species was observed, but the latter could not be isolated. The diamagnetic complexes were characterised by ¹H (Figure 9), ¹³C{¹H} and ³¹P{¹H} NMR spectroscopy, as well as MS and elemental analysis (see experimental part). The *trans* arrangement of the phosphorus atoms was deduced from the ¹³C{¹H} NMR spectrum in which the PCH₂ atoms appear as virtual triplets ($|^1J_{C,P} + ^3J_{C,P}| \approx 18$ Hz).

Scheme 4. Preparation of complexes **7** and **8**.

Figure 9. ^1H NMR spectra of **7** (top) and **8** (bottom) recorded in CDCl_3 at 300.1 MHz.

Finally, EPR spectroscopy measurements showed that, at temperatures as low as 4K, complex **8** remained diamagnetic.

Binding properties of TRANSDIP towards unsymmetrical X–M–Y rods: Another example illustrating the *trans*-chelating behaviour of **TRANSDIP** is its reaction with [PdClMe(COD)] (COD = 1,5-cyclooctadiene) in CH₂Cl₂, leading *quantitatively* to complex **9** (Scheme 5). The formation of a monomeric species was inferred from the MALDI-TOF mass spectrum, which displays a peak at *m/z* 1474.1 corresponding to the [M]⁺ cation. Again, all NMR spectra are consistent with a C₂-symmetrical species. The *trans* stereochemistry was deduced from the presence of a symmetrical methyl triplet in the ¹H NMR spectrum (³J_{H,P} = 6.8 Hz). As for the previously described complexes **5–8**, two H-5 protons of phosphinidene-capped glucose rings have undergone a significant lowfield shift (*ca.* 1.1 ppm) upon chloride encapsulation. This result is corroborated by 2D ROESY experiments, which unambiguously establish a spatial proximity between the *exo*-oriented methyl group and some H-6 protons as well as the PPh units.

Scheme 5. Preparation of complexes **9** and **10**.

It must be emphasised here that, from a steric point of view the upper part of the cavity is perfectly capable of entrapping a methyl unit. This was demonstrated by treating **TRANSDIP** with [PdMe(py)(COD)]BF₄ (py = pyridine). This reaction resulted in the *exclusive* formation of *trans*-**10** (Scheme 5), a complex with an *endo*-oriented Me group. Owing to the lability of the pyridine ligand, **10** is stable in solution only in the presence of a slight excess of pyridine. The *endo* orientation of the methyl group was deduced from a ROESY spectrum which showed cross peaks between the palladium-bound Me moiety and some of the inner-cavity

CD protons. This 2D NMR experiment also revealed that the coordinated pyridine interacts with both phenyl groups. Addition of free Cl^- anions to a solution of **10** regenerated **9**, which means that in this latter reaction the Pd-Me bond is expelled from the cavity (Scheme 5).

The affinity of the CD cavity for metal bound chlorides was also exemplified by the synthesis of complex **11**, obtained *quantitatively* by reaction of **TRANS**DIP with $[\text{RhCl}(\text{CO})(\text{COD})]$ in CH_2Cl_2 (Scheme 6). The ^1H NMR spectrum of **11** reveals that, as expected, two symmetrically sited H-5 atoms (belonging to P-capped glucose units) are significantly downfield shifted compared to the four others, owing to weak interactions with the entrapped Cl atom. Attempts to replace the encapsulated Cl atom by a hydrido ligand by treatment of **11** with NaBH_4 in ethanol produced a mixture of compounds which could not be separated. Note that entrapment of a Rh–H bond in a CD cavity was achieved recently with another, more flexible, CD-derived diphosphane.^[34]

Scheme 6. Selective Rh–Cl bond entrapment by a cyclodextrin cavity.

An interesting reaction in which the cavity behaves as a protecting funnel towards an incoming nucleophile is that between **8** and a large excess of MeLi in Et_2O at -78°C (Scheme 8). This reaction gave selectively the monosubstituted derivative **12**. The NMR spectrum of **12** shows a single Me signal (intensity 3H), at -0.94 ppm; a ROESY experiment confirmed the positioning of this group nearby the phenyl rings. Consistent with the presence of an unaffected NiBr unit lying inside the cavity, the ^1H NMR spectrum shows a H-5 signal (integral 2H; protons belonging to P-capped glucose units) that has undergone a significant low-field shift with respect to that of the free ligand. The deshielding is even more pronounced than that observed for **8** (Figure 10). The reaction leading to **12** constitutes the first example in which a $[\text{NiX}_2\text{P}_2]$ complex undergoes a *selective mono*-alkylation, whatever the stoichiometry of alkylating agent used.^[39] In other words, the protection of the cavity is

sufficient to prevent the substitution of the inner bromide. Interestingly, no reaction occurred when a solution of PhLi was added to **8**, probably because access to the metal centre by the bulkier Ph⁻ nucleophile is sterically hindered.

Scheme 7. A CD cavity acting as a protecting funnel towards an incoming nucleophile.

Figure 10. ¹H NMR spectrum of **12** recorded in C₆D₆ at 500.1 MHz. The starred signals correspond to anomeric protons.

Is TRANSDIP a perfect trans chelator ? All the complexation reactions described above, which involve group 10 metal halides, are quantitative and in none of them oligomeric complexes were formed. Therefore, **TRANSDIP** may be regarded as an excellent chelator. Moreover, all the complexes formed display trans stereochemistry. Interestingly, the PMP angles found in [PdCl₂(**TRANSDIP**)], 171.3° and 174.6°, suggest that the natural bite angle of the ligand is somewhat smaller than 180°. To confirm this assumption we studied the reaction of **TRANSDIP** with [Au(THT)(CH₂Cl₂)]PF₆ (THT = tetrahydrothiophene), leading to

13 (Figure 11). The Au^+ ion was used because of its known ability to form perfectly linear P–Au–P arrangements.^[40] As for **6**, the solid state structure of **13** reveals a non linear P–Au–P fragment, the two P–Au vectors being somewhat bent towards the cavity centre (PAuP = 163.4°). For comparison, a value of $175.1(1)^\circ$ was found in $[(\text{PhMe}_2\text{P})_2\text{Au}][\text{Au}(\text{GeCl}_3)_2]$.^[41] The P–Au bond lengths (2.319 and 2.324 Å) fall in the range expected for $[\text{AuPR}_3]_2^+$ cations.^[42] What about the flexibility of **TRANSDIP**? This question was addressed recently on studying $[\text{AgX}(\text{TRANSDIP})]$ (X = halide) chelate complexes.^[43] While PAgP angles near 120° were expected for these complexes, actual values of ca. 143° were found in the solid state. These observations illustrate the relatively weak flexibility of **TRANSDIP**, unable to accommodate an ideal trigonal planar coordination geometry. Unsurprisingly, no cis complex was formed upon reaction of **TRANSDIP** with MX_2 moieties (M = group 10 metal ions).

Figure 11. X-ray structure of the gold(I) complex **13**. The figure shows also the PF_6 anion and only one of the four $\text{C}_2\text{H}_2\text{Cl}_4$ solvent molecules.

Catalytic properties of $[\text{NiX}_2(\text{TRANSDIP})]$ complexes: An interesting property of **TRANSDIP** concerns its catalytic properties. After activation with methylaluminoxane (MAO), the complexes **7**, **8** and **12** catalyse the oligomerisation of ethene as well as that of propene.

Dimerisation of ethene. The ethene oligomerisation tests were carried out in toluene in a 100 mL steel autoclave under various conditions (Table 2). The catalytic reaction started as

soon as an ethene pressure was applied, producing a slow but steady temperature increase over a period of *ca.* 1 h [$P(\text{C}_2\text{H}_4) = 30$ bar, $\Delta T = 17\text{-}21^\circ\text{C}$], independently of the catalyst precursor used.

Table 2. Catalytic ethene dimerisation in a 100 mL steel autoclave.^[a]

Entry	Catalyst precursor	t (min.)	P(C ₂ H ₄) (bar)	[Al]/[Ni]	Yield ^[b] (g)	TOF ^[c] (/10 ⁻⁴)	Selectivity C4 ^[d] (wt-%)	α -C4 ^[e]
1	[NiBr ₂]	60	30	2000	0.0	—	—	—
2	[NiBr ₂ (DME)]	60	30	2000	0.0	—	—	—
3	7	60	30	2000	4.3	3.4	>99	50.0
4	8	60	30	400	1.9	1.5	>99	42.4
5	8	60	30	1000	3.3	2.6	>99	42.9
6	8	60	30	2000	5.4	4.3	>99	40.4
7	8	60	20	2000	5.0	3.9	>99	59.7
8	8	60	10	2000	1.5	1.2	>99	54.8
9	8	30	30	2000	2.5	4.0	>99	41.1
10	8	120	30	2000	9.2	3.6	>99	41.1
11	12	60	30	2000	5.4	4.3	>99	47.4
12	12	60	30	0	0.0	—	—	—

[a] 4.5 μmol of catalyst, toluene 22 mL, $T = 25^\circ\text{C}$, 500 rpm. For all experiments the results were averaged. [b] Yield determined by mass of final reaction mixture *versus* mass of control reaction in toluene (22 mL). [c] mol of C₂H₄ converted per mol of Ni per hour [$\text{mol}(\text{C}_2\text{H}_4) \text{ mol}(\text{Ni})^{-1} \text{ h}^{-1}$]. [d] Determined by GC. [e] Determined by ¹H NMR spectroscopy: 1-butene was identified at $\delta = 2.00, 4.95$ and 5.78 ppm; resonances for the 2-butenes appear at $\delta = 1.54$ and 5.37 (*cis* form) and at $\delta = 1.58$ and 5.55 (*trans*) ppm.

The three nickel(II) complexes turned out to be good dimerisation catalysts, the observed TOFs ranging from 12000-43000 $\text{mol}(\text{C}_2\text{H}_4) \text{ mol}(\text{Ni})^{-1} \text{ h}^{-1}$. For comparison, under similar conditions, the TOF observed for [NiBr₂(Ph₂PCH₂CH₂PPh₂)]/MAO was 34000 $\text{mol}(\text{C}_2\text{H}_4) \text{ mol}(\text{Ni})^{-1} \text{ h}^{-1}$.^[44] During catalysis, ligand dissociation is very unlikely to occur, considering the observed lack of reactivity of the [NiBr₂]/MAO and [NiBr₂(DME)]/MAO systems (entries 1 and 2, Table 2). In fact, the catalytic systems were found to be active over a period longer than 2 h, which is indicative of the high stability of the active species. The TOF reaches its maximum value after *ca.* 1 h, upon which the activity decreases very slowly, possibly owing to the increasing viscosity of the solution.

The three complexes **7**, **8** and **12** showed similar behaviour. With each catalyst, the observed butene selectivity was higher than 99%, the longest olefins detected by gas chromatography (GC) being octenes. As usually observed for [NiX₂L₂] complexes, the catalyst activity of **8** increased with the amount of MAO, but the maximum activity was not yet reached using 2000 equiv. (entries 4-6, Table 2). The proportion of 1-butene obtained with

8 depended on the reaction conditions and reached 60% in the best case [$P(C_2H_4) = 20$ bar]. On the other hand, the amount of MAO used did not affect the product distribution.

Monitoring the reaction temperature at the beginning of catalysis revealed that upon addition of MAO and ethene, the exothermicity of the reaction was more important with **7** than with **8** and **12**. This finding suggests that halide abstraction by MAO from the CD-funnel occurs more readily for chloride than for bromide, and, accordingly, that with the former complex full conversion into a catalytically active species is faster. Note that complex **12** is not active in the absence of MAO (entry 12, Table 2), confirming that no halide must be left in the first coordination sphere of the catalytically active species.

Dimerisation of propene. A propene dimerisation experiment was carried out with complex **8** in chlorobenzene in a 200 mL Büchi glass autoclave. The catalyst was generated by treatment of **8** with 2000 equiv. of MAO (Table 3). The activity of the catalyst at room temperature and under 5 bar propene, $14000 \text{ mol}(C_3H_6) \text{ mol}(\text{Ni})^{-1} \text{ h}^{-1}$, was about 8 times lower than that of $[\text{NiBr}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]/\text{MAO}$.^[45] This difference is probably due to a higher crowding about the nickel centre in **8**. As already observed in the ethene dimerisation experiments, the active species turned out to be remarkably stable during catalysis. The distribution (determined by GC/mass) of the primary products (those obtained after β -elimination) and the isomerisation products is given in Table 4.

Table 3. Catalytic propene dimerisation with **8** or $[\text{NiBr}_2(\text{dppe})]$.^[a]

Entry	Catalyst precursor	[Al]/[Ni]	Yield (g)	TOF ^[b] (10^4)	Selectivity C6 ^[c] (wt-%)	Ref.
1 ^[d]	8	2000	2.6	1.4	75.6	this work ^[45]
2	$[\text{NiBr}_2(\text{dppe})]$	400	21.7	11.5	87.0	

[a] in a 200 mL Büchi autoclave; 4.5 mmol of catalyst, chlorobenzene 30 mL, $T = 25^\circ\text{C}$, $t = 60$ min., $P(C_3H_6) = 5$ bar. [b] mol of C_3H_6 converted per mol of Ni per hour $[\text{mol}(C_3H_6) \text{ mol}(\text{Ni})^{-1} \text{ h}^{-1}]$. [c] Determined by GC. [d] The results were averaged over 3 experiments.

Table 4. Product distribution of the propene dimerisation with **8** or [NiBr₂(dppe)].

Entry	Catalyst precursor	Product distribution (mol-%) ^[a]						MP (%) ^[b]	Ref.
		4M1P	4M2P	2M1P	2M2P	Hex.	TMEN		
1 ^[c]	8	1.4	32.6	7.8	52.2	3.6	2.4	94.0	this work ^[45]
2	[NiBr ₂ (dppe)]	2.2	35.8	14.8	41.0	5.0	1.2	93.8	

[a] Determined by GC/mass. 4M1P: 4-methyl-1-pentene, 4M2P: 4-methyl-2-pentene, 2M1P: 2-methyl-1-pentene, 2M2P: 2-methyl-2-pentene, Hex.: hexenes, TMEN: 2,3-dimethyl-2-butene. [b] Total methyl-pentene (MP). [c] The results were averaged over 3 experiments.

As can be inferred from [Table 4](#), the system clearly favours the formation of methylpentenes (MP). Interestingly, the proportion of the isomerisation product 2M2P is higher than 50%. This result is somewhat surprising, in view to the fact that nickel(II) catalysts containing basic diphosphines are known to form preferentially 2,3-dimethylbutenes.^[46]

Comments on the dimerisation mechanism: in the conventional olefin dimerisation mechanism using Ni(PR₃)₂X₂/MAO mixtures, square planar [Ni(PR₃)₂(alkyl)(olefin)]⁺ intermediates adopting a cis configuration are formed before the insertion step.^[47, 48] Obviously, owing to the rather high rigidity of **TRANSDIP**, related intermediates with cis-bonded phosphines are unattainable with this chelator. Since formation of a C–C bond requires that the moieties undergoing coupling come close together, it appears likely that dimerisation with **7**, **8** or **12** involves intermediates either with a sawhorse or a trigonal bipyramidal (TBP) structure, as shown in [Figure 12](#) (complexes *a* and *b*). Note that, from a

Figure 12. Proposed intermediates in the dimerisation of ethene with **7**/MAO.

stereochemical point of view, both types of complexes allow the migratory insertion to take place inside the cavity, but we have no indication that such a process occurs. It should further be mentioned here that in view of the ease of oxidising Ni(II) species, catalytic intermediates with a Ni(III) centre can formally not be ruled out. Further experiments as well as theoretical calculations are needed to exclude or confirm these hypotheses.

Conclusion

In summary, we have shown that reaction of PhPLi_2 with the $6^{\text{A}}, 6^{\text{B}}, 6^{\text{D}}, 6^{\text{E}}$ -tetramesylated precursor **1** occurs in a regiospecific manner, resulting in the selective formation of **TRANSDIP**, an A,B:D,E capped cyclodextrin with two facing phosphane units. The restricted flexibility of this C_2 -symmetrical diphosphane is responsible for the existence of through-space spin–spin couplings between the phosphorus atoms and the eight-bond distant CH_2OMe carbon atoms of glucose units *C* and *F*.

TRANSDIP displays remarkable complexation properties, which are notably illustrated by its reaction with d^8 -metal ion halides, affording *exclusively* chelate complexes. The fact that no oligomers were formed in these reactions relies on both the imposed $\text{P}\cdots\text{P}$ separation and the ligand rigidified structure. Moreover, in all the square-planar complexes obtained from **TRANSDIP**, the phosphorus atoms are *trans* disposed. **TRANSDIP** may therefore be regarded as an *authentic trans*-spanning ligand. As pointed out above, such ligands are extremely rare. A further interesting feature of **TRANSDIP** is the presence nearby the phosphorus atoms of a receptor, which may behave as a second coordination sphere. Thus, in $[\text{NiX}_2(\text{TRANSDIP})]$ complexes ($\text{X} = \text{halide}$), the cavity provides a steric protection of one of the two $\text{M}-\text{X}$ bonds, thereby enabling an efficient discrimination of the two halides in nucleophilic substitution reactions.

Finally, our finding that $[\text{NiX}_2(\text{TRANSDIP})]$ complexes may, after activation with MAO, efficiently dimerise ethene and propene clearly indicates that the formation of intermediates in which the two phosphorus atoms are bonded in a *cis* fashion is not a requirement for achieving the CC coupling step. Elucidation of the exact mechanism leading

to the dimers, as well as the stereochemistry of the intermediates involved in such reactions are currently underway.

Experimental Section

General procedures: All commercial reagents were used as supplied. The complexes $[\text{PtCl}_2(\text{PhCN})_2]$,^[49] $[\text{PdCl}_2(\text{PhCN})_2]$,^[49] $[\text{PdClMe}(\text{COD})]$,^[50] and $[\text{AuCl}(\text{THT})]$ ^[51] were synthesised according to literature procedures. All manipulations involving phosphines were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Column chromatography was performed on silica gel 60 (particle size 40-63 μm , 230-240 mesh). CDCl_3 was passed down a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 25°C with an FT Bruker and AC300 (^1H : 300.1 MHz, ^{13}C : 75.5 MHz, ^{31}P : 121.5 MHz) instrument and an Avance 500 Bruker (^1H : 500.1 MHz, ^{13}C : 125.8 MHz) instrument. ^1H NMR spectral data were referenced to residual protiated solvents [7.26 ppm for CDCl_3 ; 7.16 ppm for C_6D_6 ; 2.05 ppm for $(\text{CD}_3)_2\text{CO}$], ^{13}C chemical shifts are reported relative to deuterated solvents [77.0 ppm for CDCl_3 ; 128.06 ppm for C_6D_6 ; 29.84 ppm for $(\text{CD}_3)_2\text{CO}$], and the ^{31}P NMR data are given relative to external H_3PO_4 . Mass spectra were recorded either on a Bruker MaldiTOF spectrometer using α -cyano-4-hydroxycinnamic acid or 1,8,9-trihydroxy anthracene (dithranol) as matrix, or on a Bruker MicroTOF spectrometer (ESI) using CH_2Cl_2 , CH_3CN or CH_3OH as solvent. IR spectra were recorded on a Perkin Elmer 1600 instrument. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus.

Assignment of the stereochemistry of the P atoms (namely *R* for both P atoms in **TRANSDIP**) was made by giving arbitrarily priority to glucose units *A* and *D* over glucose units *B* and *E*, respectively. The numbering of the atoms within a glucose unit is as follows:

Synthesis of ligands and complexes

$6^A, 6^B, 6^D, 6^E$ -Tetradecoxy- $6^A, 6^B: 6^D, 6^E$ -bis[(*R*)-phenylphosphinidene]- $2^A, 2^B, 2^C, 2^D, 2^E, 2^F, 3^A, 3^B, 3^C, 3^D, 3^E, 3^F, 6^C, 6^F$ -tetradeca-*O*-methyl- α -cyclodextrin (TRANSDIP): A solution of BuⁿLi in hexane (1.60 M, 1.7 mL, 2.72 mmol) was added dropwise to a stirred solution of PhPH₂ (0.148 g, 1.36 mmol, *ca.* 0.15 mL) in THF (25 mL) at – 78°C whereupon the yellow solution was allowed to reach room temperature. After 10 min, a yellow precipitate appeared. The resulting suspension was stirred at room temperature for an additional hour before being transferred within 1h via a cannula to a solution of tetramesylate **1** (0.400 g, 0.27 mmol) in THF (20 mL) kept at 20°C. After stirring for 14 h, the solvent was removed under vacuum and excess Li₂PPh quenched with methanol (20 mL). After removal of the solvent in vacuo, toluene was added to the residue and the resulting suspension filtered over a bed of Celite. Evaporation to dryness afforded analytically pure TRANSDIP (yield 0.348 g, 98%). *R_f* (SiO₂, CH₂Cl₂/MeOH, 92:8, v/v) = 0.37; Mp 198°C dec. ¹H NMR (500.1 MHz, CDCl₃, 25°C): δ (assignment by COSY) = 1.80 (m, 4 H, H-6a^{A,B,D,E}), 3.00 (broad dd, 2 H, ²*J*_{H-6b,H-6a} = 15.1 Hz, ²*J*_{H-6b,P} = 15.1 Hz, H-6b^{A,D or B,E}), 3.06 (s, 6 H, OMe), 3.14 (dd, 2 H, ³*J*_{H-2,H-1} = 3.2 Hz, ³*J*_{H-2,H-3} = 9.9 Hz, H-2^{B,E or A,D}), 3.19 (dd, 2 H, ³*J*_{H-2,H-1} = 3.4 Hz, ³*J*_{H-2,H-3} = 9.8 Hz, H-2^{C,F}), 3.20-3.33 (6 H, H-4^{A,B,D,E}, H-6b^{B,E or A,D}), 3.44-3.70 (12 H, H-2^{A,D or B,E}, H-3, H-4^{C,F}, H-6a^{C,F}), 3.47 (s, 6 H, OMe), 3.47 (s, 6 H, OMe), 3.52 (s, 6 H, OMe), 3.62 (s, 6 H, OMe), 3.65 (s, 6 H, OMe), 3.68 (s, 6 H, OMe), 3.99-4.06 (6 H, H-5^{A,D or B,E}, H-5^{C,F}, H-6b^{C,F}), 4.33 (m, 2 H, H-5^{B,E or A,D}), 4.98 (d, 2 H, ³*J*_{H-1,H-2} = 3.2 Hz, H-1^{B,E or A,D}), 5.03 (d, 2 H, ³*J*_{H-1,H-2} = 4.5 Hz, H-1^{A,D or B,E}), 5.04 (d, 2 H, ³*J*_{H-1,H-2} = 3.4 Hz, H-1^{C,F}), 7.18 (m, 4 H, *m*-H), 7.26 (m, 2 H, *p*-H), 7.47 (m, 4 H, *o*-H) ppm; ¹³C{¹H, ³¹P} NMR (125.8 MHz, CDCl₃, 25°C): δ (assignment by HMQC) = 26.6 (C-6^{A,D or B,E}), 34.0 (C-6^{B,E or A,D}), 57.5, 57.5, 57.6 (2-OCH₃), 58.7 (6-OCH₃), 61.6, 61.9, 62.1 (3-OCH₃), 66.2 (C-5^{A,D or B,E}), 70.5 (C-5^{C,F}), 70.7 (C-6^{C,F}), 72.9 (C-5^{B,E or A,D}), 81.1 (C-3^{B,E or A,D}), 81.6 (C-3^{C,F}), 81.7 (C-2^{B,E or A,D}), 81.9 (C-2^{C,F}), 82.2 (C-4^{C,F}), 82.4 (C-2^{A,D or B,E}), 83.5 (C-3^{A,D or B,E}), 87.8 (C-4^{A,D or B,E}), 88.8 (C-4^{B,E or A,D}), 97.6 (C-1^{A,D or B,E}), 99.9 (C-1^{B,E or A,D}), 100.3 (C-1^{C,F}), 128.3 (*m*-C), 128.5 (*p*-C), 131.8 (*o*-C), 140.4 (*ipso*-C) ppm; ³¹P{¹H} NMR (121.5 MHz, CDCl₃, 25 °C): δ = -16.8 (s) ppm; elemental analysis (%): calcd for C₆₂H₉₄O₂₆P₂•0.5 CH₂Cl₂ (1317.37 + 42.47): C 55.20, H 7.04; found: C 55.46, H 7.01; MS (FAB): *m/z* (%): 1317.4 (100) [*M* + H]⁺.

6^A,6^B,6^D,6^E-Tetradecoxy-6^A,6^B:6^D,6^E-bis[(*S*)-phenyloxophosphinidene]-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^F-tetradeca-*O*-methyl- α -cyclodextrin (2): This di(phosphine oxide) was quantitatively formed by reacting Ni(1,5-cyclooctadiene)₂ with 1 equiv. of **TRANSDIP** in toluene, then by bubbling air through the solution. Alternatively, **2** was obtained quantitatively by bubbling air for 1h through a solution of **7** (see below) in CH₂Cl₂. The product was purified by column chromatography [SiO₂, CH₂Cl₂/MeOH, 97:3 (v/v)]. *R_f* (SiO₂, CH₂Cl₂/MeOH, 92:8, v/v) = 0.35; Mp 215°C dec. ¹H NMR (300.1 MHz, CDCl₃, 25°C): δ (assignment by COSY) = 2.10 (m, 2 H, H-6a^{A,D} or B^E), 2.20 (m, 2 H, H-6a^{B,E} or A^D), 2.94 (m, 2 H, H-6b^{B,E} or A^D), 3.06 (dd, 2 H, ³*J*_{H-2,H-1} = 3.0 Hz, ³*J*_{H-2,H-3} = 10.4 Hz, H-2^{B,E} or A^D), 3.16 (dd, 2 H, ³*J*_{H-2,H-1} = 3.3 Hz, ³*J*_{H-2,H-3} = 9.7 Hz, H-2^{C,F}), 3.21-3.39 (8 H, H-2^{A,D} or B^E, H-4^{A,B,D,E}, H-6b^{A,D} or B^E), 3.33 (s, 6 H, OMe), 3.43 (s, 6 H, OMe), 3.46 (s, 6 H, OMe), 3.52 (s, 6 H, OMe), 3.52-3.3.72 (8 H, H-3, H-4^{C,F}), 3.57 (s, 6 H, OMe), 3.66 (s, 6 H, OMe), 3.71 (s, 6 H, OMe), 3.84 (m, 2 H, H-6a^{C,F}), 4.15 (m, 2 H, H-6b^{C,F}), 4.37 (m, 2 H, H-5^{A,D} or B^E), 4.44 (m, 2 H, H-5^{C,F}), 4.62 (m, 2 H, H-5^{B,E} or A^D), 4.93 (d, 2 H, ³*J*_{H-1,H-2} = 3.3 Hz, H-1^{C,F}), 4.99 (d, 2 H, ³*J*_{H-1,H-2} = 3.0 Hz, H-1^{B,E} or A^D), 5.05 (d, 2 H, ³*J*_{H-1,H-2} = 4.3 Hz, H-1^{A,D} or B^E), 7.45-7.55 (6 H, *m*-H, *p*-H), 7.71 (m, 4 H, *o*-H) ppm; ¹³C{¹H} NMR (75.5 MHz, CDCl₃, 25°C): δ (assignment by HMQC) = 34.0 (d, ¹*J*_{C,P} = 67.0 Hz, C-6^{A,D} or B^E), 40.7 (d, ¹*J*_{C,P} = 67.6 Hz, C-6^{A,D} or B^E), 57.4, 57.6, 57.6 (2-OCH₃), 58.7 (6-OCH₃), 61.7 [×2], 62.4 (3-OCH₃), 63.4 (d, ²*J*_{C,P} = 5.6 Hz, C-5^{A,D} or B^E), 66.8 (C-5^{B,E} or A^D), 71.0 [×2] (C-5^{C,F}, C-6^{C,F}), 79.9, 81.3, 81.8, 82.1, 82.3, 82.5, 82.6 (C-2, C-3, C-4^{C,F}), 87.3 (d, ³*J*_{C,P} = 11.8 Hz, C-4^{A,D} or B^E), 90.1 (d, ³*J*_{C,P} = 5.0 Hz, C-4^{B,E} or A^D), 97.6 (C-1^{A,D} or B^E), 100.2 (C-1^{C,F}), 100.7 (C-1^{B,E} or A^D), 129.0 (d, ²*J*_{C,P} = 11.8 Hz, *o*-C), 129.4 (d, ³*J*_{C,P} = 9.3 Hz, *m*-C), 131.9 (d, ⁴*J*_{C,P} = 2.5 Hz, *p*-C), 133.9 (d, *J*_{C,P} = 98.0 Hz, *ipso*-C) ppm; ³¹P{¹H} NMR (121.5 MHz, CDCl₃, 25°C): δ = 40.2 (s) ppm; elemental analysis (%): calcd for C₆₂H₉₄O₂₈P₂ (1349.34): C 55.19, H 7.02; found: C 55.08, H 6.99; MS (ESI-TOF): *m/z* (%): 1371.5 (100) [*M* + Na]⁺.

6^A,6^B,6^D,6^E-Tetradecoxy-6^A,6^B:6^D,6^E-bis[(*S*)-phenylsulfidophosphinidene]-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^F-tetradeca-*O*-methyl- α -cyclodextrin (3): Solid sulfur (0.005 g, 0.15 mmol) was added at room temperature to a solution of **TRANSDIP** (0.100 g, 0.08 mmol) in THF (10 mL) under vigorous stirring. After 3 h the reaction mixture was concentrated to 5 mL and pentane (100 mL) was added. The suspension was then filtered over Celite. Evaporation of pentane afforded analytically pure **3** as a pale yellow powder (yield: 0.103 g, 98%). *R_f* (SiO₂, CH₂Cl₂/MeOH, 92:8, v/v) = 0.34; Mp 184°C dec. ¹H NMR (300.1 MHz, CDCl₃, 25°C): δ (assignment by COSY) = 2.05 (m, 2 H, H-6a^{A,D} or B^E), 2.45 (m, 2 H,

H-6a^{B,E or A,D}), 3.02-3.33 (14 H, H-2, H-4^{A,B,D,E}, H-6b^{A,B,D,E}), 3.26 (s, 6 H, OMe), 3.45 (s, 12 H, OMe), 3.47-3.71 (8 H, H-3, H-4^{C,F}), 3.54 (s, 6 H, OMe), 3.59 (s, 6 H, OMe), 3.66 (s, 6 H, OMe), 3.74 (s, 6 H, OMe), 3.96 (m, 2 H, H-6a^{C,F}), 4.22 (m, 2 H, H-5^{C,F}), 4.32-4.44 (4 H, H-5^{B,E or A,D}, H-6b^{C,F}), 4.77 (m, 2 H, H-5^{A,B or D,E}), 4.92 (d, 2 H, $^3J_{H-1,H-2} = 2.8$ Hz, H-1^{C,F}), 4.95 (d, 2 H, $^3J_{H-1,H-2} = 2.5$ Hz, H-1^{A,D or B,E}), 5.08 (d, 2 H, $^3J_{H-1,H-2} = 4.0$ Hz, H-1^{B,E or A,D}), 7.48 (m, 4 H, *m*-H), 7.54 (m, 2 H, *p*-H), 7.96 (m, 4 H, *o*-H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl₃, 25°C): δ (assignment by HMQC) = 38.9 (d, $^1J_{C-6,P} = 52.6$ Hz, C-6^{B,E or A,D}), 43.3 (d, $^1J_{C-6,P} = 50.8$ Hz, C-6^{A,D or B,E}), 57.4, 57.5, 57.7 (2-OCH₃), 58.7 (6-OCH₃), 61.6, 61.9, 62.5 (3-OCH₃), 63.9 (m, C-5^{B,E or A,D}), 68.5 (C-5^{A,D or B,E}), 71.5 (C-5^{C,F}), 72.0 (C-6^{C,F}), 80.3, 81.3, 81.8, 82.0, 82.2, 82.2, 83.0 (C-2, C-3, C-4^{C,F}), 87.0 (m, C-4^{B,E or A,D}), 89.8 (m, C-4^{A,D or B,E}), 97.7 (C-1^{B,E or A,D}), 100.3 (C-1^{A,D or B,E}), 100.6 (C-1^{C,F}), 128.4 (m, *m*-C), 130.5 (m, *o*-C), 131.1 (*p*-C), 135.1 (d, $J_{C,P} = 78.8$ Hz, *ipso*-C) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl₃, 25°C): $\delta = 40.8$ (s) ppm; elemental analysis (%): calcd for C₆₂H₉₄O₂₆P₂S₂•2(CH₂Cl₂) (1381.47 + 169.87): C 49.55, H 6.37; found: C 49.32, H 6.48; MS (ESI-TOF): *m/z* (%): 1403.6 (100) [*M* + H]⁺. When the sulfuration reaction was carried out with one equivalent of sulfur, a mixture of starting material, monosulfide **4** and disulfide **3** (major compound) was obtained. Further treatment of the solution with additional sulfur led quantitatively to **3**. The phosphane sulfides **3** and **4** could not be separated. $^{31}\text{P}\{^1\text{H}\}$ NMR: (121.5 MHz, CDCl₃, 25°C): $\delta = 42.2$ (d, P(V), $J(\text{PP}') = 48.7$ Hz), -19.5 (d, P(III), $J(\text{PP}') = 48.7$ Hz) ppm.

Trans-*P,P'*-dichloro-{6^A,6^B,6^D,6^E-tetradecoxy-6^A,6^B:6^D,6^E-bis[(*R*)-phenylphosphinidene]-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^F-tetradeca-*O*-methyl- α -cyclodextrin}platinum(II) (5**):** A solution of [PtCl₂(PhCN)₂] (0.047 g, 0.10 mmol) and TRANS DIP (0.130 g, 0.10 mmol) in toluene (25 mL) was refluxed for 3 d. The solution was concentrated to *ca.* 5 mL and pentane (140 mL) was added to precipitate small amounts of unreacted starting complex. The solution was filtered over Celite. Evaporation of pentane afforded analytically pure **5** as a pale yellow powder (yield 0.153 g, 98%). *R*_f (SiO₂, CH₂Cl₂/MeOH, 90:10, v/v) = 0.46; Mp >250°C. ^1H NMR (300.1 MHz, CDCl₃, 25 °C): δ (assignment by COSY) = 2.28 (m, 2 H, H-6a^{A,D or B,E}), 2.63 (ddd, 2 H, $^2J_{H-6a,H-6b} = 5.5$ Hz, $^3J_{H-6a,H-5} = 5.5$ Hz, $^3J_{H-6a,P} = 14.6$ Hz, H-6a^{B,E or A,D}), 3.07-3.22 (10 H, H-2, H-4^{A,B,D,E}), 3.31-3.39 (4 H, H-6b^{A,B,D,E}), 3.43 (m, 2 H, H-3^{A,D or B,E}), 3.44 (s, 6 H, OMe), 3.47 (s, 6 H, OMe), 3.52 (s, 12 H, OMe), 3.52-3.65 (4 H, H-3^{B,E or A,D}, H-3^{C,F}), 3.64 (s, 6 H, OMe), 3.65 (s, 6 H, OMe), 3.74 (s, 6 H, OMe), 3.81 (m, 2 H, H-6a^{C,F}), 3.86 (m, 2 H, H-4^{C,F}), 4.51-4.64 (6 H, H-5^{A,D or B,E}, H-5^{C,F}, H-6b^{C,F}), 4.93 (d, 2 H, $^3J_{H-1,H-2} = 2.8$ Hz, H-1^{C,F}), 4.95 (d, 2 H, $^3J_{H-1,H-2} = 2.5$ Hz, H-1^{A,D or B,E}), 5.08 (d, 2 H, $^3J_{H-1,H-2} = 4.0$ Hz, H-1^{B,E or A,D}), 7.48 (m, 4 H, *m*-H), 7.54 (m, 2 H, *p*-H), 7.96 (m, 4 H, *o*-H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl₃, 25°C): δ (assignment by HMQC) = 38.9 (d, $^1J_{C-6,P} = 52.6$ Hz, C-6^{B,E or A,D}), 43.3 (d, $^1J_{C-6,P} = 50.8$ Hz, C-6^{A,D or B,E}), 57.4, 57.5, 57.7 (2-OCH₃), 58.7 (6-OCH₃), 61.6, 61.9, 62.5 (3-OCH₃), 63.9 (m, C-5^{B,E or A,D}), 68.5 (C-5^{A,D or B,E}), 71.5 (C-5^{C,F}), 72.0 (C-6^{C,F}), 80.3, 81.3, 81.8, 82.0, 82.2, 82.2, 83.0 (C-2, C-3, C-4^{C,F}), 87.0 (m, C-4^{B,E or A,D}), 89.8 (m, C-4^{A,D or B,E}), 97.7 (C-1^{B,E or A,D}), 100.3 (C-1^{A,D or B,E}), 100.6 (C-1^{C,F}), 128.4 (m, *m*-C), 130.5 (m, *o*-C), 131.1 (*p*-C), 135.1 (d, $J_{C,P} = 78.8$ Hz, *ipso*-C) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl₃, 25°C): $\delta = 42.2$ (d, P(V), $J(\text{PP}') = 48.7$ Hz), -19.5 (d, P(III), $J(\text{PP}') = 48.7$ Hz) ppm.

$_{1,H-2} = 4.2$ Hz, H-1^{A,D or B,E}), 5.05 (two overlapping d, 4 H, H-1^{B,E or A,D}, H-1^{C,F}), 5.23 (m, 2 H, H-5^{B,E or A,D}), 7.28-7.37 (6 H, *m*-H, *p*-H), 7.49 (m, 4 H, *o*-H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3 , 25 °C): δ (assignment by HMQC) = 30.2 (m, C-6^{A,D or B,E}), 35.8 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 26.6$ Hz, C-6^{B,E or A,D}), 57.5, 58.0, 58.7 (2-OCH₃), 59.3 (6-OCH₃), 61.7, 61.7, 62.0 (3-OCH₃), 66.1 (C-5^{A,D or B,E}), 67.9 (C-5^{B,E or A,D}), 70.6 (C-5^{C,F}), 71.8 (C-6^{C,F}), 80.6 (C-4^{C,F}), 81.1 (C-3^{C,F}), 81.3 (C-3^{B,E or A,D}), 81.4 [×2] (C-2^{A,B,D,E}), 83.0 (C-3^{A,D or B,E}), 83.2 (C-2^{C,F}), 86.5 (virtual t, $|^3J_{\text{C,P}} + ^5J_{\text{C,P}}| = 9.5$ Hz, C-4^{A,D or B,E}), 89.9 (C-4^{B,E or A,D}), 97.3 (C-1^{B,E or A,D}), 97.5 (C-1^{A,D or B,E}), 100.9 (C-1^{C,F}), 127.8 (virtual t, $|^3J_{\text{C,P}} + ^5J_{\text{C,P}}| = 10.0$ Hz, *m*-C), 129.6 (*p*-C), 131.3 (virtual t, $|^2J_{\text{C,P}} + ^4J_{\text{C,P}}| = 9.5$ Hz, *o*-C), 133.4 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 57.8$ Hz, *ipso*-C) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3 , 25 °C): $\delta = -6.5$ (s with Pt satellites, $^1J_{\text{P,Pt}} = 2463$ Hz) ppm; elemental analysis (%): calcd for $\text{C}_{62}\text{H}_{94}\text{O}_{26}\text{P}_2\text{PtCl}_2$ (1583.37): C 47.03, H 5.98; found: C 47.14, H 6.05; MS (FAB): m/z (%): 1547.2 (100) [$M - \text{Cl}$]⁺.

***Trans*-P,P'-dichloro-{6^A,6^B,6^D,6^E-tetradecoxy-6^A,6^B:6^D,6^E-bis[(*R*)-phenylphosphinidene]-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^F-tetradeca-*O*-methyl- α -cyclodextrin}**

palladium(II) (6): A solution of $[\text{PdCl}_2(\text{PhCN})_2]$ (0.047 g, 0.12 mmol) in CH_2Cl_2 (5 mL) was added at room temperature to a solution of **TRANSDIP** (0.160 g, 0.12 mmol) in CH_2Cl_2 (10 mL) under vigorous stirring. After 0.5 h the reaction mixture was concentrated to 5 mL and pentane (100 mL) was added. The suspension was then filtered over Celite. Evaporation of pentane afforded analytically pure **6** as a pale yellow powder. Washings of the Celite layer with hot heptane afforded further amounts of **6** (yield: 0.174 g, 97 %). R_f (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 90:10, v/v) = 0.45; Mp 219-223 °C. ^1H NMR (300.1 MHz, CDCl_3 , 25 °C): $\delta =$ 2.13 (m, 2 H, H-6a^{A,D or B,E}), 2.63 (ddd, 2 H, $^2J_{\text{H-6a,H-6b}} = 4.7$ Hz, $^3J(\text{H-6a,H-5}) = 4.7$ Hz, $^3J_{\text{H-6a,P}} = 14.7$ Hz, H-6a^{B,E or A,D}), 3.08-3.22 (10 H, H-2, H-4^{A,B,D,E}), 3.33-3.37 (4 H, H-6b^{A,B,D,E}), 3.41 (m, 2 H, H-3^{A,D or B,E}), 3.45 (s, 6 H, OMe), 3.47 (s, 6 H, OMe), 3.52 (s, 12 H, OMe), 3.54-3.68 (4 H, H-3^{B,E or A,D}, H-3^{C,F}), 3.64 (s, 6 H, OMe), 3.65 (s, 6 H, OMe), 3.73 (s, 6 H, OMe), 3.79-3.88 (4 H, H-4^{C,F}, H-6a^{C,F}), 4.48-4.62 (6 H, H-5^{A,D or B,E}, H-5^{C,F}, H-6b^{C,F}), 4.93 (d, 2 H, $^3J_{\text{H-1,H-2}} = 4.2$ Hz, H-1^{A,D or B,E}), 5.05 (d, 4 H, $^3J_{\text{H-1,H-2}} = 3.4$ Hz, H-1^{B,E or A,D}, H-1^{C,F}), 5.23 (m, 2 H, H-5^{B,E or A,D}), 7.30-7.36 (6 H, *m*-H, *p*-H), 7.51 (m, 4 H, *o*-H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3 , 25 °C): $\delta =$ 30.2 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 25.0$ Hz, C-6^{A,D or B,E}), 36.2 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 20.0$ Hz, C-6^{B,E or A,D}), 57.5, 58.0, 58.6 (2-OCH₃), 59.4 (6-OCH₃), 61.7, 61.7, 62.0 (3-OCH₃), 66.0 (br signal with triplet shape, C-5^{A,D or B,E}), 68.3 (br signal with triplet shape, C-5^{B,E or A,D}), 70.8 (C-5^{C,F}), 72.0 (C-6^{C,F}), 80.9, 81.0, 81.1, 81.3, 81.4, 82.9, 83.1 (C-2, C-3, C-4^{C,F}), 86.6 (virtual t, $|^3J_{\text{C,P}} + ^5J_{\text{C,P}}| = 9.5$ Hz, C-4^{A,D or B,E}), 89.9 (br signal with triplet shape, C-

$4^{B,E \text{ or } A,D}$), 97.5 [$\times 2$] ($C-1^{A,B,D,E}$), 101.0 ($C-1^{C,F}$), 127.9 (virtual t, $|^3J_{C,P} + ^5J_{C,P}| = 9.5$ Hz, $m-C$), 129.6 ($p-C$), 131.3 (virtual t, $|^2J_{C,P} + ^4J_{C,P}| = 9.5$ Hz, $o-C$), 134.5 (virtual t, $|^1J_{C,P} + ^3J_{C,P}| = 50.0$ Hz, $ipso-C$) ppm; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = -0.4$ (s) ppm; elemental analysis (%): calcd for $C_{62}H_{94}O_{26}P_2PdCl_2 \cdot 0.5 CH_2Cl_2$ (1494.68 + 42.47): C 48.84, H 6.23; found: C 48.73, H, 6.30; MS (Maldi TOF): m/z (%): 1494.1 (19) $[M]^+$, 1459.1 (70) $[M - Cl]^+$, 1422.2 (100) $[M - 2Cl]^+$.

***Trans-P,P'*-dichloro- $\{6^A,6^B,6^D,6^E$ -tetradecoxy- $6^A,6^B:6^D,6^E$ -bis[(*R*)-phenylphosphinidene]- $2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^F$ -tetradeca-*O*-methyl- α -cyclodextrin}nickel(II)**

(7): A suspension of $NiCl_2$ (0.018 g, 0.14 mmol) in ethanol (2 mL) was added to a solution of **TRANS DIP** (0.180 g, 0.14 mmol) in CH_2Cl_2 (10 mL), under vigorous stirring. After 4 hours at 25°C the solvent was evaporated, whereupon the product was dissolved in CH_2Cl_2 (5 mL) and pentane (150 mL) was added to precipitate unreacted compounds, which were then filtered off over Celite. Evaporation of pentane afforded **7** as a violet powder (yield 0.183 g, 93%). R_f (SiO_2 , $CH_2Cl_2/MeOH$, 90:10, v/v) = 0.41; Mp 193°C dec. 1H NMR (300.1 MHz, $CDCl_3$, 25°C): δ (assignment by COSY) = 1.92 (m, 2 H, $H-6a^{A,D \text{ or } B,E}$), 2.49 (m, 2 H, $H-6a^{B,E \text{ or } A,D}$), 2.64 (m, 2 H, $H-6b^{B,E \text{ or } A,D}$), 3.05-3.31 (12 H, $H-2$, $H-4^{A,B,D,E}$, $H-6b^{A,D \text{ or } B,E}$), 3.40-3.79 (8 H, $H-3$, $H-6a^{C,F}$), 3.43 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.52 (s, 6 H, OMe), 3.56 (s, 6 H, OMe), 3.64 (s, 6 H, OMe), 3.65 (s, 6 H, OMe), 3.79 (s, 6 H, OMe), 3.92 (virtual t, 2 H, $^3J_{H-4,H-3} = ^3J_{H-4,H-5} = 9.0$ Hz, $H-4^{C,F}$), 4.36 (m, 2 H, $H-5^{A,D \text{ or } B,E}$), 4.44 (m, 2 H, $H-6b^{C,F}$), 4.69 (m, 2 H, $H-5^{C,F}$), 4.98 (two overlapping d, 4 H, $H-1^{A,B,D,E}$), 5.08 (m, 2 H, $H-5^{B,E \text{ or } A,D}$), 5.11 (d, 2 H, $^3J_{H-1,H-2} = 3.6$ Hz, $H-1^{C,F}$), 5.35 (m, 2 H, $H-5^{B,E \text{ or } A,D}$), 7.37-7.39 (6 H, $m-H$, $p-H$), 8.02 (m, 4 H, $o-H$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ (assignment by HMQC) = 27.0 (virtual t, $|^1J_{C,P} + ^3J_{C,P}| = 18.1$ Hz, $C-6^{A,D \text{ or } B,E}$), 34.8 (m, $C-6^{B,E \text{ or } A,D}$), 56.9, 57.8, 58.8, 58.8, 61.1, 61.3, 61.4 (2- OCH_3 , 3- OCH_3 , 6- OCH_3), 64.8 ($C-5^{A,D \text{ or } B,E}$), 68.2 ($C-5^{B,E \text{ or } A,D}$), 70.7 ($C-5^{C,F}$), 71.9 ($C-6^{C,F}$), 79.9, 80.8, 81.0, 81.1, 81.2, 82.9, 83.0, 85.0, 89.5 ($C-2$, $C-3$, $C-4$), 96.6 ($C-1^{B,E \text{ or } A,D}$), 97.1 ($C-1^{A,D \text{ or } B,E}$), 100.5 ($C-1^{C,F}$), 127.9 ($m-C$, $p-C$), 129.5 ($o-C$), 131.6 ($ipso-C$) ppm; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25°C): $\delta = -9.5$ (s) ppm; elemental analysis (%): calcd for $C_{62}H_{94}Cl_2NiO_{26}P_2 \cdot CH_2Cl_2$ (1446.98 + 84.93): C 49.40, H 6.32; found: C 49.59, H 6.69; MS (ESI-TOF): m/z (%): 1481.4 (100) $[M + Cl]^-$.

***Trans-P,P'*-dibromo- $\{6^A,6^B,6^D,6^E$ -tetradecoxy- $6^A,6^B:6^D,6^E$ -bis[(*R*)-phenylphosphinidene]- $2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^F$ -tetradeca-*O*-methyl- α -cyclodextrin}nickel(II)**

(8): A suspension of $NiBr_2$ (0.030 g, 0.14 mmol) in ethanol (2 mL) was added to a solution of **TRANS DIP** (0.180 g, 0.14 mmol) in CH_2Cl_2 (10 mL), under vigorous stirring. After 4 hours

at 25°C the solvent was evaporated, whereupon the product was dissolved in CH₂Cl₂ (5 mL) and pentane (150 mL) was added to precipitate unreacted compounds, which were then filtered off over Celite. Evaporation of pentane afforded **8** as a green powder (yield 0.175 g, 83%). *R_f* (SiO₂, CH₂Cl₂/MeOH, 90:10, v/v) = 0.38; Mp 186°C dec. ¹H NMR (300.1 MHz, CDCl₃, 25°C): δ (assignment by COSY) = 2.09 (m, 2 H, H-6a^{A,D} or B,E), 2.54 (m, 2 H, H-6a^{B,E} or A,D), 2.84 (m, 2 H, H-6b^{B,E} or A,D), 3.04-3.28 (10 H, H-2, H-4^{A,B,D,E}), 3.33 (m, 2 H, H-6b^{A,D} or B,E), 3.45-3.70 (6 H, H-3), 3.48 (s, 6 H, OMe), 3.53 (s, 6 H, OMe), 3.56 (s, 6 H, OMe), 3.58 (s, 6 H, OMe), 3.66 (s, 6 H, OMe), 3.68 (s, 6 H, OMe), 3.81 (s, 6 H, OMe), 3.90-4.01 (4 H, H-4^{C,F}, H-6a^{C,F}), 4.49 (m, 2 H, H-5^{A,D} or B,E), 4.74 (m, 2 H, H-6b^{C,F}), 4.86 (m, 2 H, H-5^{C,F}), 4.97 (d, 2 H, ³J_{H-1,H-2} = 4.1 Hz, H-1^{A,D} or B,E), 5.10 (two overlapping d, 4 H, H-1^{B,E} or A,D, H-1^{C,F}), 5.35 (m, 2 H, H-5^{B,E} or A,D), 7.36-7.41 (6 H, *m*-H, *p*-H), 7.81 (m, 4 H, *o*-H) ppm; ¹³C{¹H} NMR (75.5 MHz, CDCl₃, 25 °C): δ (assignment by HMQC) = 28.4 (virtual t, |¹J_{C,P} + ³J_{C,P}| = 17.6 Hz, C-6^{A,D} or B,E), 35.1 (C-6^{B,E} or A,D), 56.2, 57.2, 58.2, 58.3, 60.5, 60.7, 61.0 (2-OCH₃, 3-OCH₃, 6-OCH₃), 65.0 (C-5^{A,D} or B,E), 67.4 (C-5^{B,E} or A,D), 69.9 (C-5^{C,F}), 71.4 (C-6^{C,F}), 79.7, 80.3, 80.4, 80.5, 80.5, 82.3, 82.4, 84.5, 88.8 (C-2, C-3, C-4), 96.1 (C-1^{B,E} or A,D), 96.4 (C-1^{A,D} or B,E), 99.8 (C-1^{C,F}), 127.0 (*m*-C), 128.6 (*p*-C), 130.6 (*o*-C), 136.4 (*ipso*-C) ppm; ³¹P{¹H} NMR (121.5 MHz, CDCl₃, 25°C): δ = -6.9 (s) ppm; elemental analysis (%): calcd for C₆₂H₉₄Br₂NiO₂₆P₂•2(CH₂Cl₂) (1535.84 + 169.87): C 45.07, H 5.79; found: C 44.81, H 5.92; MS (ESI-TOF): *m/z* (%): 1525.3 (16) [*M* – Br + 2Cl][–], 1571.3 (73) [*M* + Cl][–], 1615.2 (100) [*M* + Br][–].

Trans-*P,P'*-chloro-methyl-{6^A,6^B,6^D,6^E-tetradecoxy-6^A,6^B:6^D,6^E-bis[(*R*)-phenylphosphini dene]-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^F-tetradeca-*O*-methyl- α -cyclodextrin}palladium(II) (9): A solution of [PdClMe(1,5-cyclooctadiene)] (0.024 g, 0.08 mmol) in CH₂Cl₂ (3 mL) was added to a solution of **TRANSDIP** (0.110 g, 0.08 mmol) in CH₂Cl₂ (20 mL) under vigorous stirring. After stirring for 14 h, the solution was concentrated to 5 mL and pentane (120 mL) was added. Filtration through Celite and subsequent precipitation afforded pure **9** as a pale yellow powder (yield 0.117 g, 95 %). *R_f* (SiO₂, CH₂Cl₂/MeOH, 90:10, v/v) = 0.45; Mp 198-201°C. ¹H NMR (500.1 MHz, CDCl₃, 25 °C): δ (assignment by COSY and ROESY) = -0.68 (t, 3 H, ³J_{H,P} = 6.8 Hz, CH₃), 2.07 (m, 2 H, H-6a^{A,D} or B,E), 2.37 (m, 2 H, H-6a^{B,E} or A,D), 3.06-3.20 (10 H, H-2, H-4^{A,B,D,E}), 3.23 (m, H-6b^{A,D} or B,E), 3.32 (m, 2 H, H-6b^{B,E} or A,D), 3.39 (s, 6 H, OMe), 3.46-3.71 (8 H, H-3, H-6a^{C,F}), 3.46 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.50 (s, 6 H, OMe), 3.63 (s, 6 H, OMe), 3.64 (s, 6 H, OMe), 3.70 (s, 6 H, OMe), 3.78 (virtual triplet, 2 H, ³J_{H-4,H-3} = ³J_{H-4,H-5} = 9.0 Hz, H-4^{C,F}), 4.47 (dd, 2 H, ³J_{H-6b,H-5} = 2.9 Hz, ²J_{H-6b,H-6a} = 10.8 Hz,

H-6b^{C,F}), 4.70-4.76 (4 H, H-5^{A,D} or ^{B,E}, H-5^{C,F}), 4.91 (d, 2 H, $^3J_{H-1,H-2} = 4.3$ Hz, H-1^{A,D} or ^{B,E}), 5.01 (d, 2 H, $^3J_{H-1,H-2} = 3.6$ Hz, H-1^{C,F}), 5.03 (d, 2 H, $^3J_{H-1,H-2} = 3.3$ Hz, H-1^{B,E} or ^{A,D}), 5.40 (m, 2 H, H-5^{B,E} or ^{A,D}), 7.29 (m, 2 H, *p*-H), 7.34 (m, 4 H, *m*-H), 7.40 (m, 4 H, *o*-H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3 , 25 °C): δ (assignment by HMQC) = 6.2 (br signal with triplet shape, CH_3), 29.4 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 22.0$, C-6^{A,D} or ^{B,E}), 35.8 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 18.5$ Hz, C-6^{B,E} or ^{A,D}), 57.5, 57.8, 58.3 (2-OCH₃), 59.2 (6-OCH₃), 61.7, 61.8, 62.1 (3-OCH₃), 65.7 (br signal with triplet shape, C-5^{A,D} or ^{B,E}), 68.3 (virtual t, $|^2J_{\text{C,P}} + ^4J_{\text{C,P}}| = 9.0$ Hz, C-5^{B,E} or ^{A,D}), 70.3 (C-5^{C,F}), 72.0 (C-6^{C,F}), 81.0 [$\times 2$] (C-3^{B,E} or ^{A,D}, C-3^{C,F}), 81.3 (C-4^{C,F}), 81.4 (C-2^{B,E} or ^{A,D}), 81.7 (C-2^{C,F}), 82.8 (C-3^{A,D} or ^{B,E}), 83.2 (C-2^{A,D} or ^{B,E}), 87.4 (virtual t, $|^3J_{\text{C,P}} + ^5J_{\text{C,P}}| = 9.0$ Hz, C-4^{A,D} or ^{B,E}), 89.9 (C-4^{B,E} or ^{A,D}), 97.6 (C-1^{A,D} or ^{B,E}), 98.0 (C-1^{B,E} or ^{A,D}), 101.0 (C-1^{C,F}), 128.3 (virtual t, $|^3J_{\text{C,P}} + ^5J_{\text{C,P}}| = 9.0$ Hz, *m*-C), 129.2 (*p*-C), 130.6 (virtual t, $|^2J_{\text{C,P}} + ^4J_{\text{C,P}}| = 10.0$ Hz, *o*-C), 135.4 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 42.5$ Hz, *ipso*-C) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3 , 25 °C): $\delta = 3.8$ (s) ppm; elemental analysis (%): calcd for $\text{C}_{63}\text{H}_{97}\text{ClO}_{26}\text{P}_2\text{Pd}$ (1474.26): C 51.33, H 6.63; found: C 51.50, H 6.69; MS (Maldi TOF): *m/z* (%): 1474.1 (6) [M]⁺, 1459.1 (22) [$M - \text{Me}$]⁺, 1437.2 (15) [$M - \text{Cl}$]⁺, 1422 (66) [$M - \text{Me} - \text{Cl}$]⁺.

***Trans-P,P'*-methyl-{6^A,6^B,6^D,6^E-tetradecoxy-6^A,6^B:6^D,6^E-bis[(*R*)-phenylphosphinidene]-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^F-tetradeca-*O*-methyl- α -cyclodextrin}(pyridine) palladium(II)tetrafluoroborate (10):** A solution of AgBF_4 (0.024 g, 0.12 mmol) in THF (1 mL) was added to a solution of $[\text{PdClMe}(\text{COD})]$ (0.032 g, 0.12 mmol) in CH_2Cl_2 (3 mL). After stirring the suspension vigorously for 5 min, the precipitate was collected on Celite and the filtrate directly added to a solution of **TRANSDIP** (0.169 g, 0.12 mmol) in CH_2Cl_2 /pyridine (83:17, v/v, 12 mL) under agitation at 0°C. The reaction mixture was then stirred at room temperature for 30 min. before being concentrated to *ca.* 5 mL. Addition of pentane (80 mL) caused the product to precipitate and filtration through a Schlenk type fritté afforded pure **10** as a pale yellow solid (yield 0.170 g, 96%). Complex **10** decomposes on silica (SiO_2); Mp 183 °C dec. ^1H NMR (300.1 MHz, $(\text{CD}_3)_2\text{CO}$, 25°C): δ (assignment by COSY and ROESY) = 1.12 (t, 3 H, $^3J_{\text{H,P}} = 7.3$ Hz, CH_3), 2.21 (m, 2 H, H-6a^{A,D} or ^{B,E}), 2.86 (m, 2 H, H-6a^{B,E} or ^{A,D}), 3.14-3.87 (22 H, H-2, H-3, H-4, H-6b^{A,B,D,E}), 3.47 (s, 6 H, 6-OMe), 3.55 (s, 6 H, OMe), 3.55 (s, 6 H, OMe), 3.56 (s, 6 H, OMe), 3.60 (s, 6 H, OMe), 3.65 (s, 6 H, OMe), 3.71 (s, 6 H, OMe), 4.07 (m, 2 H, H-6a^{C,F}), 4.24-4.44 (6 H, H-5^{A,D} or ^{B,E}, H-5^{C,F}, H-6b^{C,F}), 4.84 (m, 2 H, H-5^{B,E} or ^{A,D}), 5.10 (d, 2 H, $^3J_{H-1,H-2} = 4.5$ Hz, H-1^{A,D} or ^{B,E}), 5.11 (d, 2 H, $^3J_{H-1,H-2} = 4.4$ Hz, H-1^{C,F}), 5.26 (d, 2 H, $^3J_{H-1,H-2} = 3.1$ Hz, H-1^{B,E} or ^{A,D}), 6.70 (m, 2 H, *m*-H of M-pyridine), 7.04-7.69 (11 H, *p*-H of M-pyridine, aromatic H of P-phenyl), 7.74 (m, 2 H, *o*-H

of M-pyridine) ppm, small amounts of free pyridine were also detected; $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$, 25 °C): δ (assignment by HMQC) = 29.7 (m, C-6^{A,D} or B,E), 34.7 (m, C-6^{B,E} or A,D), 57.4, 58.6, 59.5, 60.2, 61.6, 61.7, 61.8 (2-OCH₃, 3-OCH₃, 6-OCH₃), 66.7 (C-5^{A,D} or B,E), 68.1 (C-5^{C,F}), 69.5 (C-5^{B,E} or A,D), 72.9 (C-6^{C,F}), 81.4, 82.1, 82.2, 82.3, 82.4, 83.9, 84.3, 85.8, 89.7 (C-2, C-3, C-4), 97.8 (C-1^{A,D} or B,E), 98.1 (C-1^{B,E} or A,D), 101.3 (C-1^{C,F}), 126.2-132.6 (aromatic C) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $(\text{CD}_3)_2\text{CO}$, 25°C): δ = -7.1 (s) ppm; C₆₃H₉₇ClO₂₆P₂Pd (1474.26); MS (ESI-TOF): m/z (%): 1437.5 (100) [$M - \text{BF}_4 - \text{py}$]⁺. We do not provide microanalytical data for the cationic palladium(II) complexes reported in this study since this species was obtained only in the presence of excess pyridine.

Trans-P,P'-chloro-carbonyl-{6^A,6^B,6^D,6^E-tetradecoxy-6^A,6^B:6^D,6^E-bis[(R)-phenylphosphini dene]-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^F-tetradeca-O-methyl- α -cyclodextrin}rhodium(I) (11):

A solution of $[\text{RhCl}(\text{CO})_2]_2$ (0.024 g, 0.06 mmol) in CH_2Cl_2 (5 mL) was added to a solution of **TRANSDIP** (0.160 g, 0.12 mmol) in CH_2Cl_2 (5 mL) under vigorous stirring. After 30 min. the mixture was concentrated to 2 mL and pentane (80 mL) was added to precipitate unreacted starting materials, which were filtered off over a bed of Celite. Evaporation of the solvent afforded **11** as a pale yellow powder (yield 0.172 g, 97%). R_f (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 90:10, v/v) = 0.41; Mp 171°C dec. IR (KBr) ν/cm^{-1} : 1982.1 ($\text{C}\equiv\text{O}$). ^1H NMR (300.1 MHz, CDCl_3 , 25°C): δ (assignment by COSY) = 2.37 (m, 2 H, H-6a^{A,D} or B,E), 2.80 (m, 2 H, H-6a^{B,E} or A,D), 3.19-3.31 (10 H, H-2, H-4^{A,B,D,E}), 3.33 (s, 6 H, OMe), 3.35 (s, 6 H, OMe), 3.37 (s, 6 H, OMe), 3.47 (s, 6 H, OMe), 3.57 (s, 6 H, OMe), 3.61 (m, 2 H, H-6b^{B,E} or A,D), 3.74 (s, 6 H, OMe), 3.79-3.93 (8 H, H-3, H-6b^{A,D} or B,E), 3.85 (s, 6 H, OMe), 4.07 (d, 2 H, $^2J_{\text{H-6a,H-6b}} = 11.1$ Hz, H-6a^{C,F}), 4.18 (m, 2 H, H-4^{C,F}), 4.80 (d, 2 H, $^3J_{\text{H-1,H-2}} = 4.3$ Hz, H-1^{A,D} or H-1^{B,E}), 5.00 (broad d, 2 H, $^3J_{\text{H-5,H-4}} = 8.8$ Hz, H-5^{C,F}), 5.06-5.17 (6 H, H-1^{C,F}, H-5^{A,D} or B,E, H-6b^{C,F}), 5.40 (d, 2 H, $^3J_{\text{H-1,H-2}} = 3.0$ Hz, H-1^{B,E} or H-1^{A,D}), 5.68 (m, 2 H, H-5^{B,E} or A,D), 6.96-7.01 (2 H, *p*-H), 7.08 (m, 4 H, *m*-H), 7.75 (m, 4 H, *o*-H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6 , 25 °C): δ (assignment by HMQC) = 32.0 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 22.3$, C-6^{A,D} or B,E), 38.0 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 18.5$ Hz, C-6^{B,E} or A,D), 57.3 [$\times 2$], 58.3, 59.4 (2-OCH₃, 6-OCH₃), 61.5, 61.8, 61.9 (3-OCH₃), 66.6 (br signal with triplet shape, C-5^{A,B} or D,E), 68.5 (br signal with triplet shape, C-5^{B,E} or A,D), 71.1 (C-5^{C,F}), 73.0 (C-6^{C,F}), 81.3, 81.4 and 83.7 (C-3), 81.8 (C-4^{C,F}), 82.6, 82.7 and 84.0 (C-2), 88.0 (virtual t, $|^3J_{\text{C,P}} + ^5J_{\text{C,P}}| = 9.5$ Hz, C-4^{A,D} or B,E or C-4^{B,E} or A,D), 90.6 (C-4^{B,E} or A,D or C-4^{A,D} or B,E), 98.0 (C-1^{A,D} or B,E or C-1^{B,E} or A,D), 98.1 (C-1^{B,E} or A,D or C-1^{A,D} or B,E), 101.6 (C-1^{C,F}), 128.7 (virtual t, $|^3J_{\text{C,P}} + ^5J_{\text{C,P}}| = 8.0$ Hz, *m*-C), 129.3 (*p*-C), 130.4 (virtual t, $|^2J_{\text{C,P}} + ^4J_{\text{C,P}}| = 10.0$ Hz, *o*-C), 140.8 (virtual t, $|^1J_{\text{C,P}} + ^3J_{\text{C,P}}| = 43.5$ Hz, *ipso*-C)

ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3 , 25°C): $\delta = -0.16$ (d, $J_{\text{P,Rh}} = 120.3$ Hz) ppm; elemental analysis (%): calcd for $\text{C}_{63}\text{H}_{94}\text{ClO}_{27}\text{P}_2\text{Rh}$ (1483.71): C 51.0, H 6.39; found: C 50.71, H 6.40; MS (ESI-TOF): m/z (%): 1447.1 (100) $[\text{M} - \text{Cl}]^+$.

***Trans-P,P'*-bromo-methyl- $\{6^{\text{A}},6^{\text{B}},6^{\text{D}},6^{\text{E}}$ -tetradecoxy- $6^{\text{A}},6^{\text{B}}:6^{\text{D}},6^{\text{E}}$ -bis[(*R*)-phenylphosphinidene]- $2^{\text{A}},2^{\text{B}},2^{\text{C}},2^{\text{D}},2^{\text{E}},2^{\text{F}},3^{\text{A}},3^{\text{B}},3^{\text{C}},3^{\text{D}},3^{\text{E}},3^{\text{F}},6^{\text{C}},6^{\text{F}}$ -tetradeca-*O*-methyl- α -cyclodextrin}**

nickel(II) (12): MeLi (0.0035 g, *ca.* 0.10 mL 1.6 M, 0.15 mmol) were added to a solution of **8** (0.110 g, 0.07 mmol) in Et_2O (10 mL) at -78°C. The reaction mixture was stirred for 1 h, before being evaporated to dryness. Toluene was added and the product filtered over a bed of Celite. Evaporation of the solvent afforded **12** as a beige solid (yield 0.060 g, 86%). Complex **12** decomposes on silica (SiO_2); Mp 148°C dec. ^1H NMR (500.1 MHz, C_6D_6 , 25°C): δ (assignment by COSY and ROESY) = -0.94 (t, 3 H, $^2J_{\text{H,P}} = 10.2$ Hz, CH_3), 2.20 (m, 2 H, H-6a $^{\text{A,D}}$ or B,E), 2.59 (m, 2 H, H-6a $^{\text{B,E}}$ or A,D), 3.15 (virtual t, 2 H, $^3J_{\text{H-4,H-3}} = ^3J_{\text{H-4,H-5}} = 8.9$ Hz, H-4 $^{\text{B,E}}$ or A,D), 3.24-3.48 (10 H, H-2, H-4 $^{\text{A,B}}$ or D,E , H-6b $^{\text{B,E}}$ or A,D), 3.31 (s, 6 H, OMe), 3.37 (s, 6 H, OMe), 3.39 (s, 6 H, OMe), 3.40 (s, 6 H, OMe), 3.57 (m, 2 H, H-6b $^{\text{A,D}}$ or B,E), 3.64-4.02 (8 H, H-3, H-6a $^{\text{C,F}}$), 3.71 (s, 6 H, OMe), 3.74 (s, 6 H, OMe), 3.76 (s, 6 H, OMe), 3.78 (virtual triplet, 2 H, $^3J_{\text{H-4,H-3}} = ^3J_{\text{H-4,H-5}} = 9.0$ Hz, H-4 $^{\text{C,F}}$), 4.75 (d, 2 H, $^3J_{\text{H-1,H-2}} = 4.0$ Hz, H-1 $^{\text{A,D}}$ or B,E), 5.00 (m, 2 H, H-6b $^{\text{C,F}}$), 5.15 (m, 2 H, H-5 $^{\text{A,D}}$ or B,E), 5.19 (d, 2 H, $^3J_{\text{H-1,H-2}} = 3.7$ Hz, H-1 $^{\text{C,F}}$), 5.24 (m, 2 H, H-5 $^{\text{C,F}}$), 5.41 (d, 2 H, $^3J_{\text{H-1,H-2}} = 3.0$ Hz, H-1 $^{\text{B,E}}$ or A,D), 5.93 (m, 2 H, H-5 $^{\text{B,E}}$ or A,D), 7.03 (broad t, 2 H, $^3J_{\text{p-H},m\text{-H}} = 7.4$ Hz, *p*-H), 7.13 (broad t, 4 H, $^3J_{m\text{-H},p\text{-H}} = 7.4$ Hz, *m*-H), 7.79 (m, 4 H, *o*-H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6 , 25 °C): δ (assignment by HMQC) = -2.1 (m, CH_3), 29.3 (m, C-6 $^{\text{A,D}}$ or B,E), 35.7 (C-6 $^{\text{B,E}}$ or A,D), 57.0, 57.1, 57.7, 57.8, 59.0, 69.4, 61.6 (2-OCH₃, 3-OCH₃, 6-OCH₃), 66.4 (m with triplet shape, C-5 $^{\text{A,D}}$ or B,E), 68.7 (m with triplet shape, C-5 $^{\text{B,E}}$ or A,D), 71.8 (C-5 $^{\text{C,F}}$), 72.8 (C-6 $^{\text{C,F}}$), 71.6, 81.7, 81.8, 82.6, 82.7, 83.8, 84.3, 86.9, 90.5 (C-2, C-3, C-4), 97.6 (C-1 $^{\text{B,E}}$ or A,D), 97.8 (C-1 $^{\text{A,D}}$ or B,E), 101.6 (C-1 $^{\text{C,F}}$), aromatic CH signals overlap with C_6D_6 signal, 138.4 (*ipso*-C) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6 , 25°C): $\delta = 0.5$ (s) ppm; elemental analysis (%): calcd for $\text{C}_{63}\text{H}_{97}\text{BrO}_{26}\text{P}_2\text{Ni}\cdot 3(\text{CH}_2\text{Cl}_2)$ (1470.97 + 254.79): C 45.93, H 6.02; found: C 45.61, H 6.29. Attempts to detect complex **12** by mass spectrometry were unsuccessful.

***P,P'*- $\{6^{\text{A}},6^{\text{B}},6^{\text{D}},6^{\text{E}}$ -Tetradecoxy- $6^{\text{A}},6^{\text{B}}:6^{\text{D}},6^{\text{E}}$ -bis[(*R*)-phenylphosphinidene]- $2^{\text{A}},2^{\text{B}},2^{\text{C}},2^{\text{D}},2^{\text{E}},2^{\text{F}},3^{\text{A}},3^{\text{B}},3^{\text{C}},3^{\text{D}},3^{\text{E}},3^{\text{F}},6^{\text{C}},6^{\text{F}}$ -tetradeca-*O*-methyl- α -cyclodextrin}**gold(I) hexafluorophosphate (**13**): To a stirred solution of TRANS DIP (0.160 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was added a solution of $[\text{AuCl}(\text{THT})]$ (0.040 g, 0.12 mmol) in CH_2Cl_2 (10 mL). After 0.5 h

the solution was added to a suspension of thallium hexafluorophosphate (0.044 g, 0.12 mmol) in acetonitrile (2 mL). After stirring for 5 min., the white precipitate was filtered through a bed of Celite and the filtered solution was concentrated to *ca.* 5 mL. Addition of pentane yielded complex **13** as a colourless precipitate (yield 0.180 g, 91%). R_f (SiO₂, CH₂Cl₂/MeOH, 90:10, v/v) = 0.31; Mp >250°C. ¹H NMR (300.1 MHz, CDCl₃, 25°C): δ (assignment by COSY) = 2.18 (m, 2 H, H-6a^{A,D} or ^{B,E}), 2.62 (m, 2 H, H-6a^{B,E} or ^{A,D}), 2.79 (s, 6 H, OMe), 3.07-3.73 (24 H, H-2, H-3, H-4, H-6b^{A,B,D,E}, H-6a^{C,F}), 3.47 (s, 6 H, OMe), 3.53 (s, 6 H, OMe), 3.57 (s, 6 H, OMe), 3.63 (s, 6 H, OMe), 3.65 (s, 6 H, OMe), 3.66 (s, 6 H, OMe), 3.89 (m, 2 H, H-5^{C,F}), 4.16 (m, 2 H, H-6b^{C,F}), 4.24 (m, 2 H, H-5^{B,E} or ^{A,D}), 4.36 (m, 2 H, H-5^{A,D} or ^{B,E}), 4.83 (d, 2 H, ³J_{H-1,H-2} = 3.2 Hz, H-1^{A,D} or ^{B,E}), 5.05 (two overlapping d, 4 H, H-1^{B,E} or ^{A,D}, H-1^{C,F}), 7.41-7.61 (10 H, aromatic H) ppm; ¹³C{¹H} NMR (75.5 MHz, CDCl₃, 25 °C): δ (assignment by HMQC) = 27.9 (m, C-6^{B,E} or ^{A,D}), 37.2 (m, C-6^{A,D} or ^{B,E}), 57.8, 58.0, 58.2 (2-OCH₃), 59.8 (6-OCH₃), 61.5, 61.6, 62.0 (3-OCH₃), 64.2 (C-5^{B,E} or ^{A,D}), 71.7 (m, C-5^{A,D} or ^{B,E}), 72.9 (C-5^{C,F}), 73.5 (C-6^{C,F}), 80.6, 80.9 [×2], 81.1, 81.3, 82.6, 83.9 (C-2, C-3, C-4^{C,F}), 86.1 (m, C-4^{B,E} or ^{A,D}), 88.3 (C-4^{A,D} or ^{B,E}), 98.8 (C-1^{B,E} or ^{A,D}), 99.5 (C-1^{A,D} or ^{B,E}), 100.4 (C-1^{C,F}), 129.7 (virtual t, |³J_{C,P} + ⁵J_{C,P}| = 11.2 Hz, *m*-C), 132.2 (virtual t, |²J_{C,P} + ⁴J_{C,P}| = 13.0 Hz, *o*-C); 132.6 (*p*-C) ppm; ¹⁹F{¹H} NMR (282.4 MHz, CDCl₃, 25°C): δ = -72.8 (d, ¹J_{F,P} = 716 Hz) ppm; ³¹P{¹H} NMR (121.5 MHz, CDCl₃, 25°C): δ = 38.6 (s), -144.3 (h, ¹J_{P,F} = 716 Hz) ppm; elemental analysis (%): calcd for C₆₂H₉₄AuF₆O₂₆P₃ (1659.27): C 44.88, H 5.71; found: C 44.71, H 5.83; MS (ESI-TOF): *m/z* (%): 1513.1 (100) [*M* - PF₆]⁺.

X-ray crystallographic data of **6:** 2 PdP₂C₆₂H₉₄Cl₂O₂₆•2C₅H₁₂, *Mr* = 3275.32, triclinic, *P*1, *a* = 14.419(5), *b* = 14.913(5), *c* = 19.382(5) Å, α = 79.985(7), β = 79.750(8), γ = 87.252(8)°, *V* = 4038(1) Å³, *Z* = 1, *D_x* = 1.347 Mg.m⁻³, λ (MoK α) = 0.71073 Å, μ = 4.82 cm⁻¹, *F*(000) = 1720, *T* = 110(1) K. Single crystals were obtained by slow diffusion of pentane into a chloroform solution of **6**. A sample was studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatised MoK α radiation (λ = 0.71069 Å). The data collection^[52] (2 θ _{max} = 54°, ω scan frames via 0.7° ω rotation and 20 s per frame, range HKL: H -8–21; K -21–21; L -27–27) gave 28266 reflections. The data led to 20976 independent reflections from which 9809 had *I* > 2.0 σ (*I*). The structure was solved with SIR-97,^[53] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, the hydrogen atoms were located by use of a Fourier Difference. The whole structure was refined with SHELXL-97^[54] by the full-matrix least-square techniques (use of *F*² magnitude; *x*, *y*, *z*, β_{ij} for C, Cl, O, P and Pd atoms, *x*, *y*, *z* in riding mode for H atoms; 1685 variables and 9809

observations with $I > 2.0 \sigma(I)$; calc. $w = 1/[\sigma^2(F_o^2) + (0.03 P)^2]$ where $P = (F_o^2 + 2 F_c^2)/3$ with the resulting $R = 0.125$, $R_w = 0.314$ and $S_w = 1.096$, $\Delta\rho < 3.5 \text{ e}\text{\AA}^{-3}$. Flack's parameter: 0.03 (5). The unit cell contains two slightly different molecules and two molecules of pentane. Owing to crystals of medium quality (probably arising from the presence of the solvent molecules), and as frequently observed in cyclodextrin structures, the refinement did not fully converge.

X-ray crystallographic data of **13:** $\text{AuP}_2\text{C}_{62}\text{H}_{94}\text{F}_6\text{O}_{26}\text{P} \cdot 4 \text{C}_2\text{Cl}_4\text{H}_2$, $M_r = 2330.59$, triclinic, $P1$, $a = 13.8155(6)$, $b = 14.3165(6)$, $c = 15.1126(7)\text{\AA}$, $\alpha = 112.842(4)$, $\beta = 110.568(4)$, $\gamma = 100.381(3)^\circ$, $V = 2399.2(2) \text{\AA}^3$, $Z = 1$, $D_x = 1.209 \text{ Mg}\cdot\text{m}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.71073\text{\AA}$, $\mu = 21.09 \text{ cm}^{-1}$, $F(000) = 1180$, $T = 100(1) \text{ K}$. Single crystals were obtained by cooling a solution of the complex in $\text{C}_2\text{Cl}_4\text{H}_2$. A sample was studied on a Bruker AXS X8-APEX II with graphite monochromatized $\text{MoK}\alpha$ radiation. The data collection^[55] ($2\theta_{\text{max}} = 54^\circ$, distance detector = 60mm, ϕ scan frames via $0.7^\circ \phi$ rotation and 20 s per frame, range HKL : H -19,16 K -19,20 L -21,21) gave 23078 reflections. The data led to 16677 independent reflections from which 14250 with $I > 2.0 \sigma(I)$. The structure was solved with SIR-97,^[53] which revealed the non hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined with SHELXL97^[54] by the full-matrix least-square techniques (use of F square magnitude; x, y, z, β_{ij} for Au, P, Cl, C and O atoms, x, y, z in riding mode for H atoms; 1100 variables and 14250 observations with $I > 2.0 \sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.172 P)^2]$ where $P = (F_o^2 + 2 F_c^2)/3$ with the resulting $R = 0.068$, $R_w = 0.179$ and $S_w = 0.882$, $\Delta\rho < 6.1\text{e}\text{\AA}^{-3}$. Flack's parameter: 0.03 (5). The molecule crystallises with four solvent molecules, one of which lies inside the CD. CCDC reference numbers 648501 (**6**) and 631157 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedures for olefin dimerisation: $[\text{NiBr}_2]$ and $[\text{NiBr}_2(\text{DME})]$ were purchased from Aldrich and used without further purification. Methylaluminoxane (MAO) 10 wt % (Aldrich) was used as a white powder which was obtained after evaporation of the solvent (60°C , 3 h). This treatment reduces the amount of residual trimethylaluminium to *ca.* 3%. The resulting solid residue was dried during 3 h at 60°C under vacuum. All Ni complexes and MAO were weighed in a dry box (dry argon); the autoclave was charged under a slight flow of ethene or propene. Toluene and chlorobenzene were dried by conventional methods and distilled immediately prior to use. Gas chromatographic (GC) analysis were performed on a

VARIAN 3900 gas chromatograph using a WCOT Fused Silica Column (25 m, 0.32 mm intern diameter, 0.25 mm film thickness).

Ethene dimerisation: A 100 mL steel autoclave was heated at 100°C under vacuum for 2 h, cooled to room temperature and filled with ethene. The catalyst (4.50 μ mol) was dissolved in toluene (12 mL) before being introduced into the autoclave *via* a syringe under low ethene pressure. The solution was stirred for 15 min. whereupon the reactor was vented before a solution of MAO [400 equiv. (0.090 g, *ca.* 1.80 mmol) to 2000 equiv. (0.450 g, *ca.* 9.00 mmol)] in toluene (10 mL) was added. The reactor was pressurised at 25°C and stirred for the desired reaction time. At the end of the run, the autoclave was cooled down to 7°C, then depressurised over 1 h. The flask containing the reaction mixture was immediately after weighed in order to limit loss of butane products. The yield was determined by mass comparison of the reaction mixture with a control solution (22 mL of toluene stirred for 30 min. at 25°C under ethene pressure; depressurisation was carried out as for the reaction mixture).^[56] The mass of MAO used for catalysis was taken into account in the final yield determination. The products were analysed by ¹H NMR spectroscopy and GC.^[56] But-1-ene was identified by ¹H NMR resonances at δ 2.00, 4.95 and 5.78 ppm. Resonances for the *cis* and *trans* isomers of but-2-ene appear at δ 1.54 and 4.95 ppm, respectively δ 1.58 and 5.55 ppm.

Propene dimerisation: A 200 mL Büchi glass autoclave was heated at 100°C under vacuum for 2 h, then cooled to room temperature and filled with propene. A solution of **8** (0.007 g, 4.50 μ mol) in chlorobenzene (20 mL) was introduced into the autoclave *via* a syringe under a low propene flow. The solution was stirred for 15 min. whereupon the reactor was vented before a solution of MAO (2000 equiv., 0.450 g, *ca.* 9.00 mmol) in chlorobenzene (10 mL) was added. The reactor was pressurised at 25°C and stirred for 1 h. At the end of the run, the autoclave was cooled down to 5°C, then depressurised over 1 h. The yield was determined as for the dimerisation of ethene. Finally, heptane (1 mL) was added as internal standard and a sample of the reaction mixture was taken for GC analysis.

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Supporting information

Synthesis and properties of TRANSDIP, a rigid chelator built upon a cyclodextrin cavity. Is TRANSDIP an authentic *trans-spanning* ligand ?

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Figure SI1. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **TRANS DIP** recorded in CDCl_3 at 125.8 MHz. Enlargements of the regions I-IX are found in [Fig. SI2](#).

Figure S12. Relevant signal enlargements of the $^{13}\text{C}\{^1\text{H}\}$ (upper parts) and $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ (lower parts) NMR spectra of **TRANS DIP** recorded in CDCl_3 at 125.8 MHz. The C-6 $^{\text{C},\text{F}}$ signal is singled out.