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Synthesis and Properties of TRANSDIP, a Rigid Chelator Built upon a Cyclodextrin Cavity: Is TRANSDIP an Authentic *trans*-Spanning Ligand?

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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 treating $6^A,6^B,6^D,6^E$-tetramesylated, permethylated α-cyclodextrin with $PPhLi_2$ in excess. The double cascade cyclisation thus produced is regioselective as phosphinidene capping involves only adjacent glucose units. It is also stereospecific, as both lone pairs on the phosphorus atoms are orientated towards the cyclodextrin axis. The restricted flexibility of the phosphorus atoms, which are part of nine-membered heterocyclic rings, is responsible for $J_{P,C}$ spin–spin couplings with the eight-bond distant CH_2OMe carbon atoms of glucose units C and F. The treatment of TRANSDIP with Group 10 metal dihalides quantitatively gave 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 lone pairs on the phosphorus atoms rule out the possibility of forming binuclear complexes or higher oligomers. Further, in all the complexes, the phosphorus atoms are in a *trans* arrangement. TRANSDIP may therefore be regarded as an authentic *trans*-spanning diphosphane. In the complex $[NiBr_2{\cdot}TRANSDIP]$, 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: alkene dimerisation · cavitands · cyclodextrins · phosphane ligands · transition metals

Introduction

Speculation began early in the 20th century concerning the possibility of a bidentate ligand that spanned the opposite sites of a complex with 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 1930s 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, thus leading to coordination oligomers and polymers.[9]

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

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]

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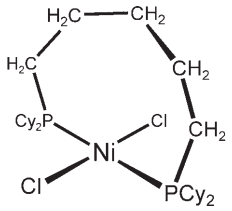


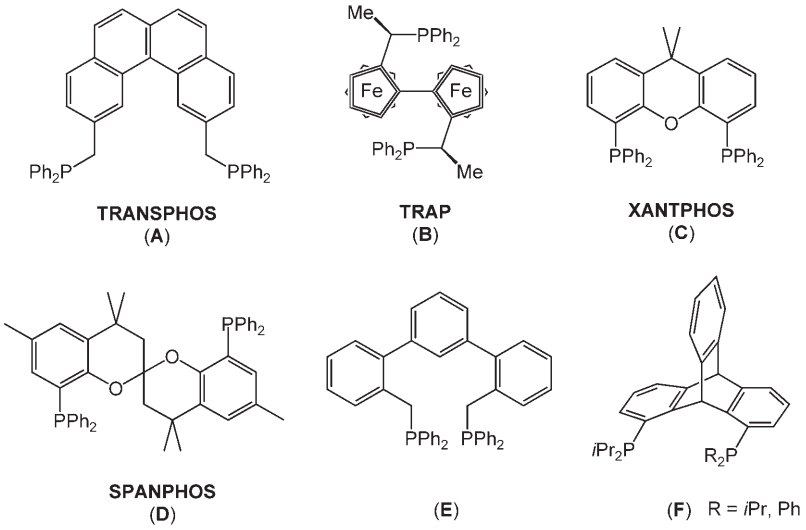
Scheme 1. The first *trans*-spanned diphosphane complex, as reported by Issleib and Hohlfeld in 1961.[10]

In 1974, Venanzi and co-workers described the TRANSPHOS ligand **A**, the first *trans*-spanning diphosphane with a rigid backbone (Scheme 2).[14,15] Built upon a benzo[*c*]phenanthrene scaffold, this ligand was said to have a consistent preference for *trans*-coordination.[14,16] Since then, other diphosphanes conceived as *trans*-spanning ligands were prepared, notably arylTRAPs **B** prepared by Ito and co-workers,[17,18] XANTPHOS **C**[19–21] and SPANPHOS **D** prepared by van Leeuwen and co-workers,[22] a *meta*-terphenyl-based pincer **E** prepared by Smith and Protasiewicz,[23] and triptycene-derived bidentates **F** prepared by Gelman and co-workers[24,25] (Scheme 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.

While the initial results were consistent with exclusive *trans*-spanning ligands, later experiments showed that all of 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 diphosphanes with 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 [$PdCl_2$(**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.[24,25] Further, the treatment of TRAP with *trans*-[$PtCl_2(MeCN)_2$] afforded, along with the hoped-for *trans* complex, the corresponding *cis* chelate as well.[17] Likewise, about six years after their first report that dealt with TRANSPHOS, Venanzi and co-workers admitted that the latter also acts as a *cis*-spanning ligand towards the $PtCl_2$ unit.[29] Finally, van Leeuven and co-workers recently published a report entitled "SPANPHOS: *trans*-spanning diphosphanes as *cis*-chelating ligands!", which described cationic rhodium(I) SPANPHOS complexes with a *cis* configuration.[30] Note that all of the above-described diphosphanes **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 diphosphanes may range from the stabilisation of exotic metal geometries to unusual selectivities in various catalytic processes, their preparation still remains a challenge.

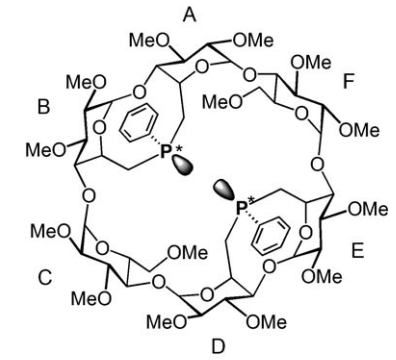
We describe the synthesis of a large diphosphane, TRANSDIP, which leads exclusively to a chelate complex when treated with a transition-metal ion able to accept two two-electron donors. TRANSDIP is based on a α-cyclodextrin platform. The synthetic strategy outlined hereafter allowed not only positioning of the two coordinating atoms above the primary face of the cyclodextrin macrocycle but also control over the orientation of the lone pairs on the phosphorus atoms. Because of the rigidity of the ligand and the appropriate phosphorus–phosphorus separation, we anticipated that this diphosphane should selectively result in complexes with *trans* stereochemistry when treated with the metal halides of Group 9 and 10. It has to be mentioned that *trans*-chelating diphosphanes built upon a cavity (e.g., calixarenes[31,32] and cyclodextrins[33,34]) have been reported previously, but all these also form either *cis* complexes or coordination oligomers. A preliminary study on the synthesis of TRANSDIP has been reported previously.[35]

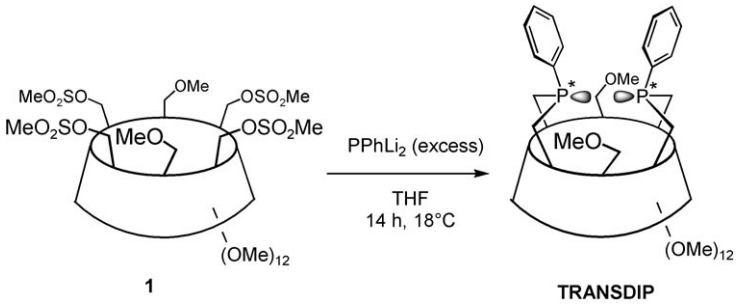


Scheme 2. Some well-known *trans*-spanning diphosphanes.

Results and Discussion

Ligand synthesis: TRANSDIP was synthesised from the previously described tetramesylate **1**[35] by treatment with an excess of the lithiated dianion $PhPLi_2$ at 18 °C (Scheme 3). The resulting cyclisations produced a single diastereoisomer in high yield (>95%). The formulation of the diphosphane





Scheme 3. Synthesis of TRANSDIP.

was inferred from its FAB mass spectrum, which revealed a strong signal for the $[M+H]^+$ ion (m/z 1317.4). The presence of three doublets for the H-1 atoms and seven singlets for the methyl groups in the ^{1}H NMR spectrum is consistent with a C_2-symmetrical molecule. The signals of the anomeric protons appear in a narrow range ($\Delta\delta = 0.06$ ppm), hence suggesting that the cyclodextrin 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 and oligomerisation, even when operating in concentrated solutions. In accord with the C_2 symmetry of the compound, the $^{31}P\{^1H\}$ NMR spectrum shows a single peak at $\delta = -16.8$ ppm. Careful examination of the ^{13}C NMR spectra (see Figures 1 and 2 and the Supporting Information) revealed an unexpected coupling between the phosphorus atoms and each of the symmetrically sited C-6^C and C-6^F atoms. The corresponding assignments were made by HMQC (see the Experimental Section). The couplings are likely to occur through through-space interactions involving the H-6^C, H-6^F atoms and the introverted lone pairs on the phosphorus atoms (Figure 3). Through-bond $J_{P,C\text{-}6^{C,F}}$ interactions can reasonably be ruled out as the C-6^{C,F} atoms are separated from each phosphorus atom by eight single bonds. Note that as a result of overlapping signals the corresponding $J_{P,H\text{-}6}$ couplings could not be identified. Preliminary molecular mechanics calculations (MM2) reveal that in the minimised structure the H-6^{C,F} and phosphorus atoms lie roughly in the same plane (Figure 3). We note that the C-6^{A,B} and C-6^{D,E} atoms also experience coupling interactions with both phosphorus atoms. Overall, these findings reflect the high rigidity of the two capping units.

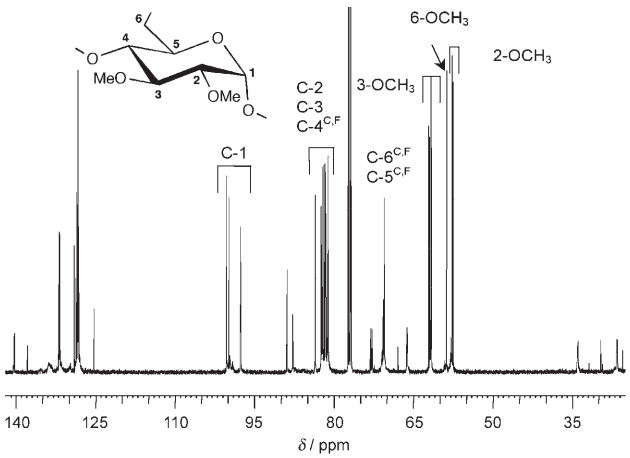


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of TRANSDIP recorded in $CDCl_3$ at 125.8 MHz. Enlargements are found in Figure 2 and in the Supporting Information.

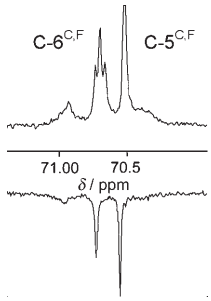


Figure 2. Signals of the C-6^{C,F} and C-5^{C,F} atoms in TRANSDIP in the $^{13}C\{^1H\}$ (top) and $^{13}C\{^1H,^{31}P\}$ (bottom) NMR spectra recorded in $CDCl_3$ at 125.8 MHz.

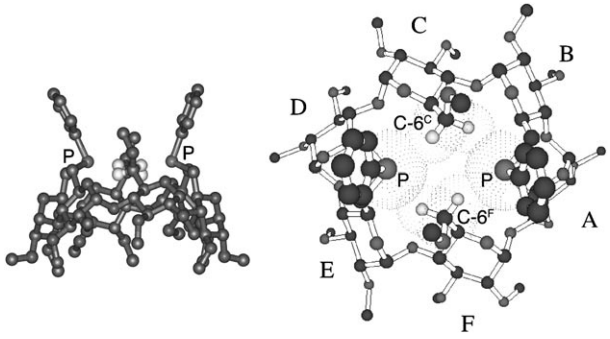
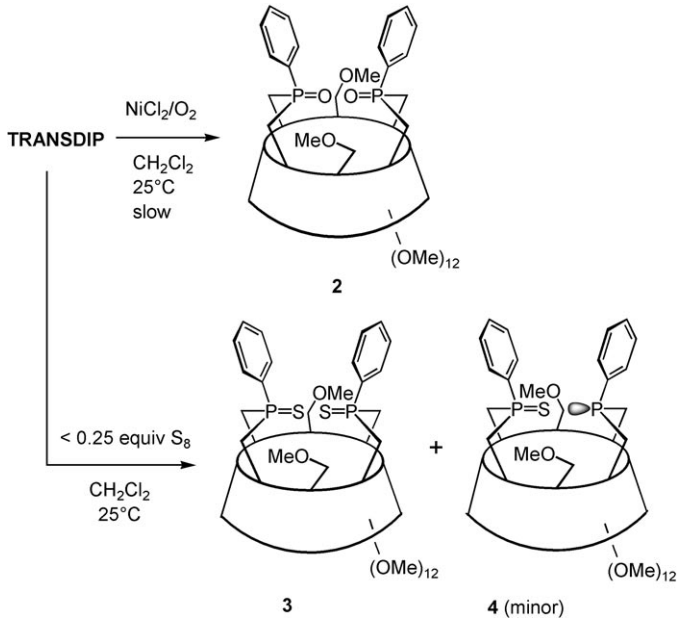


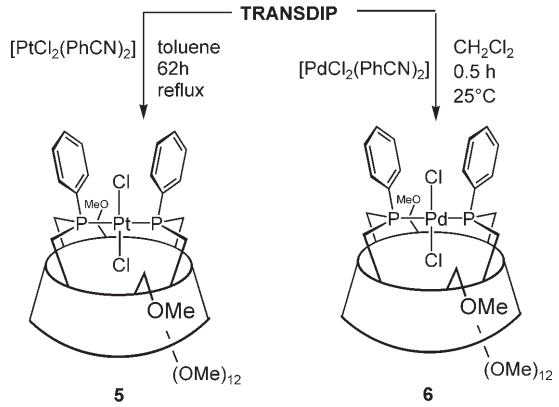
Figure 3. Calculated structure (MM2) of free TRANSDIP (right: view along the cyclodextrin axis from the primary face; left: side view).

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



Scheme 4. Formation of phosphorus(V) derivatives of TRANSDIP.

***trans*-Chelating properties of TRANSDIP**: According to Corey–Pauling–Koltun (CPK) models, TRANSDIP possesses the correct 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 forming square-planar metal complexes. Thus, the treatment of TRANSDIP with a mixture of *cis* and *trans* isomers of [$PtCl_2(PhCN)_2$] quantitatively afforded complex **5** (Scheme 5). It should be mentioned that this reaction takes



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

about three days in refluxing toluene to be completed, and ^{31}P{^{1}H} NMR spectroscopic monitoring showed that neither *cis* nor oligomeric compounds were formed during the complexation. Complex **5** is characterised by a sharp ^{31}P{^{1}H} NMR signal at $\delta = -6.5$ ppm, flanked by Pt satellites with a $^1J_{P,Pt}$ coupling constant ($J = 2463$ Hz) that lies in the range expected for complexes of *trans* stereochemistry.[36]

The palladium analogue **6**, which was quantitatively obtained from [$PdCl_2(PhCN)_2$] (Scheme 5), is characterised by a singlet at $\delta = -0.4$ ppm in the ^{31}P{^{1}H} NMR spectrum. The presence in the ^{13}C{^{1}H} NMR spectrum of a virtual triplet for the carbon atom of each P*C*H$_2$ moiety in the A,D and B,E glucose units ($|{}^1J_{C,P} + {}^3J_{C,P'}| = 20.0$ 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 the mass spectrum that corresponded to the $[M]^+$ ion (m/z 1494.1). In contrast to the demanding reaction conditions required for the preparation of **5** (see above), the reaction between TRANSDIP and the palladium(II) precursor is complete within 30 minutes in CH_2Cl_2 at room temperature. As for the ligand, the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of complexes **5** and **6** show clear evidence for twofold molecular symmetry. The location of the chlorine atoms along the cyclodextrin axis could be unambiguously deduced from the ^{1}H NMR spectra. The latter reveal a strong deshielding effect ($\Delta\delta = > 0.9$ ppm with respect to the free ligand) of two inwardly pointing H-5 atoms, thus indicating weak C-H^5···Cl interactions (Figure 4). 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 cyclodextrin species 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

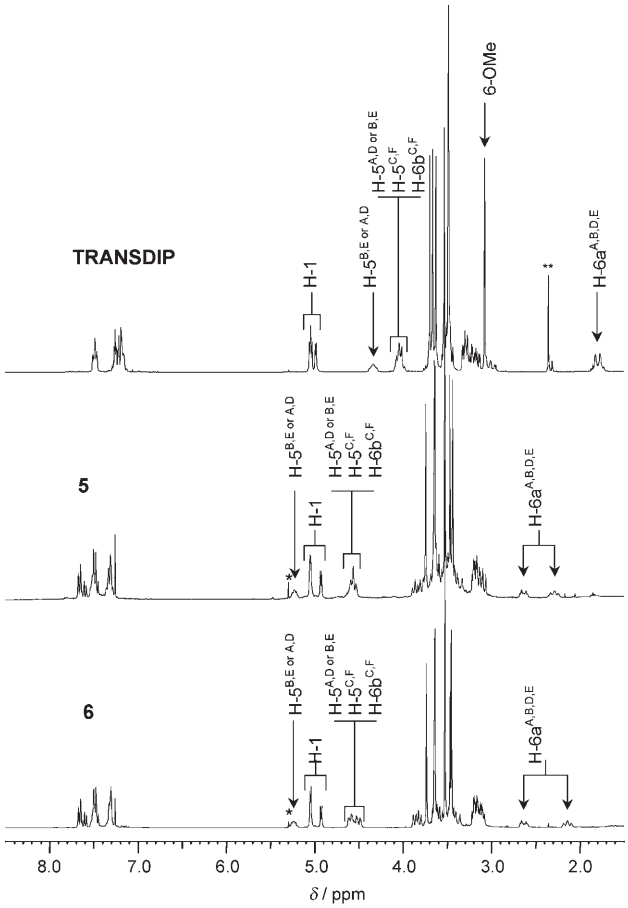


Figure 4. ^{1}H NMR spectra of TRANSDIP (top), **5** (middle), and **6** (bottom) recorded in $CDCl_3$ at 300.1 MHz. The asterisks denote residual solvents (CH_2Cl_2 or toluene).

meta-carbon atoms in the $^{13}C\{^{1}H\}$ NMR spectra (see the Experimental Section). Each triplet becomes a singlet after ^{31}P decoupling.

An X-ray diffraction study confirmed the *trans* disposition of the phosphorus atoms (Figure 5 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 cyclodextrin species. The data nevertheless provide clear information about the most important structural features of the complex. The unit cell contains two distinct molecules (denoted a and b), which display nonsignificant structural differences.

Table 1. Selected bond lengths and angles for [$\mathbf{6}_2$·2(C_5H_{12})].

Molecule a		Molecule b	
Bond lengths and distances [Å]			
P(1)–Pd(1)	2.394(5)	P(1)–Pd(1)	2.331(5)
P(2)–Pd(1)	2.343(5)	P(2)–Pd(1)	2.353(5)
Pd(1)–Cl(1)	2.271(5)	Pd(1)–Cl(1)	2.329(6)
Pd(1)–Cl(2)	2.337(5)	Pd(1)–Cl(2)	2.306(5)
Cl(1)···H^5(5)	2.652	Cl(1)···H^5(5)	2.629
Cl(1)···H^5(55)	2.852	Cl(1)···H^5(55)	2.747
Cl(1)···H^5(45)	2.956	Cl(1)···H^5(45)	2.932
Angles [°]			
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 cyclodextrin cavity, whereas the other is *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) (Cl···H-5 distances: 2.652, 2.852, and 2.956 Å, respectively; Figure 5). Similar short separations were found in molecule b (Table 1), which is consistent with the previously established chlorophilicity of methylated α-cyclodextrin species.[34,38] The stereochemistry of the palladium centre deviates in both molecules from an ideal square-planar coordination geometry, thus resulting in slightly bent Cl-Pd-Cl and P-Pd-P units, but the nonlinearity 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, as the whole molecule is no longer C_2-symmetric. Both P–C(aryl) bonds are inclined towards one side of the cyclodextrin torus, with the *exo*-chlorine atom being obviously pushed away by the phenyl rings (Cl(2)-Pd(1)-P-C(Ar) torsion angles in molecule a are 34.7 and −29.6°). On the other hand, repulsion of the *endo*-chlorine atom by the cyclodextrin 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 (Figure 6). This motion could not, however, be frozen out on the NMR timescale on cooling a solution of the complex in CD_2Cl_2 down to −80 °C.

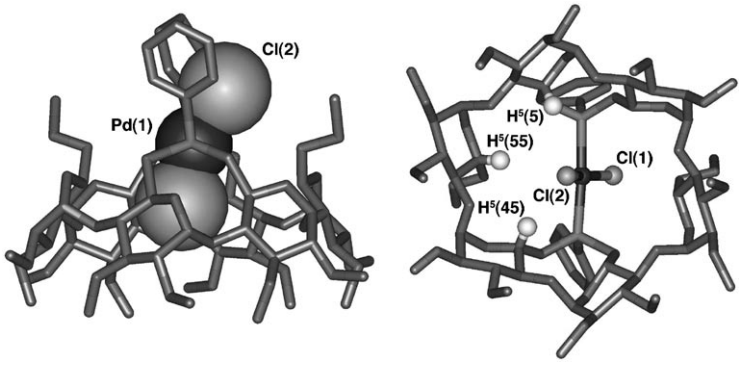


Figure 5. Molecular structure of complex **6**. Side (left) and bottom views (right) show the slightly bent Cl-Pd-Cl rod (only molecule a is represented). Hydrogen atoms and solvent molecules are omitted for clarity (except three H-5 atoms).

The coordination properties of TRANSDIP were further assessed towards nickel(II)

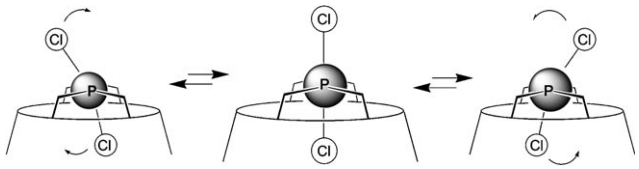
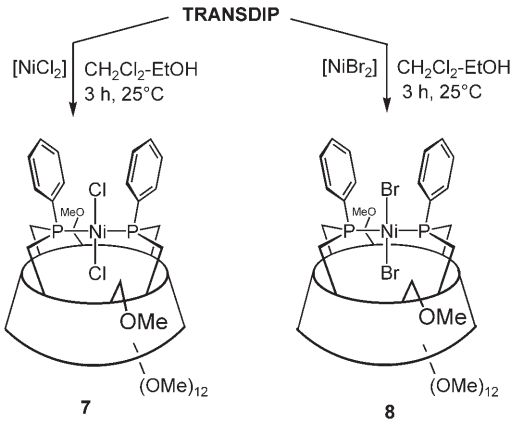


Figure 6. Proposed fast oscillation of the Cl-Pd-Cl unit about the P–P axis in complex **6**.

centres. Thus, the violet nickel complex **7** and the green complex **8** were quantitatively formed by the reaction of TRANSDIP with $NiCl_2$ and $NiBr_2$, respectively (Scheme 6).



Scheme 6. Preparation of complexes **7** and **8**.

In both reactions, a transient red species was observed, but could not be isolated. The diamagnetic complexes were characterised by ^{1}H (Figure 7), $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectroscopic, mass-spectrometric, and elemental analysis (see the Experimental Section). The *trans* arrangement of the phosphorus atoms was deduced from the $^{13}C\{^{1}H\}$ NMR spectrum, in which the PCH_2 carbon atoms appear as virtual triplets ($|{}^{1}J_{C,P}+{}^{3}J_{C,P'}| \approx 18$ Hz). Finally, electron paramagnetic resonance (EPR) spectroscopic measurements showed that complex **8** remained diamagnetic at temperatures as low as 4 K.

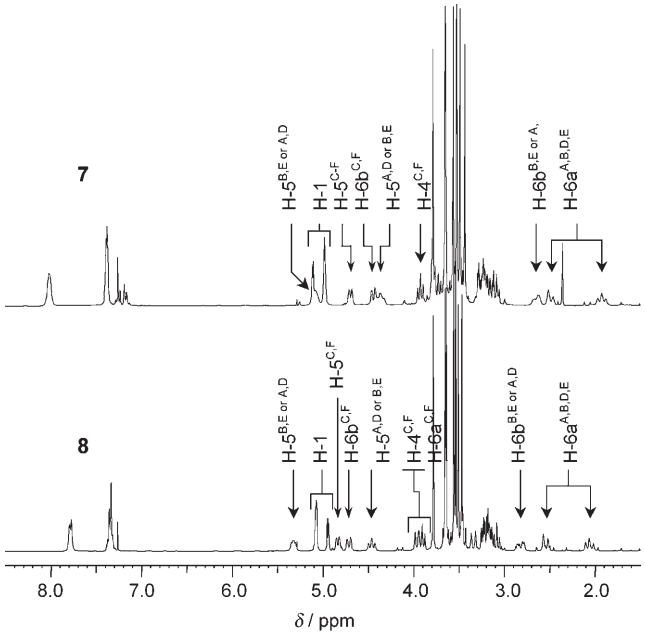
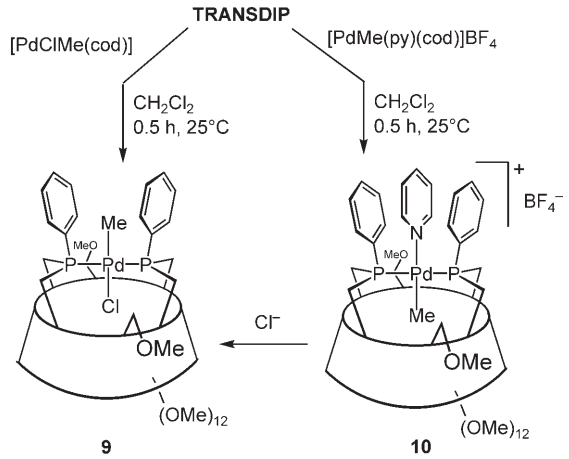


Figure 7. ^{1}H NMR spectra of **7** (top) and **8** (bottom) recorded in $CDCl_3$ at 300.1 MHz.

Binding properties of TRANSDIP towards unsymmetrical X-M-Y rods: Another example that illustrates the *trans*-chelating behaviour of TRANSDIP is its reaction with [PdClMe(cod)] (cod = 1,5-cyclooctadiene) in CH_2Cl_2, thus leading to the quantitative formation of complex **9** (Scheme 7). The formation of a monomeric species was inferred from the MALDI-TOF mass spectrum, which displays a peak at m/z 1474.1 and corresponds to the $[M]^+$ ion. Again, all the NMR spectra are consistent with a C_2-symmetrical species. The *trans* stereochemistry was deduced from the presence of a symmetrical methyl triplet in the ^{1}H NMR spectrum ($^{3}J_{H,P} = 6.8$ Hz). As for the previously described complexes **5**–**8**, two H-5 atoms of the phosphinidene-capped glucose rings underwent a significant lowfield shift ($\Delta\delta \approx 1.1$ 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 atoms as well as the PPh units.

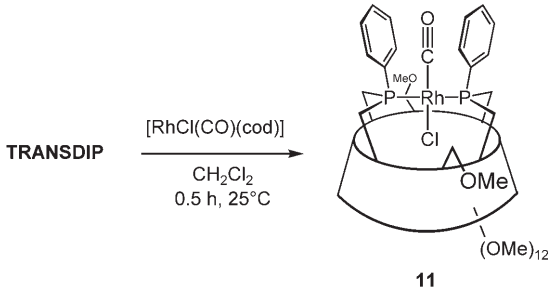


Scheme 7. Preparation of complexes **9** and **10**.

It must be emphasised that from a steric point of view the upper part of the cavity is perfectly capable of entrapping a methyl unit. This ability was demonstrated by treating TRANSDIP with $[PdMe(py)(cod)]BF_4$ (py = pyridine). This reaction resulted in the exclusive formation of *trans*-**10** (Scheme 7), a complex with an *endo*-oriented methyl group. As a result of 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 that showed cross peaks between

the palladium-bound methyl moiety and some of the inner-cavity protons of the cyclodextrin species. This 2D NMR spectroscopic experiment also revealed that the coordinated pyridine moiety interacts with both phenyl groups. The addition of free Cl^- ions to a solution of **10** regenerated **9**, which means that the Pd–Me bond is expelled from the cavity in this latter reaction (Scheme 7).

The affinity of the cyclodextrin cavity for metal-bound chloride ions was also exemplified by the synthesis of complex **11**, obtained quantitatively by reaction of TRANSDIP with [RhCl(CO)(cod)] in CH_2Cl_2 (Scheme 8). The ^{1}H NMR

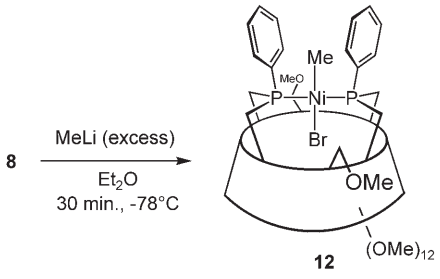


11

Scheme 8. Selective entrapment of the Rh–Cl bond within a cyclodextrin cavity.

spectrum of **11** reveals that, as expected, two symmetrically situated H-5 atoms (belonging to phosphorus-capped glucose units) are significantly downfield shifted relative to the four other H-5 atoms, as a result of weak interactions with the entrapped chlorine atom. Attempts to replace the encapsulated chlorine atom with a hydrido ligand by treatment of **11** with $NaBH_4$ in ethanol produced a mixture of compounds that could not be separated. Note that the entrapment of a Rh–H bond in a cyclodextrin cavity was achieved recently with another, more flexible, cyclodextrin-derived diphosphane.[34]

An interesting reaction in which the cavity behaves as a protecting funnel towards an incoming nucleophile is the reaction between **8** and a large excess of MeLi in Et_2O at −78 °C (Scheme 9). This reaction selectively gave the monosubstituted derivative **12**. The ^{1}H NMR spectrum of **12** shows a single methyl signal (intensity 3H) at $\delta = -0.94$ ppm; furthermore, a ROESY experiment confirmed



12

Scheme 9. A cyclodextrin cavity acting as a protecting funnel towards an incoming nucleophile.

the positioning of this group as close to the phenyl rings. Consistent with the presence of an unaffected NiBr unit lying inside the cavity, the ^{1}H NMR spectrum shows a signal for H-5 (integral: 2H; the protons belong to the phosphorus-capped glucose units) that has undergone a significant lowfield shift with respect to that of the free ligand. The deshielding is even more pronounced than that observed for **8** (Figure 8). The reaction that leads to **12** constitutes the first

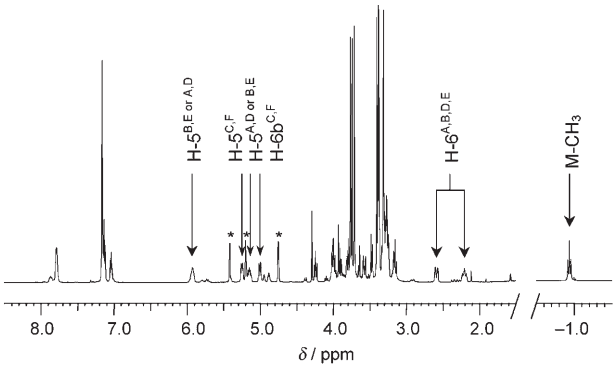


Figure 8. ^{1}H NMR spectrum of **12** recorded in C_6D_6 at 500.1 MHz. The starred signals correspond to anomeric protons.

example in which a $[NiX_2P_2]$ complex undergoes a selective monoalkylation, regardless of the stoichiometry of the 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.

Is TRANSDIP a perfect *trans*-chelator? All the complexation reactions described above, which involve Group 10 metal halides, are quantitative, and oligomeric complexes were not formed in any of these reactions. Therefore, TRANSDIP may be regarded as an excellent chelator. Moreover, all the complexes formed display *trans* stereochemistry. Interestingly, the P-M-P angles found in $[PdCl_2$(TRANSDIP)] (i.e., 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 $[Au(tht)(CH_2Cl_2)]PF_6$ (tht = tetrahydrothiophene), which leads to **13** (Figure 9). 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 nonlinear P-Au-P fragment, with the two P–Au vectors somewhat bent towards the cavity centre (P-Au-P = 163.4°). For comparison, a value of 175.1(1)° was found in $[Au(PhMe_2P)_2][Au(GeCl_3)_2]$.[41] The P–Au bond lengths (i.e., 2.319 and 2.324 Å) fall into the range expected for $[(AuPR_3)_2]^+$ ions.[42] What about the flexibility of TRANSDIP? This question was addressed recently by studying [AgX(TRANSDIP)] (X = halide) chelate complexes.[43] While P-Ag-P angles near to 120° were expected for these

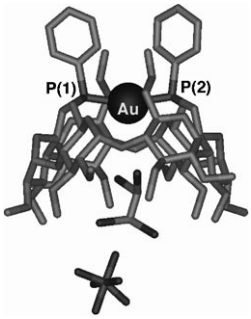


Figure 9. X-ray structure of the gold(I) complex **13**. The PF_6 anion and only one of the four $C_2H_2Cl_4$ solvent molecules are shown.

complexes, actual values of approximately 143° were found in the solid state. These observations illustrate the relatively weak flexibility of TRANSDIP, which is, 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).

Catalytic properties of [NiX_2(TRANSDIP)] complexes: An interesting property of TRANSDIP concerns its catalytic properties. After activation with methylaluminoxane (MAO), complexes **7**, **8**, and **12** catalyse the oligomerisation of ethene and propene.

Dimerisation of ethene: The investigations into ethene oligomerisation 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, thus producing a slow but steady temperature increase over a period of approximately one hour ($P(C_2H_4) = 30$ bar, $\Delta T =$ 17–21 °C) independently of the catalyst precursor used.

The three nickel(II) complexes turned out to be good catalysts for dimerisation, the observed turnover frequencies (TOFs) ranged from 10000 to 43000 mol(C_2H_4) mol(Ni)$^{-1}$ h^{-1}. For comparison, under similar conditions, the TOF observed for [$NiBr_2(Ph_2PCH_2CH_2PPh_2)$]/MAO was 34000 mol$(C_2H_4)$ mol(Ni)$^{-1}$ h^{-1}.[44] During catalysis, ligand dissociation is very unlikely to occur, considering the observed lack of reactivity of the [$NiBr_2$]/MAO and [$NiBr_2$(dme)]/MAO (dme = dimethyl ether) systems (Table 2, entries 1 and 2). In fact, the catalytic systems were found to be active over a period longer than two hours, which is indicative of the high stability of the active species. The TOF reaches its maximum value after approximately one hour, upon which the activity decreases very slowly, possibly as a result of 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) were octenes. As usually observed for [NiX_2L_2] (L = ligand) complexes, the catalytic activity of **8** increased with the amount of MAO, but the maximum activity had not been reached using 2000 equivalents (Table 2, entries 4–6). 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 the 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 cyclodextrin funnel occurs more readily for chloride than bromide ions, and, accordingly, that full conversion into a catalytically active species is faster with the former complex. Note that complex **12** is not active in the absence of MAO (Table 2, entry 12), thus confirming that no halide must be left in the first coordination sphere of the catalytically active species.

Dimerisation of propene: An investigation into propene dimerisation 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 equivalents of MAO (Table 3). The activity of the catalyst at room temperature and under propene ($P(C_3H_6)$ 5 bar) was about eightfold lower (i.e., TOF = 14000 mol(C_3H_6) mol(Ni)$^{-1}$ h^{-1}) than that of [$NiBr_2(Ph_2PCH_2CH_2PPh_2)$]/MAO.[45] This difference is probably a result of greater crowding about the nickel centre in **8**. As already observed in the studies of ethene dimerisation, the active species turned out to be remarkably stable during catalysis. The distribution (determined by GC/MS) of the primary products

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

Entry	Catalyst precursor	t [min]	$P(C_2H_4)$ [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] Conditions: catalyst = 4.5 μmol, toluene = 22 mL, $T = 25$ °C, 500 rpm; for all experiments the results were averaged. [b] Yield determined by the mass of the final reaction mixture versus the mass of the control reaction in toluene (22 mL). [c] Measurement: mol of C_2H_4 converted per mol of Ni per hour [mol(C_2H_4) mol(Ni)$^{-1}$ h^{-1}]. [d] Determined by GC analysis. [e] Determined by ^{1}H NMR spectroscopic analysis: 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*) and 1.58 and 5.55 ppm (*trans*).

Table 3. Catalytic propene dimerisation with **8** or $[NiBr_2(dppe)]$.[a]

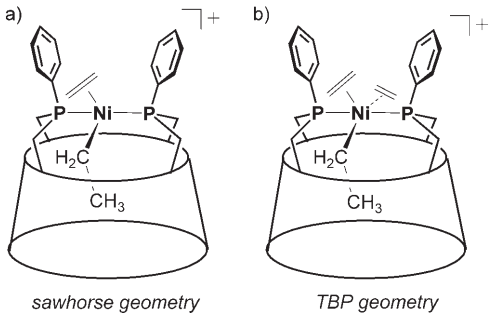
Entry	Catalyst precursor	[Al]/[Ni]	Yield [g]	TOF[b] [10^4]	Selectivity C6[c] [wt%]	Ref.
1[d]	**8**	2000	2.6	1.4	75.6	this study
2	$[NiBr_2(dppe)]$	400	21.7	11.5	87.0	[45]

[a] Conditions: carried out in a 200-mL Büchi autoclave, catalyst = 4.5 mmol, chlorobenzene = 30 mL, $T = 25\,^{\circ}C$, $t = 60$ min, $P(C_3H_6) = 5$ bar. [b] Measurement: mol of C_3H_6 converted per mol of Ni per hour [mol(C_3H_6) mol$(Ni)^{-1}h^{-1}$]. [c] Determined by GC analysis. [d] The results were averaged over three experiments. dppe = 1,2-bis(diphenylphosphino)ethane.

(those obtained after β-elimination) and the isomerisation products is given in Table 4.

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

The dimerisation mechanism: In the conventional olefin-dimerisation mechanism using mixtures of $[Ni(PR_3)_2X_2]$/MAO, square-planar $[Ni(PR_3)_2(alkyl)(olefin)]^+$ intermediates that adopt a *cis* configuration are formed before the insertion step.[47,48] Obviously, as a result of the rather high rigidity of TRANSDIP, related intermediates with *cis*-bonded phosphanes are unattainable with this chelator. Since the formation of a C–C bond requires the moieties undergoing coupling to 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 (Scheme 10; complexes a and b). Note that, from a stereochemical point of view, both types of complexes allow migratory insertion to take place inside the cavity, but we have no indication that such a process occurs. It should further be mentioned that in view of the ease nickel(II) species undergo oxidation, catalytic intermediates with a nickel(III) centre can not be formally ruled out. Further experimental investigations and theoretical calculations are needed to exclude or confirm these hypotheses.



Scheme 10. Proposed intermediates in the dimerisation of ethene with **7**/MAO.

Conclusion

In summary, we have shown that the reaction of $PhPLi_2$ with the $6^A,6^B,6^D,6^E$-tetramesylated precursor **1** occurs in a regiospecific manner, thus 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 carbon atoms in the CH_2OMe units of glucose units C and F.

TRANSDIP displays remarkable complexation properties, which are notably illustrated by its reaction with d^8-metal ion halides, thus affording chelate complexes exclusively. The fact that no oligomers were formed in these reactions relies on both the imposed P···P separation and the rigidified ligand 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 of a receptor close to the phosphorus atoms, which may behave as a second coordination sphere. Thus, in $[NiX_2(TRANSDIP)]$ complexes, the cavity provides steric protection for one of the two M–X bonds, thereby enabling efficient discrimination of the two halides in nucleophilic substitution reactions.

Finally, our finding that $[NiX_2(TRANSDIP)]$ 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 C–C coupling step. Elucidation of the exact mechanism that leads to the dimers, and the stereochemistry of the intermediates involved in such reactions, is currently underway.

Table 4. Product distribution of the propene dimerisation with **8** or $[NiBr_2(dppe)]$.

Entry	Catalyst precursor	Product distribution [mol%][a]						MP [%][b]	Ref.
		4M1P	4M2P	2M1P	2M2P	Hexane	TMEN		
1[c]	**8**	1.4	32.6	7.8	52.2	3.6	2.4	94.0	this study
2	$[NiBr_2(dppe)]$	2.2	35.8	14.8	41.0	5.0	1.2	93.8	[45]

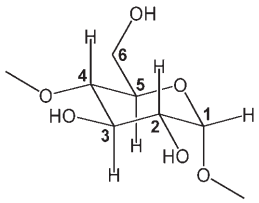
[a] Determined by GC/mass-spectrometric analysis. [b] Total amount of MP obtained. [c] The results were averaged over three experiments. 4M1P: 4-methyl-1-pentene, 4M2P: 4-methyl-2-pentene, 2M1P: 2-methyl-1-pentene, 2M2P: 2-methyl-2-pentene, MP: methylpentene, TMEN: 2,3-dimethyl-2-butene.

Experimental Section

General procedures: All the commercial reagents were used as supplied. Complexes $[PtCl_2(PhCN)_2]$,[49] $[PdCl_2(PhCN)_2]$,[49] $[PdClMe(cod)]$,[50] and $[AuCl(tht)]$[51] were synthesised according to previously reported procedures. All manipulations involving phosphanes were performed in Schlenk-type flasks under dry nitro-

gen. 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 an alumina column (thickness: 5 cm) and stored under nitrogen over molecular sieves (4 Å). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 25 °C with an FT Bruker and AC300 (^{1}H: 300.1, ^{13}C: 75.5, ^{31}P: 121.5 MHz) instrument and an Avance 500 Bruker (^{1}H: 500.1, ^{13}C: 125.8 MHz) instrument. ^{1}H NMR spectral data were referenced to residual protiated solvents ($\delta = 7.26$, 7.16, and 2.05 ppm for $CDCl_3$, C_6D_6, and $(CD_3)_2CO$, respectively), ^{13}C NMR spectral data to deuterated solvents ($\delta = 77.0$, 128.06, and 29.84 ppm for $CDCl_3$, C_6D_6, and $(CD_3)_2CO$, respectively), and the ^{31}P NMR data 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 the matrix or on a Bruker MicroTOF spectrometer (ESI) using CH_2Cl_2, CH_3CN, or CH_3OH as the 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 phosphorus atoms (i.e., *R* for both phosphorus atoms in TRANSDIP) was made by giving arbitrary priority to glucose units A and D over B and E, respectively. The numbering of the atoms within the glucose unit:



Synthesis of ligands and complexes

6^A,6^B,6^D,6^E-Tetradeoxy-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 *n*BuLi in hexane (1.60 M, 1.7 mL, 2.72 mmol) was added dropwise to a stirred solution of $PhPH_2$ (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 1 h through 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 Li_2PPh quenched with methanol (20 mL). After removal of the solvent in vacuo, toluene was added to the residue and the resulting suspension filtered over celite. Evaporation to dryness afforded analytically pure TRANSDIP (yield: 0.348 g, 98 %). R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, v/v) = 0.37; m.p. 198 °C (decomp): ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 1.80 (m, 4H, H-6a^{A,B,D,E}), 3.00 (broad dd, 2H, $^2J_{H\text{-}6b,H\text{-}6a}$ = 15.1, $^2J_{H\text{-}6b,P}$ = 15.1 Hz, H-6b$^{A,D\text{ or }B,E}$), 3.06 (s, 6H, OMe), 3.14 (dd, 2H, $^3J_{H\text{-}2,H\text{-}1}$ = 3.2, $^3J_{H\text{-}2,H\text{-}3}$ = 9.9 Hz, H-2$^{B,E\text{ or }A,D}$), 3.19 (dd, 2H, $^3J_{H\text{-}2,H\text{-}1}$ = 3.4, $^3J_{H\text{-}2,H\text{-}3}$ = 9.8 Hz, H-2^{C,F}), 3.20–3.33 (6H, H-4 ^{A,B,D,E}, H-6b$^{B,E\text{ or }A,D}$), 3.44–3.70 (12H, H-2$^{A,D\text{ or }B,E}$, H-3, H-4^{C,F}, H-6a^{C,F}), 3.47 (s, 6H, OMe), 3.47 (s, 6H, OMe), 3.52 (s, 6H, OMe), 3.62 (s, 6H, OMe), 3.65 (s, 6H, OMe), 3.68 (s, 6H, OMe), 3.99–4.06 (6H, H-5$^{A,D\text{ or }B,E}$, H-5^{C,F}, H-6b^{C,F}), 4.33 (m, 2H, H-5$^{B,E\text{ or }A,D}$), 4.98 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, H-1$^{B,E\text{ or }A,D}$), 5.03 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.5 Hz, H-1$^{A,D\text{ or }B,E}$), 5.04 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, H-1^{C,F}), 7.18 (m, 4H, *m*-H), 7.26 (m, 2H, *p*-H), 7.47 (m, 4H, *o*-H) ppm; ^{13}C{^{1}H,^{31}P} NMR (125.8 MHz, $CDCl_3$, 25 °C): δ (assignment by HMQC) = 26.6 (C-6$^{A,D\text{ or }B,E}$), 34.0 (C-6$^{B,E\text{ or }A,D}$), 57.5, 57.5, 57.6 (2-OCH_3), 58.7 (6-OCH_3), 61.6, 61.9, 62.1 (3-OCH_3), 66.2 (C-5$^{A,D\text{ or }B,E}$), 70.5 (C-5^{C,F}), 70.7 (C-6^{C,F}), 72.9 (C-5$^{B,E\text{ or }A,D}$), 81.1 (C-3$^{B,E\text{ or }A,D}$), 81.6 (C-3^{C,F}), 81.7 (C-2$^{B,E\text{ or }A,D}$), 81.9 (C-2^{C,F}), 82.2 (C-4^{C,F}), 82.4 (C-2$^{A,D\text{ or }B,E}$), 83.5 (C-3$^{A,D\text{ or }B,E}$), 87.8 (C-4$^{A,D\text{ or }B,E}$), 88.8 (C-4$^{B,E\text{ or }A,D}$), 97.6 (C-1$^{A,D\text{ or }B,E}$), 99.9 (C-1$^{B,E\text{ or }A,D}$), 100.3 (C-1^{C,F}), 128.3 (*m*-C), 128.5 (*p*-C), 131.8 (*o*-C), 140.4 (*ipso*-C) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = -16.8$ (s) ppm; elemental analysis (%) calcd for $C_{62}H_{94}O_{26}P_2 \cdot 0.5\,CH_2Cl_2$ (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-Tetradeoxy-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): The bis(phosphane oxide) was quantitatively formed by treating [Ni(cod)$_2$] with 1 equiv of TRANSDIP in toluene, then by bubbling air through the solution. Alternatively, **2** was obtained quantitatively by bubbling air through a solution of **7** (see below) in CH_2Cl_2 for 1 h. The product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 97:3, v/v). R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, v/v) = 0.35; m.p. 215 °C (decomp); ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 2.10 (m, 2H, H-6a$^{A,D\text{ or }B,E}$), 2.20 (m, 2H, H-6a$^{B,E\text{ or }A,D}$), 2.94 (m, 2H, H-6b$^{B,E\text{ or }A,D}$), 3.06 (dd, 2H, $^3J_{H\text{-}2,H\text{-}1}$ = 3.0, $^3J_{H\text{-}2,H\text{-}3}$ = 10.4 Hz, H-2$^{B,E\text{ or }A,D}$), 3.16 (dd, 2H, $^3J_{H\text{-}2,H\text{-}1}$ = 3.3, $^3J_{H\text{-}2,H\text{-}3}$ = 9.7 Hz, H-2^{C,F}), 3.21–3.39 (8H, H-2$^{A,D\text{ or }B,E}$, H-4^{A,B,D,E}, H-6b$^{A,D\text{ or }B,E}$), 3.33 (s, 6H, OMe), 3.43 (s, 6H, OMe), 3.46 (s, 6H, OMe), 3.52 (s, 6H, OMe), 3.52–3.72 (8H, H-3, H-4^{C,F}), 3.57 (s, 6H, OMe), 3.66 (s, 6H, OMe), 3.71 (s, 6H, OMe), 3.84 (m, 2H, H-6a^{C,F}), 4.15 (m, 2H, H-6b^{C,F}), 4.37 (m, 2H, H-5$^{A,D\text{ or }B,E}$), 4.44 (m, 2H, H-5^{C,F}), 4.62 (m, 2H, H-5$^{B,E\text{ or }A,D}$), 4.93 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1^{C,F}), 4.99 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, H-1$^{B,E\text{ or }A,D}$), 5.05 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.3 Hz, H-1$^{A,D\text{ or }B,E}$), 7.45–7.55 (6H, *m*-H, *p*-H), 7.71 (m, 4H, *o*-H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ (assignment by HMQC) = 34.0 (d, $^1J_{C,P}$ = 67.0 Hz, C-6$^{A,D\text{ or }B,E}$), 40.7 (d, $^1J_{C,P}$ = 67.6 Hz, C-6$^{A,D\text{ or }B,E}$), 57.4, 57.6, 57.6 (2-OCH_3), 58.7 (6-OCH_3), 61.7 (×2], 62.4 (3-OCH_3), 63.4 (d, $^2J_{C,P}$ = 5.6 Hz, C-5$^{A,D\text{ or }B,E}$), 66.8 (C-5$^{B,E\text{ or }A,D}$), 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, $^3J_{C,P}$ = 11.8 Hz, C-4$^{A,D\text{ or }B,E}$), 90.1 (d, $^3J_{C,P}$ = 5.0 Hz, C-4$^{B,E\text{ or }A,D}$), 97.6 (C-1$^{A,D\text{ or }B,E}$), 100.2 (C-1^{C,F}), 100.7 (C-1$^{B,E\text{ or }A,D}$), 129.0 (d, $^2J_{C,P}$ = 11.8 Hz, *o*-C), 129.4 (d, $^3J_{C,P}$ = 9.3 Hz, *m*-C), 131.9 (d, $^4J_{C,P}$ = 2.5 Hz, *p*-C), 133.9 (d, $J_{C,P}$ = 98.0 Hz, ips*o*-C) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 40.2$ (s) ppm; elemental analysis (%) calcd for $C_{62}H_{94}O_{28}P_2$ (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-Tetradeoxy-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 the pentane afforded analytically pure **3** as a pale-yellow powder (yield: 0.103 g, 98 %). R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, v/v) = 0.34; m.p. 184 °C (decomp); ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 2.05 (m, 2H, H-6a$^{A,D\text{ or }B,E}$), 2.45 (m, 2H, H-6a$^{B,E\text{ or }A,D}$), 3.02–3.33 (14H, H-2, H-4^{A,B,D,E}, H-6b^{A,B,D,E}), 3.26 (s, 6H, OMe), 3.45 (s, 12H, OMe), 3.47–3.71 (8H, H-3, H-4^{C,F}), 3.54 (s, 6H, OMe), 3.59 (s, 6H, OMe), 3.66 (s, 6H, OMe), 3.74 (s, 6H, OMe), 3.96 (m, 2H, H-6a^{C,F}), 4.22 (m, 2H, H-5^{C,F}), 4,32–4.44 (4H, H-5$^{B,E\text{ or }A,D}$, H-6b^{C,F}), 4.77 (m, 2H, H-5$^{A,B\text{ or }D,E}$), 4.92 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.8 Hz, H-1^{C,F}), 4.95 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.5 Hz, H-1$^{A,D\text{ or }B,E}$), 5.08 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.0 Hz, H-1$^{B,E\text{ or }A,D}$), 7.48 (m, 4H, *m*-H), 7.54 (m, 2H, *p*-H), 7.96 (m, 4H, *o*-H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ (assignment by HMQC) = 38.9 (d, $^1J_{C\text{-}6,P}$ = 52.6 Hz, C-6$^{B,E\text{ or }A,D}$), 43.3 (d, $^1J_{C\text{-}6,P}$ = 50.8 Hz, C-6$^{A,D\text{ or }B,E}$), 57.4, 57.5, 57.7 (2-OCH_3), 58.7 (6-OCH_3), 61.6, 61.9, 62.5 (3-OCH_3), 63.9 (m, C-5$^{B,E\text{ or }A,D}$), 68.5 (C-5$^{A,D\text{ or }B,E}$), 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$^{B,E\text{ or }A,D}$), 89.8 (m, C-4$^{A,D\text{ or }B,E}$), 97.7 (C-1$^{B,E\text{ or }A,D}$), 100.3 (C-1$^{A,D\text{ or }B,E}$), 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}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 40.8$ (s) ppm; elemental analysis (%) calcd for $C_{62}H_{94}O_{26}P_2S_2 \cdot 2\,CH_2Cl_2$ (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**; phosphane sulfides **3** and **4** could not be separated; ^{31}P{^{1}H} NMR: (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 42.2$ (d, P^V, $J_{P,P'}$ = 48.7 Hz), −19.5 (d, P^{III}, $J_{P,P'}$ = 48.7 Hz) ppm.

***trans*-P,P′-Dichloro-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-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 [$PtCl_2(PhCN)_2$] (0.047 g, 0.10 mmol) and TRANSDIP (0.130 g, 0.10 mmol) in toluene (25 mL) was refluxed for 3 days. The solution was concentrated to approximately 5 mL, and pentane (140 mL) was added to precipitate small amounts of starting complex. The solution was filtered over celite. Evaporation of the pentane afforded analytically pure **5** as a pale-yellow powder (yield: 0.153 g, 98%). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, v/v) = 0.46; m.p. >250°C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): δ (assignment by COSY) = 2.28 (m, 2H, H-6a$^{A,D\ or\ B,E}$), 2.63 (ddd, 2H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 5.5, $^3J_{H\text{-}6a,H\text{-}5}$ = 5.5, $^3J_{H\text{-}6a,P}$ = 14.6 Hz, H-6a$^{B,E\ or\ A,D}$), 3.07–3.22 (10H, H-2, H-4^{A,B,D,E}), 3.31–3.39 (4H, H-6b^{A,B,D,E}), 3.43 (m, 2H, H-3$^{A,D\ or\ B,E}$), 3.44 (s, 6H, OMe), 3.47 (s, 6H, OMe), 3.52 (s, 12H, OMe), 3.52–3.65 (4H, H-3$^{B,E\ or\ A,D}$, H-3^{C,F}), 3.64 (s, 6H, OMe), 3.65 (s, 6H, OMe), 3.74 (s, 6H, OMe), 3.81 (m, 2H, H-6a^{C,F}), 3.86 (m, 2H, H-4^{C,F}), 4.51–4.64 (6H, H-5$^{A,D\ or\ B,E}$, H-5^{C,F}, H-6b^{C,F}), 4.93 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.2 Hz, H-1$^{A,D\ or\ B,E}$), 5.05 (two overlapping d, 4H, H-1$^{B,E\ or\ A,D}$, H-1^{C,F}), 5.23 (m, 2H, H-5$^{B,E\ or\ A,D}$), 7.28–7.37 (6H, *m*-H, *p*-H), 7.49 (m, 4H, *o*-H) ppm; ^{13}C{^{1}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, $|^1J_{C,P}+{}^3J_{C,P'}|$ = 26.6 Hz, C-6$^{B,E\ or\ A,D}$), 57.5, 58.0, 58.7 (2-OCH_3), 59.3 (6-OCH_3), 61.7, 61.7, 62.0 (3-OCH_3), 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, $|^3J_{C,P}+{}^5J_{C,P'}|$ = 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, $|^3J_{C,P}+{}^5J_{C,P'}|$ = 10.0 Hz, *m*-C), 129.6 (*p*-C), 131.3 (virtual t, $|^2J_{C,P}+{}^4J_{C,P'}|$ = 9.5 Hz, *o*-C), 133.4 (virtual t, $|^1J_{C,P}+{}^3J_{C,P'}|$ = 57.8 Hz, *ipso*-C) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C): δ = −6.5 (s with Pt satellites, $^1J_{PPt}$ = 2463 Hz) ppm; elemental analysis (%) calcd for $C_{62}H_{94}O_{26}P_2PtCl_2$ (1583.37): C 47.03, H 5.98; found: C 47.14, H 6.05; MS (FAB): *m/z* (%): 1547.2 (100) $[M-Cl]^+$.

***trans*-P,P′-Dichloro-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-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 [$PdCl_2(PhCN)_2$] (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 the 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, CH_2Cl_2/MeOH, 90:10, v/v) = 0.45; m.p. 219–223°C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): δ = 2.13 (m, 2H, H-6a$^{A,D\ or\ B,E}$), 2.63 (ddd, 2H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 4.7, ^3J(H-6a,H-5) = 4.7, $^3J_{H\text{-}6a,P}$ = 14.7 Hz, H-6a$^{B,E\ or\ A,D}$), 3.08–3.22 (10H, H-2, H-4^{A,B,D,E}), 3.33–3.37 (4H, H-6b^{A,B,D,E}), 3.41 (m, 2H, H-3$^{A,D\ or\ B,E}$), 3.45 (s, 6H, OMe), 3.47 (s, 6H, OMe), 3.52 (s, 12H, OMe), 3.54–3.68 (4H, H-3$^{B,E\ or\ A,D}$, H-3^{C,F}), 3.64 (s, 6H, OMe), 3.65 (s, 6H, OMe), 3.73 (s, 6H, OMe), 3.79–3.88 (4H, H-4^{C,F}, H-6a^{C,F}), 4.48–4.62 (6H, H-5$^{A,D\ or\ B,E}$, H-5^{C,F}, H-6b^{C,F}), 4.93 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.2 Hz, H-1$^{A,D\ or\ B,E}$), 5.05 (d, 4H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, H-1$^{B,E\ or\ A,D}$, H-1^{C,F}), 5.23 (m, 2H, H-5$^{B,E\ or\ A,D}$), 7.30–7.36 (6H, *m*-H, *p*-H), 7.51 (m, 4H, *o*-H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 30.2 (virtual t, $|^1J_{C,P}+{}^3J_{C,P'}|$ = 25.0 Hz, C-6$^{A,D\ or\ B,E}$), 36.2 (virtual t, $|^1J_{C,P}+{}^3J_{C,P'}|$ = 20.0 Hz, C-6$^{B,E\ or\ A,D}$), 57.5, 58.0, 58.6 (2-OCH_3), 59.4 (6-OCH_3), 61.7, 61.7, 62.0 (3-OCH_3), 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, $|^3J_{C,P}+{}^5J_{C,P'}|$ = 9.5 Hz, C-4$^{A,D\ or\ B,E}$), 89.9 (br signal with triplet shape, C-4$^{B,E\ or\ A,D}$), 97.5 (×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{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C): δ = −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}-tetradeoxy-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 TRANSDIP (0.180 g, 0.14 mmol) in CH_2Cl_2 (10 mL) under vigorous stirring. After 4 h 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 the starting materials, which were then filtered over celite. Evaporation of the 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; m.p. 193°C (decomp); ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): δ (assignment by COSY) = 1.92 (m, 2H, H-6a$^{A,D\ or\ B,E}$), 2.49 (m, 2H, H-6a$^{B,E\ or\ A,D}$), 2.64 (m, 2H, H-6b$^{B,E\ or\ A,D}$), 3.05–3.31 (12H, H-2, H-4^{A,B,D,E}, H-6b$^{A,D\ or\ B,E}$), 3.40–3.79 (8H, H-3, H-6a^{C,F}), 3.43 (s, 6H, OMe), 3.49 (s, 6H, OMe), 3.52 (s, 6H, OMe), 3.56 (s, 6H, OMe), 3.64 (s, 6H, OMe), 3.65 (s, 6H, OMe), 3.79 (s, 6H, OMe), 3.92 (virtual t, 2H, $^3J_{H\text{-}4,H\text{-}3}$ = $^3J_{H\text{-}4,H\text{-}5}$ = 9.0 Hz, H-4^{C,F}), 4.36 (m, 2H, H-5$^{A,D\ or\ B,E}$), 4.44 (m, 2H, H-6b^{C,F}), 4.69 (m, 2H, H-5^{C,F}), 4.98 (two overlapping d, 4H, H-1^{A,B,D,E}), 5.08 (m, 2H, H-5$^{B,E\ or\ A,D}$), 5.11 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, H-1^{C,F}), 5.35 (m, 2H, H-5$^{B,E\ or\ A,D}$), 7.37–7.39 (6H, *m*-H, *p*-H), 8.02 (m, 4H, *o*-H) ppm; ^{13}C{^{1}H} 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$^{A,D\ or\ B,E}$), 34.8 (m, C-6$^{B,E\ or\ A,D}$), 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$^{A,D\ or\ B,E}$), 68.2 (C-5$^{B,E\ or\ A,D}$), 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$^{B,E\ or\ A,D}$), 97.1 (C-1$^{A,D\ or\ B,E}$), 100.5 (C-1^{C,F}), 127.9 (*m*-C, *p*-C), 129.5 (*o*-C), 131.6 (*ipso*-C) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C): δ = −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}-tetradeoxy-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 TRANSDIP (0.180 g, 0.14 mmol) in CH_2Cl_2 (10 mL) under vigorous stirring. After 4 h 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 starting materials, which were then filtered over celite. Evaporation of the pentane afforded **8** as a green powder (yield: 0.175 g, 83%). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, v/v) = 0.38; m.p. 186°C (decomp); ^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): δ (assignment by COSY) = 2.09 (m, 2H, H-6a$^{A,D\ or\ B,E}$), 2.54 (m, 2H, H-6a$^{B,E\ or\ A,D}$), 2.84 (m, 2H, H-6b$^{B,E\ or\ A,D}$), 3.04–3.28 (10H, H-2, H-4^{A,B,D,E}), 3.33 (m, 2H, H-6b$^{A,D\ or\ B,E}$), 3.45–3.70 (6H, H-3), 3.48 (s, 6H, OMe), 3.53 (s, 6H, OMe), 3.56 (s, 6H, OMe), 3.58 (s, 6H, OMe), 3.66 (s, 6H, OMe), 3.68 (s, 6H, OMe), 3.81 (s, 6H, OMe), 3.90–4.01 (4H, H-4^{C,F}, H-6a^{C,F}), 4.49 (m, 2H, H-5$^{A,D\ or\ B,E}$), 4.74 (m, 2H, H-6b^{C,F}), 4.86 (m, 2H, H-5^{C,F}), 4.97 (d, 2H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.1 Hz, H-1$^{A,D\ or\ B,E}$), 5.10 (two overlapping d, 4H, H-1$^{B,E\ or\ A,D}$, H-1^{C,F}), 5.35 (m, 2H, H-5$^{B,E\ or\ A,D}$), 7.36–7.41 (6H, *m*-H, *p*-H), 7.81 (m, 4H, *o*-H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 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-OCH_3, 3-OCH_3, 6-OCH_3), 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$^{A,D\ or\ B,E}$), 96.4 (C-1$^{B,E\ or\ A,D}$), 99.8 (C-1^{C,F}), 127.0 (*m*-C), 128.6 (*p*-C), 130.6 (*o*-C), 136.4 (*ipso*-C) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C): δ = −6.9 (s) ppm; elemental analysis (%) calcd for $C_{62}H_{94}Br_2NiO_{26}P_2{\cdot}2\,CH_2Cl_2$ (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′-Chloromethyl-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-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) (9)**: A solution of [PdClMe(cod)] (0.024 g, 0.08 mmol) in CH_2Cl_2 (3 mL) was added to a solution of TRANSDIP (0.110 g, 0.08 mmol) in CH_2Cl_2 (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 (SiO_2, CH_2Cl_2/MeOH, 90:10, v/v) = 0.45; m.p. 198–201°C; ^{1}H NMR (500.1 MHz, $CDCl_3$, 25°C): δ (assignment by COSY and ROESY) = −0.68 (t, 3H, $^3J_{H,P}$ = 6.8 Hz, CH_3), 2.07 (m, 2H, H-6a$^{A,D\ or\ B,E}$), 2.37 (m, 2H, H-6a$^{B,E\ or\ A,D}$), 3.06–3.20 (10H, H-2, H-4^{A,B,D,E}), 3.23 (m, 2H, H-6b$^{A,D\ or\ B,E}$), 3.32 (m, 2H, H-6b$^{B,E\ or\ A,D}$), 3.39 (s, 6H, OMe), 3.46–3.71 (8H, H-3, H-6a^{C,F}), 3.46 (s, 6H, OMe), 3.49 (s, 6H, OMe), 3.50 (s, 6H, OMe), 3.63 (s, 6H, OMe), 3.64 (s, 6H, OMe), 3.70 (s, 6H, OMe), 3.78 (virtual triplet, 2H, $^3J_{H\text{-}4,H\text{-}3}$ = $^3J_{H\text{-}4,H\text{-}5}$ = 9.0 Hz, H-4^{C,F}), 4.47 (dd, 2H,

$^{3}J_{H\text{-}6b,H\text{-}5}$ = 2.9, $^{2}J_{H\text{-}6b,H\text{-}6a}$ = 10.8 Hz, H-6b^{C,F}), 4.70–4.76 (4H, H-5$^{A,D\text{ or }B,E}$, H-5^{C,F}), 4.91 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 4.3 Hz, H-1$^{A,D\text{ or }B,E}$), 5.01 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, H-1^{C,F}), 5.03 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1$^{B,E\text{ or }A,D}$), 5.40 (m, 2H, H-5$^{B,E\text{ or }A,D}$), 7.29 (m, 2H, *p*-H), 7.34 (m, 4H, *m*-H), 7.40 (m, 4H, *o*-H) ppm; $^{13}C\{^{1}H\}$ 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, $|^{1}J_{C,P}+{}^{3}J_{C,P'}|$ = 22.0, C-6$^{A,D\text{ or }B,E}$), 35.8 (virtual t, $|^{1}J_{C,P}+{}^{3}J_{C,P'}|$ = 18.5 Hz, C-6$^{B,E\text{ or }A,D}$), 57.5, 57.8, 58.3 (2-OCH_3), 59.2 (6-OCH_3), 61.7, 61.8, 62.1 (3-OCH_3), 65.7 (br signal with triplet shape, C-5$^{A,D\text{ or }B,E}$), 68.3 (virtual t, $|^{2}J_{C,P}+{}^{4}J_{C,P'}|$ = 9.0 Hz, C-5$^{B,E\text{ or }A,D}$), 70.3 (C-5^{C,F}), 72.0 (C-6^{C,F}), 81.0 (×2; C-3$^{B,E\text{ or }A,D}$, C-3^{C,F}), 81.3 (C-4^{C,F}), 81.4 (C-2$^{B,E\text{ or }A,D}$), 81.7 (C-2^{C,F}), 82.8 (C-3$^{A,D\text{ or }B,E}$), 83.2 (C-2$^{A,D\text{ or }B,E}$), 87.4 (virtual t, $|^{3}J_{C,P}+{}^{5}J_{C,P'}|$ = 9.0 Hz, C-4$^{A,D\text{ or }B,E}$), 89.9 (C-4$^{B,E\text{ or }A,D}$), 97.6 (C-1$^{A,D\text{ or }B,E}$), 98.0 (C-1$^{B,E\text{ or }A,D}$), 101.0 (C-1^{C,F}), 128.3 (virtual t, $|^{3}J_{C,P}+{}^{5}J_{C,P'}|$ = 9.0 Hz, *m*-C), 129.2 (*p*-C), 130.6 (virtual t, $|^{2}J_{C,P}+{}^{4}J_{C,P'}|$ = 10.0 Hz, *o*-C), 135.4 (virtual t, $|^{1}J_{C,P}+{}^{3}J_{C,P'}|$ = 42.5 Hz, *ipso*-C) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 3.8 (s) ppm; elemental analysis (%) calcd for $C_{63}H_{97}ClO_{26}P_2Pd$ (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) $[M-Me]^+$, 1437.2 (15) $[M-Cl]^+$, 1422 (66) $[M-Me-Cl]^+$.

***trans*-P,P′-Methyl-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-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 [PdClMe(cod)] (0.032 g, 0.12 mmol) in CH_2Cl_2 (3 mL). After the suspension was stirred 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 (12 mL, 83:17, v/v) under agitation at 0 °C. The reaction mixture was then stirred at room temperature for 30 min before being concentrated to approximately 5 mL. Addition of pentane (80 mL) caused the product to precipitate, and filtration through a Schlenk-type frit afforded pure **10** as a pale yellow solid (yield: 0.170 g, 96 %). Complex **10** decomposes on silica (SiO_2); m.p. 183 °C (decomp); ^{1}H NMR (300.1 MHz, $(CD_3)_2CO$, 25 °C): δ (assignment by COSY and ROESY) = 1.12 (t, 3H, $^{3}J_{H,P}$ = 7.3 Hz, CH_3), 2.21 (m, 2H, H-6a$^{A,D\text{ or }B,E}$), 2.86 (m, 2H, H-6a$^{B,E\text{ or }A,D}$), 3.14–3.87 (22H, H-2, H-3, H-4, H-6b^{A,B,D,E}), 3.47 (s, 6H, 6-OMe), 3.55 (s, 6H, OMe), 3.55 (s, 6H, OMe), 3.56 (s, 6H, OMe), 3.60 (s, 6H, OMe), 3.65 (s, 6H, OMe), 3.71 (s, 6H, OMe), 4.07 (m, 2H, H-6a^{C,F}), 4.24–4.44 (6H, H-5$^{A,D\text{ or }B,E}$, H-5^{C,F}, H-6b^{C,F}), 4.84 (m, 2H, H-5$^{B,E\text{ or }A,D}$), 5.10 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 4.5 Hz, H-1$^{A,D\text{ or }B,E}$), 5.11 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 4.4 Hz, H-1^{C,F}), 5.26 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1$^{B,E\text{ or }A,D}$), 6.70 (m, 2H, *m*-H of M−pyridine), 7.04–7.69 (11H, *p*-H of M−pyridine, aromatic H of P−phenyl), 7.74 (m, 2H, *o*-H of M−pyridine) ppm, small amounts of free pyridine were also detected; $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $(CD_3)_2CO$, 25 °C): δ (assignment by HMQC) = 29.7 (m, C-6$^{A,D\text{ or }B,E}$), 34.7 (m, C-6$^{B,E\text{ or }A,D}$), 57.4, 58.6, 59.5, 60.2, 61.6, 61.7, 61.8 (2-OCH_3, 3-OCH_3, 6-OCH_3), 66.7 (C-5$^{A,D\text{ or }B,E}$), 68.1 (C-5^{C,F}), 69.5 (C-5$^{B,E\text{ or }A,D}$), 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$^{A,D\text{ or }B,E}$), 98.1 (C-1$^{B,E\text{ or }A,D}$), 101.3 (C-1^{C,F}), 126.2–132.6 (aromatic C) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $(CD_3)_2CO$, 25 °C): δ = −7.1 (s) ppm; $C_{63}H_{97}ClO_{26}P_2Pd$ (1474.26); MS (ESI-TOF): *m/z* (%): 1437.5 (100) $[M-BF_4-py]^+$; there is no microanalytical data for the cationic palladium(II) complexes reported in this study as this species was obtained only in the presence of excess pyridine.

***trans*-P,P′-Chlorocarbonyl-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-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}rhodium(I) (11)**: A solution of $[\{RhCl(CO)_2\}_2]$ (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 reaction mixture was concentrated to 2 mL and pentane (80 mL) was added to precipitate the starting materials, which were filtered over celite. Evaporation of the solvent afforded **11** as a pale-yellow powder (yield: 0.172 g, 97 %). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, v/v) = 0.41; m.p. 171 °C (decomp); IR (KBr) ν: 1982.1 (C=O) cm^{-1}; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 2.37 (m, 2H, H-6a$^{A,D\text{ or }B,E}$), 2.80 (m, 2H, H-6a$^{B,E\text{ or }A,D}$), 3.19–3.31 (10H, H-2, H-4^{A,B,D,E}), 3.33 (s, 6H, OMe), 3.35 (s, 6H, OMe), 3.37 (s, 6H, OMe), 3.47 (s, 6H, OMe), 3.57 (s, 6H, OMe), 3.61 (m, 2H, H-6b$^{B,E\text{ or }A,D}$), 3.74 (s, 6H, OMe), 3.79–3.93 (8H, H-3, H-6b$^{A,D\text{ or }B,E}$), 3.85 (s, 6H, OMe), 4.07 (d, 2H, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 11.1 Hz, H-6a^{C,F}), 4.18 (m, 2H, H-4^{C,F}), 4.80 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 4.3 Hz, H-1^{A,D} or H-1^{B,E}), 5.00 (broad d, 2H, $^{3}J_{H\text{-}5,H\text{-}4}$ = 8.8 Hz, H-5^{C,F}), 5.06–5.17 (6H, H-1^{C,F}, H-5$^{A,D\text{ or }B,E}$, H-6b^{C,F}), 5.40 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, H-1^{B,E} or H-1^{A,D}), 5.68 (m, 2H, H-5$^{B,E\text{ or }A,D}$), 6.96–7.01 (2H, *p*-H), 7.08 (m, 4H, *m*-H), 7.75 (m, 4H, *o*-H) ppm; $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ (assignment by HMQC) = 32.0 (virtual t, $|^{1}J_{C,P}+{}^{3}J_{C,P'}|$ = 22.3, C-6$^{A,D\text{ or }B,E}$), 38.0 (virtual t, $|^{1}J_{C,P}+{}^{3}J_{C,P'}|$ = 18.5 Hz, C-6$^{B,E\text{ or }A,D}$), 57.3 (×2), 58.3, 59.4 (2-OCH_3, 6-OCH_3), 61.5, 61.8, 61.9 (3-OCH_3), 66.6 (br signal with triplet shape, C-5$^{A,D\text{ or }B,E}$), 68.5 (br signal with triplet shape, C-5$^{B,E\text{ or }A,D}$), 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, $|^{3}J_{C,P}+{}^{5}J_{C,P'}|$ = 9.5 Hz, C-4$^{A,D\text{ or }B,E}$ or C-4$^{B,E\text{ or }A,D}$), 90.6 (C-4$^{B,E\text{ or }A,D}$ or C-4$^{A,D\text{ or }B,E}$), 98.0 (C-1$^{A,D\text{ or }B,E}$ or C-1$^{B,E\text{ or }A,D}$), 98.1 (C-1$^{B,E\text{ or }A,D}$ or C-1$^{A,D\text{ or }B,E}$), 101.6 (C-1^{C,F}), 128.7 (virtual t, $|^{3}J_{C,P}+{}^{5}J_{C,P'}|$ = 8.0 Hz, *m*-C), 129.3 (*p*-C), 130.4 (virtual t, $|^{2}J_{C,P}+{}^{4}J_{C,P'}|$ = 10.0 Hz, *o*-C), 140.8 (virtual t, $|^{1}J_{C,P}+{}^{3}J_{C,P'}|$ = 43.5 Hz, *ipso*-C) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = −0.16 (d, $J_{P,Rh}$ = 120.3 Hz) ppm; elemental analysis (%) calcd for $C_{63}H_{94}ClO_{27}P_2Rh$ (1483.71): C 51.0, H 6.39; found: C 50.71, H 6.40; MS (ESI-TOF): *m/z* (%): 1447.1 (100) $[M-Cl]^+$.

***trans*-P,P′-Bromomethyl-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-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) (12)**: MeLi (0.0035 g, ca. 0.10 mL 1.6 M, 0.15 mmol) was 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 celite. Evaporation of the solvent afforded **12** as a beige solid (yield: 0.060 g, 86 %). Complex **12** decomposes on silica (SiO_2); m.p. 148 °C (decomp); ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ (assignment by COSY and ROESY) = −0.94 (t, 3H, $^{2}J_{H,P}$ = 10.2 Hz, CH_3), 2.20 (m, 2H, H-6a$^{A,D\text{ or }B,E}$), 2.59 (m, 2H, H-6a$^{B,E\text{ or }A,D}$), 3.15 (virtual t, 2H, $^{3}J_{H\text{-}4,H\text{-}3}$ = $^{3}J_{H\text{-}4,H\text{-}5}$ = 8.9 Hz, H-4$^{B,E\text{ or }A,D}$), 3.24–3.48 (10H, H-2, H-4$^{A,D\text{ or }B,E}$, H-6b$^{B,E\text{ or }A,D}$), 3.31 (s, 6H, OMe), 3.37 (s, 6H, OMe), 3.39 (s, 6H, OMe), 3.40 (s, 6H, OMe), 3.57 (m, 2H, H-6b$^{A,D\text{ or }B,E}$), 3.64–4.02 (8H, H-3, H-6a^{C,F}), 3.71 (s, 6H, OMe), 3.74 (s, 6H, OMe), 3.76 (s, 6H, OMe), 3.78 (virtual triplet, 2H, $^{3}J_{H\text{-}4,H\text{-}3}$ = $^{3}J_{H\text{-}4,H\text{-}5}$ = 9.0 Hz, H-4^{C,F}), 4.75 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 4.0 Hz, H-1$^{A,D\text{ or }B,E}$), 5.00 (m, 2H, H-6b^{C,F}), 5.15 (m, 2H, H-5$^{A,D\text{ or }B,E}$), 5,19 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, H-1^{C,F}), 5.24 (m, 2H, H-5^{C,F}), 5.41 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.0 Hz, H-1$^{B,E\text{ or }A,D}$), 5.93 (m, 2H, H-5$^{B,E\text{ or }A,D}$), 7.03 (broad t, 2H, $^{3}J_{p\text{-}H,m\text{-}H}$ = 7.4 Hz, *p*-H), 7.13 (broad t, 4H, $^{3}J_{m\text{-}H,p\text{-}H}$ = 7.4 Hz, *m*-H), 7.79 (m, 4H, *o*-H) ppm; $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ (assignment by HMQC) = −2.1 (m, CH_3), 29.3 (m, C-6$^{A,D\text{ or }B,E}$), 35.7 (C-6$^{B,E\text{ or }A,D}$), 57.0, 57.1, 57.7, 57.8, 59.0, 69.4, 61.6 (2-OCH_3, 3-OCH_3, 6-OCH_3), 66.4 (m with triplet shape, C-5$^{A,D\text{ or }B,E}$), 68.7 (m with triplet shape, C-5$^{B,E\text{ or }A,D}$), 71.8 (C-5^{C,F}), 72.8 (C-6^{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$^{B,E\text{ or }A,D}$), 97.8 (C-1$^{A,D\text{ or }B,E}$), 101.6 (C-1^{C,F}), aromatic CH signals overlap with C_6D_6 signal, 138.4 (*ipso*-C) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, 25 °C): δ = 0.5 (s) ppm; elemental analysis (%) calcd for $C_{63}H_{97}BrO_{26}P_2Ni\cdot 3CH_2Cl_2$ (1470.97 + 254.79): C 45.93, H 6.02; found: C 45.61, H 6.29; attempts to detect complex **12** by mass-spectrometric analysis were unsuccessful.

P,P′-{6^{A},6^{B},6^{D},6^{E}-Tetradeoxy-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}gold(I) hexafluorophosphate (13): A solution of [AuCl(tht)] (0.040 g, 0.12 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of TRANSDIP (0.160 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 celite and the filtered solution was concentrated to approximately 5 mL. Addition of pentane yielded complex **13** as a colourless precipitate (yield: 0.180 g, 91 %). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, v/v) = 0.31; m.p. >250 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 2.18 (m, 2H, H-6a$^{A,D\text{ or }B,E}$), 2.62 (m, 2H, H-6a$^{B,E\text{ or }A,D}$), 2.79 (s, 6H, OMe), 3.07–3.73 (24H, H-2, H-3, H-4, H-6b^{A,B,D,E}, H-6a^{C,F}), 3.47 (s, 6H, OMe), 3.53 (s, 6H, OMe), 3.57 (s, 6H, OMe), 3.63 (s, 6H, OMe), 3.65 (s, 6H, OMe), 3.66 (s, 6H, OMe), 3.89 (m, 2H, H-5^{C,F}), 4.16 (m, 2H, H-6b^{C,F}), 4.24 (m, 2H, H-5$^{B,E\text{ or }A,D}$), 4.36 (m, 2H, H-5$^{A,D\text{ or }B,E}$), 4.83 (d, 2H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, H-1$^{A,D\text{ or }B,E}$), 5.05 (two overlapping d, 4H, H-1$^{B,E\text{ or }A,D}$, H-1^{C,F}), 7.41–7.61 (10H, aromatic H) ppm; $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ (assignment by

HMQC) = 27.9 (m, C-6$^{B,E\text{ or }A,D}$), 37.2 (m, C-6$^{A,D\text{ or }B,E}$), 57.8, 58.0, 58.2 (2-OCH_3), 59.8 (6-OCH_3), 61.5, 61.6, 62.0 (3-OCH_3), 64.2 (C-5$^{B,E\text{ or }A,D}$), 71.7 (m, C-5$^{A,D\text{ or }B,E}$), 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$^{B,E\text{ or }A,D}$), 88.3 (C-4$^{A,D\text{ or }B,E}$), 98.8 (C-1$^{B,E\text{ or }A,D}$), 99.5 (C-1$^{A,D\text{ or }B,E}$), 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; $^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$, 25 °C): $\delta=-72.8$ (d, $^1J_{F,P}=716$ Hz) ppm; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta=38.6$ (s), −144.3 (h, $^1J_{P,F}=716$ Hz) ppm; elemental analysis (%) calcd for $C_{62}H_{94}AuF_6O_{26}P_3$ (1659.27): C 44.88, H 5.71; found: C 44.71, H 5.83; MS (ESI-TOF): *m/z* (%): 1513.1 (100) $[M-PF_6]^+$.

X-ray crystallographic data of 6: $PdP_2C_{62}H_{94}Cl_2O_{26}\cdot 2C_5H_{12}$, $M_r=3275.32$, triclinic, *P*1, $a=14.419(5)$, $b=14.913(5)$, $c=19.382(5)$ Å, $\alpha=79.985(7)$, $\beta=79.750(8)$, $\gamma=87.252(8)°$, $V=4038(1)$ Å^3, $Z=1$, $\rho_{calcd}=1.347$ Mg m^{-3}, $\lambda(Mo_{K\alpha})=0.71073$ Å, $\mu=4.82$ cm^{-1}, $F(000)=1720$, $T=110(1)$ K. Single crystals were obtained by slow diffusion of pentane into a solution of **6** in $CHCl_3$. A sample was studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatised $Mo_{K\alpha}$ radiation ($\lambda=0.71069$ Å). The data collection[52] ($2\theta_{max}=54°$, ω scan frames through 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 $I>2.0\,\sigma(I)$. 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 $I>2.0\sigma(I)$; calcd $w=1/[\sigma^2(F_o^2)+(0.03\ P)^2]$ where $P=(F_o^2+2\ F_c^2)/3$ with the resulting $R=0.125$, $R_w=0.314$, and $S_w=1.096$; $\Delta\rho<3.5$ e Å^{-3}. Flack parameter: 0.03(5). The unit cell contains two slightly different molecules and two molecules of pentane. As a result of 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: $AuP_2C_{62}H_{94}F_6O_{26}P\cdot 4C_2Cl_4H_2$, $M_r=2330.59$, triclinic, *P*1, $a=13.8155(6)$, $b=14.3165(6)$, $c=15.1126(7)$ Å, $\alpha=112.842(4)$, $\beta=110.568(4)$, $\gamma=100.381(3)°$, $V=2399.2(2)$ Å^3, $Z=1$, $\rho_{calcd}=1.209$ Mg m^{-3}, $\lambda(Mo_{K\alpha})=0.71073$ Å, $\mu=21.09$ cm^{-1}, $F(000)=1180$, $T=100(1)$ K. Single crystals were obtained by cooling a solution of the complex in $C_2H_2Cl_4$. A sample was studied on a Bruker AXS X8-APEX II with graphite monochromatised $Mo_{K\alpha}$ radiation. The data collection[55] ($2\theta_{max}=54°$, distance detector = 60 mm, φ scan frames through 0.7°, φ 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 SHELXL-97[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 $I>2.0\sigma(I)$; calcd $w=1/[\sigma^2(Fo^2)+(0.172\ P)^2]$ where $P=(Fo^2+2Fc^2)/3$ with the resulting $R=0.068$, $R_w=0.179$, and $S_w=0.882$, $\Delta\rho<6.1$ e Å^{-3}. Flack parameter: 0.03(5). The molecule crystallises with four solvent molecules, one of which lies inside the cyclodextrin unit. CCDC-648501 (**6**) and CCDC-631157 (**13**) contain the supplementary crystallographic data for this report. 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: $NiBr_2$ and $[NiBr_2(dme)]$ 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 decreases the amount of residual trimethylaluminium to approximately 3%. The resulting solid residue was dried over 3 h at 60 °C under vacuum. All the nickel 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 (length: 25 m, internal diameter: 0.32 mm, film thickness: 0.25 mm).

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 μmol) was dissolved in toluene (12 mL) before being introduced into the autoclave through 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 weighed immediately afterwards to limit the loss of the 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 spectroscopic and GC analysis.[56] But-1-ene was identified by signals at $\delta=2.00$, 4.95, and 5.78 ppm in the ^1H NMR spectra. Resonances appear at $\delta=1.54$ and 4.95 ppm for the *cis*-but-2-ene and at $\delta=1.58$ and 5.55 ppm the *trans* isomer.

Propene dimerisation: A 200-mL Büchi glass autoclave was heated at 100 °C under vacuum for 2 h, cooled to room temperature, and filled with propene. A solution of **8** (0.007 g, 4.50 μmol) in chlorobenzene (20 mL) was introduced into the autoclave through 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 an internal standard and a sample of the reaction mixture was taken for GC analysis.

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