A cavity-shaped diphosphane displaying *os-chelating* behaviour[**]

Rafael Gramage-Doria, Dominique Armspach, Dominique Matt,* and Loic Toupet*

[*] R. Gramage-Doria, Prof. D. Armspach, Dr. D. Matt
Laboratoire de Chimie Inorganique Moléculaire et Catalyse,
Institut de Chimie UMR 7177 CNRS
Université de Strasbourg
67008 Strasbourg Cedex (France)
Dr. L. Toupet
Groupe Matière Condensée et Matériaux, UMR 6626 CNRS
Université de Rennes 1
35042 Rennes Cedex (France)
[**] This work was supported by the CNRS and the Région Alsace (grant to RGD)

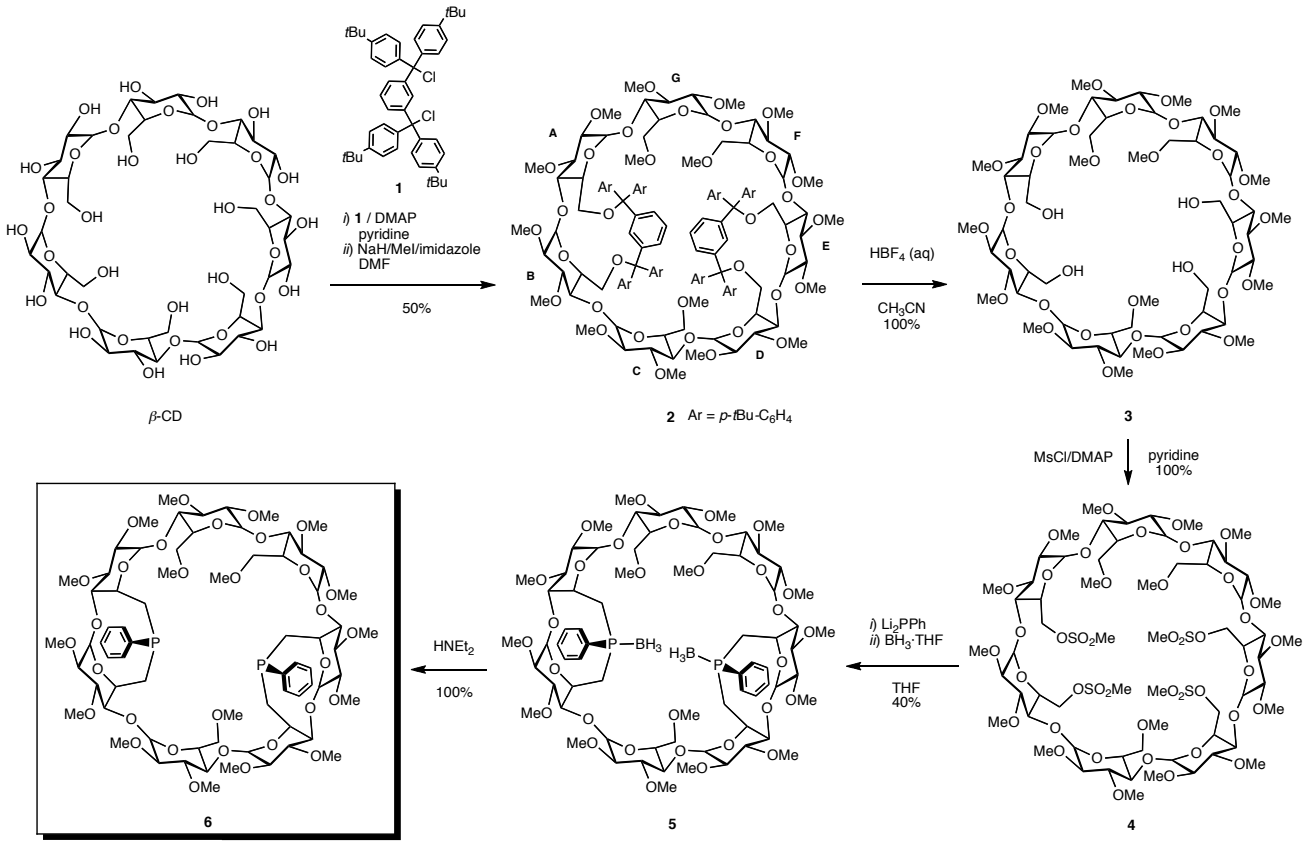
Molecules that combine the properties of a transition metal with those of an appended cavity have attracted a great deal of attention.[1-3] So far, research in this area has focused on four main objectives: a) the design and synthesis of systems exploiting the binding properties of a receptor unit linked to a transition metal centre, with the aim of producing catalysts that mimic an enzyme;[4-8] b) the study of metal-centered reactions taking place in a confined environment thereby favouring highly regio-, stereo- and shape-selective reactions;[9-13] c) the metal-assisted entrapment and recognition of ionic species;[14-16] d) the construction of sensors capitalising on a electro- or photoactive metal-unit covalently attached to a close, cavity-shaped receptor.[17,18]

While the coordination chemistry of many multitopic ligands giving rise to 3-D architectures such as capsules, cages, bowls and boxes has been thoroughly investigated,[19-25] the use of such ligands for generating oscillatory motion about a metal metal ion has not been considered yet, although examples of transition metals moving around the periphery of such an object are known.[26] Herein we show how a cavity bearing two introverted donor atoms may behave as a balance wheel swinging about a central metal unit. Our approach is based on the use of a rigid, cyclodextrin-based diphosphane characterised by a long P...P separation that results in highly unsymmetrical chelation.

Diphosphine **6** was obtained in 20% overall yield according to Scheme 1. Its synthesis began with a regioselective *double capping* of native *β*-cyclodextrin (*β*-CD) using the bulky dialkylating reagent **1**.[27] The non-alkylated hydroxyl groups were subsequently methylated with NaH/MeI, resulting in the *ABDE*-functionalised intermediate **2** (yield 50% !). Deprotection with HBF_4, leading to tetrol **3**, followed by reaction with mesyl chloride in pyridine afforded tetramesylate **4**. Reaction of the latter with Li_2PPh in THF gave diphosphine **6** in *ca*. 70% yield beside two other, unidentified products. Work-up required the preparation of the diborane adduct **5**, which was separated chromatographically. Finally, **5** was treated with $HNEt_2$ to afford quantitatively **6**. As expected, the ^{31}P NMR spectrum of **6** in C_6D_6 shows two very near singlets, seen at δ = –15.0 and –15.2 ppm, respectively (in $CDCl_3$ the spectrum showed but a unique peak). Prolonged standing in air of a solution of **6** in MeOH produced the di(phosphine oxide) **7**, the structure of which was determined by an X-ray diffraction study (Fig. 1). In the solid state, the two P=O vectors of **7** point towards the interior of the cavity, the P...P separation being 6.91 Å. Two non-bridged glucose units are tipped towards the CD axis, reflecting some strain within the CD.

Despite the long separation between the two phosphorus atoms, diphosphine **6** turned out to be suitable for chelation. Thus, for example, reaction with $[Au(tht)(thf)]PF_6$ (tht =

tetrahydrothiophene; THF = tetrahydrofuran) led *quantitatively* to complex **8**. The mass spectrum of **8** showed an intense peak at *m/z* = 1717.62 having exactly the isotopic profile expected for [Au•**6**]$^{+}$. Furthermore, the ^{31}P NMR (CD_2Cl_2, 25°C) spectrum displayed an AB pattern with a *J*(PP) coupling constant of 326 Hz, a value which is in accord with a very large bite angle. Molecular models indicate that the bite angle is close to 160°. The good chelating properties of **6** were further



Scheme 1. Stepwise buildup of **6**

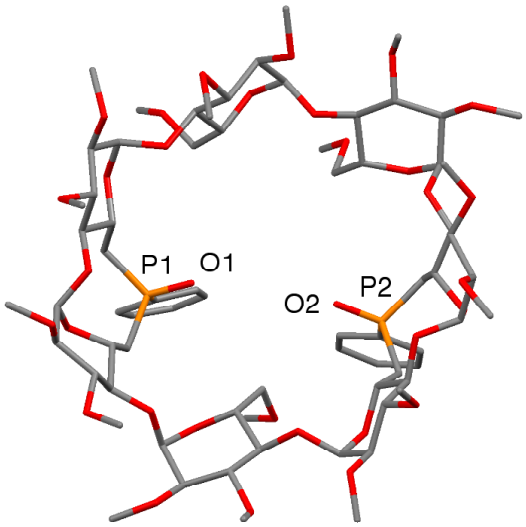
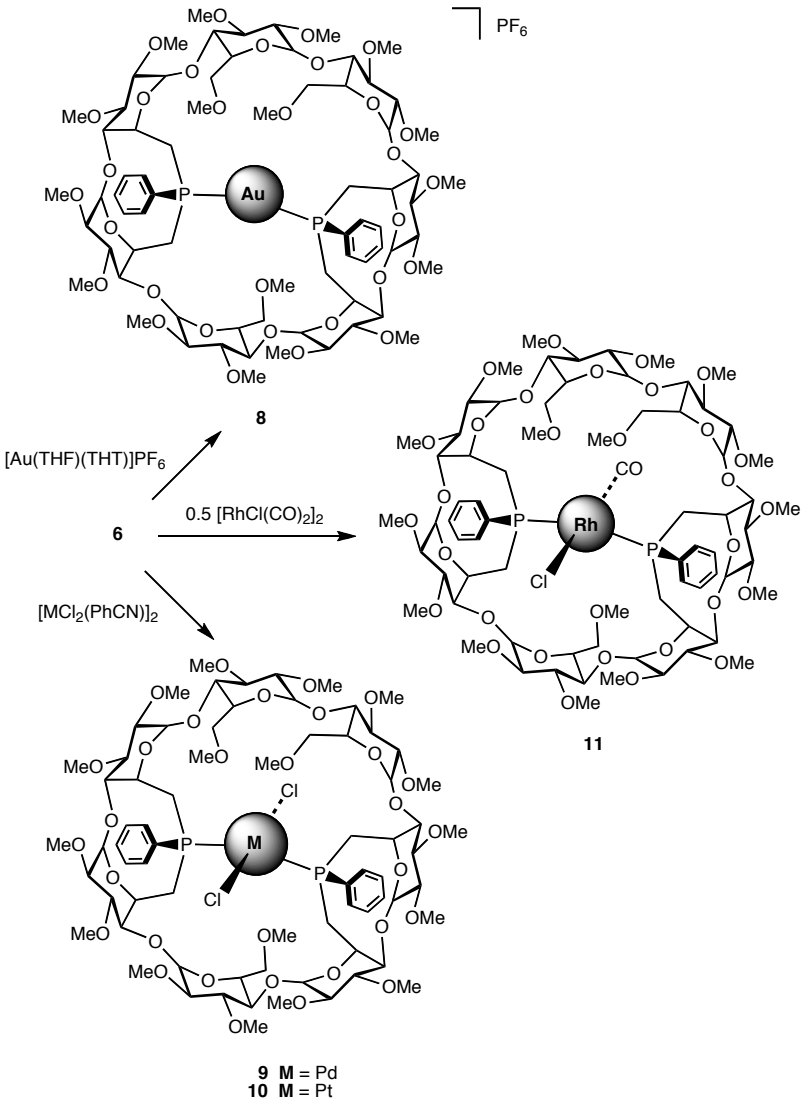


Figure 1. X-ray structure of the di(phosphine oxide) **7** (view from the secondary face). Solvent molecules have been omitted. Important distances (Å): P1-P2 6.91; O1-O2 4.32.

confirmed by its reaction with $[PdCl_2(PhCN)_2]$, $[PtCl_2(PhCN)_2]$, and $[RhCl(CO)_2]_2$ leading to the chelate complexes **9-11,** respectively, in 100% yield (Scheme 2 and SI). As in **8**, the corresponding large *J*(PP') coupling constants (see SI) reflect the large bite angle of the ligand.[28,29]



Scheme 2. Synthesis of complexes **8**-**11**.

As shown by a variable temperature NMR study, complex **10** displays fluxional behaviour in solution. The ^{31}P NMR (CD_2Cl_2) spectrum of **10**, measured at –80°C, revealed the presence of two species (**10a** and **10b**) present in a 1:1 ratio, each caracterised by an ABX pattern (^2J(AB) = 492 and 476 Hz, respectively; ^1J(PPt) coupling poorly resolved) (Fig. 2, bottom). Upon raising the temperature, the signals first broadened, then coalesced near –15°C, and finally merged into a single ABX spectrum (^2J(AB) = 496 Hz, ^1J(PPt) = 2510 Hz) (Fig. 2, top). The observed data are consistent with exchange between two complexes both of which contain a close to linear P–Pt–P unit. A variable temperature ^{1}H NMR study was also carried out which confirmed the 1:1 stoichiometry of the equilibrating species. Both series of experiments led to a free energy of activation $\Delta G^{\neq}$ = 11.3 ± 0.2 kcal mol^{-1}. Interestingly, the low temperature ^{31}P

NMR spectra revealed two AB patterns with a large separation between the A and B parts (*ca.* 12 ppm), indicating that the two P atoms of each complex are coordinated to the platinum atom with unequal strength. Note that one of the phosphorus signals appears near the midpoint between the signal of the free ligand and that of the other signal. As shown by an off-resonance $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ ROESY NMR experiment (SI), the "strongly" coordinated phosphorus atom of each species is in exchange with the "weakly" coordinated phosphorus atom of the other isomer.

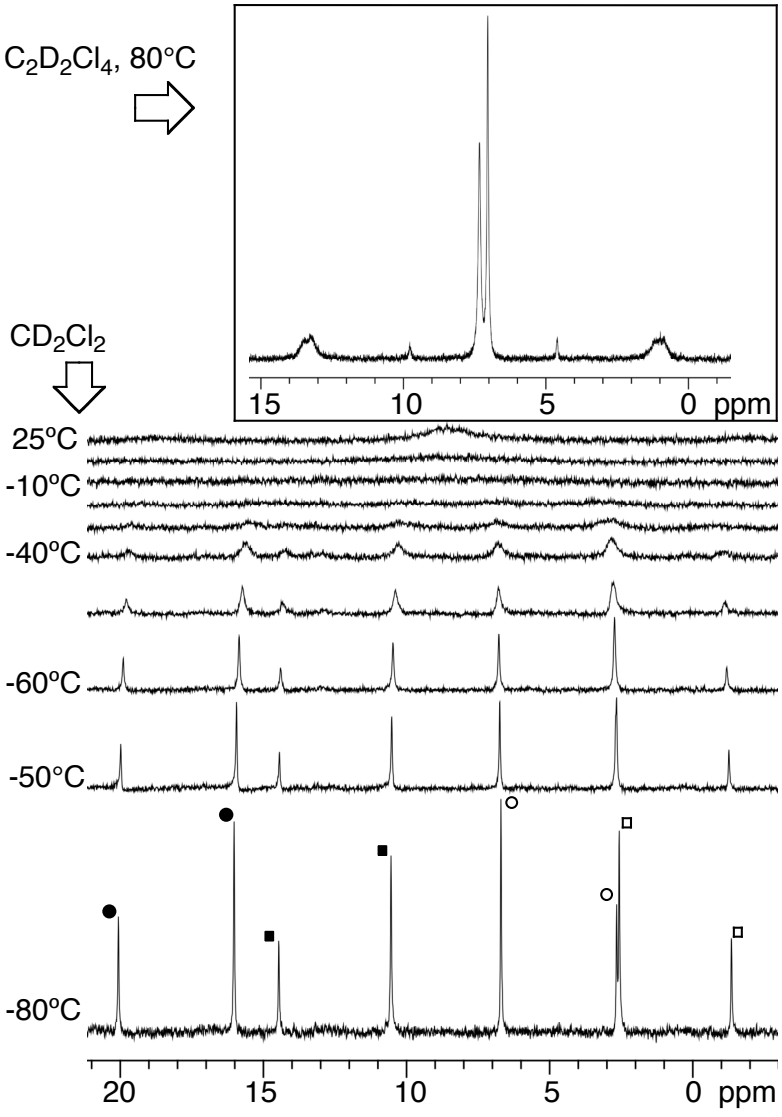
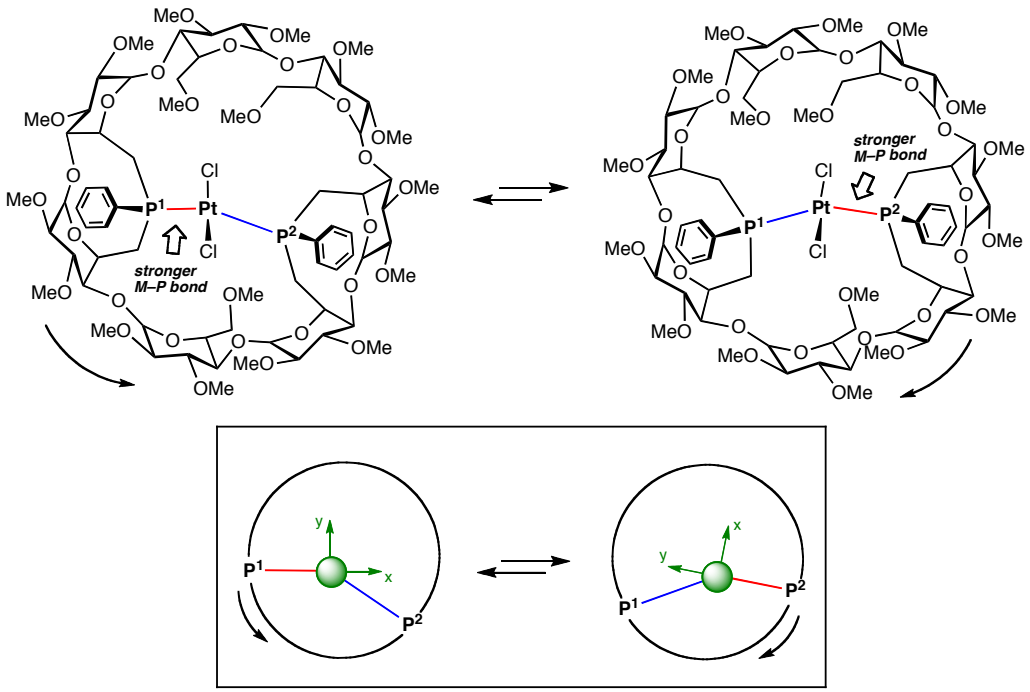


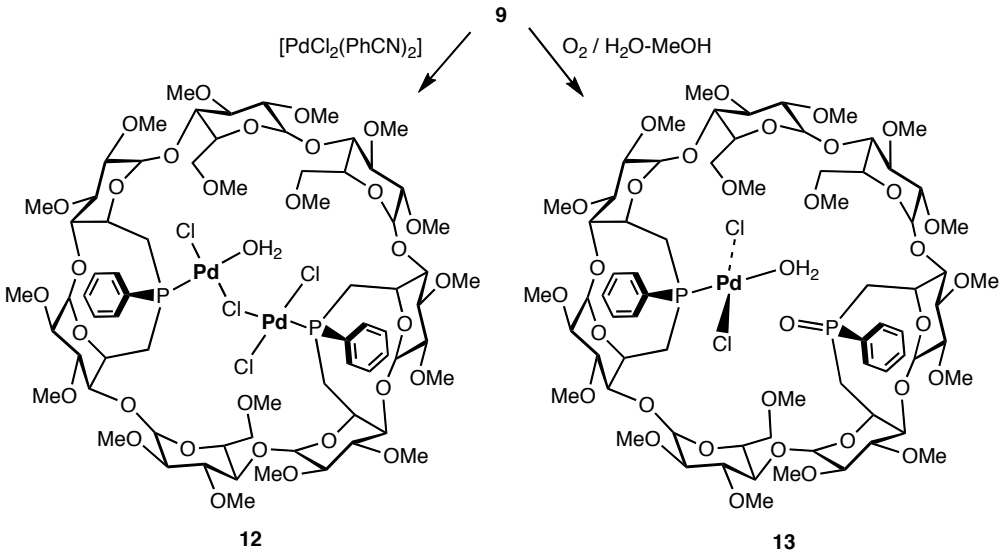
Figure 2. $^{31}P\{^{1}H\}$-NMR variable temperature study of the platinum complex **10**. The AB patterns of the two equilibrating species are represented by dots and squares. Filled symbols are for the A parts, open symbols for the B parts.



Scheme 3. Balance wheel movement of ligand **6** in complex **10** (view along the CD axis). The green arrows in the lower part indicate the orientations of the d_{x2-y2} orbital involved in formation of the two MP bonds.

Overall, the best way to describe these findings is to consider that the d_{x2-y2} orbital involved in formation of the M–P bonds changes its orientation in a pendular fashion so as to adopt in alternation different overlaps with each of the two convergent, but *non-aligned* phosphorus lone pairs. Consequently, metal binding to the two phosphorus donors is inequivalent in a given species (Scheme 3). The observed isomerisation is probably also accompanied by a slight displacement of the metal centre. Thus, being unable to form an authentic *trans*-complex (*i.e.* with a P–M–P angle of 180°), diphosphane **6** may be regarded as a frustrated chelator, which compensates the metal electron deficiency generated at one coordination site by oscillating about the complexed metal ion. We propose to term this type of bidentate ligand an *os-chelating* (contraction of "oscillating" and "chelating") species. It is worth mentioning here that the observed fluxionality is different from that found in complexes containing hemilabile ligands, the latter leading to intermediates in which one end is totally dissociated.[30-33] It should be emphasized that similar dynamics were observed for all three complexes **8**, **9** and **11**. Furthermore, for all four complexes investigated the *J*(PP') coupling constants persisted over the temperature range –80°C / +80°C. In other words, the observed

dynamic behaviour occurs without dissociation of the M–P bonds. This phenomenon may be regarded as a variant of bond-stretch isomerism.[34,35]



Scheme 4. Exploiting the *os-chelating* property of **6**

We anticipated that the dynamic nature of **6** in the chelate complexes would weaken the P–M bonds. In fact, treatment of **9** with $[PdCl_2(PhCN)_2]$ led formally to insertion of a $PdCl_2$ fragment into one of the Pd–P bonds of **9**. The resulting complex, **12**, crystallised with a water molecule coordinated to one of the palladium atoms (Scheme 4, Fig. 3). It is likely that owing to its rigidity, diphosphine **6** cannot adapt to a $Pd_2Cl_2(\mu\text{-}Cl)_2$ fragment having the usual flat or roof structure and therefore prefers to cap a Pd_2Cl_4 unit having only a single chlorido bridge. Another reaction directly related to the *os-chelating* behaviour of **6** is the reaction between **9** and O_2/H_2O in methanol, giving **13**, seemingly formed by cleavage of one of the Pd–P bonds and its substitution by a bond to H_2O, followed by oxidation of the dissociated P atom.[36] The P...P' separation in **13** (6.6 Å)

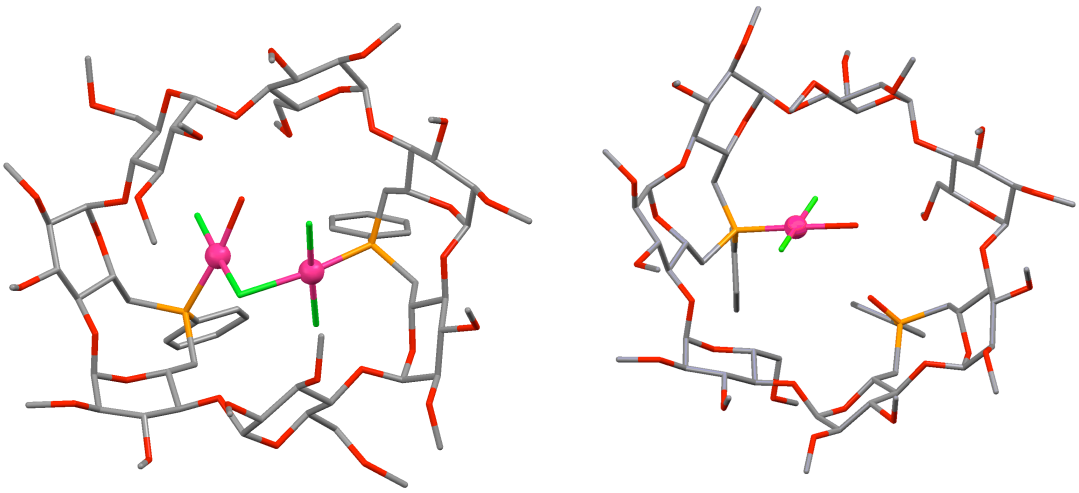


Figure 3. X-ray structures of complex **12** (left) and the monophosphine-Pd complex **13** (right)

is close to the one found in **7**. We note that both complexes, **12** and **13**, contain a "(phosphine)$PdX_2(H_2O)$" unit, thus constituting rare examples of $[LL'PdX_2]$ complexes containing a single phosphine ligand. Overall, the coordinative properties of **6** are markedly different from those of the previously reported α-CD analogue (TRANSDIP).[37]

In conclusion, using a capping methodology that relies on the use of the bulky dialkylating agent **1**, we have synthesised the first large bite angle diphosphine (**6**) based on a β-CD backbone. Owing to the rigidity of this ligand as well as the large separation between the phosphorus atoms, **6** behaves towards transition metal ions in an unsymmetrical chelator, inducing rapid oscillation of the chelate about the coordinated metal centre. This phenomenon occurs without dissociation of the phosphorus atoms. The unprecedented chelating behaviour of **6** enables the formation of monophosphine complexes located inside a CD, thereby opening a way to the further study of organometallic catalysts operating in a confined environment.

Experimental Section

Full experimental details including X-ray structural data are given in the Supporting Information. CCDC-756653, 758028 and 770728 contain the supplementary crystallographic data for **7**, **12** and, **13**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6: ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 1.73 (m, 2 H, H-6a$^{A,D\text{ or }B,E}$), 1.87 (m, 2 H, H-6a$^{B,E\text{ or }A,D}$), 2.81 (td, 2 H, $^{2}J_{H\text{-}6b,P} = {}^{2}J_{H\text{-}6b,H\text{-}6a}$ = 13.5 Hz, $^{3}J_{H\text{-}6b,H\text{-}5}$ = 3.9 Hz, H-6b$^{A,D\text{ or }B,E}$), 3.05–3.29 (12 H, H-2, H-6a^{C,F,G}, H-6b$^{B,E\text{ or }A,D}$), 3.11 (s, 3 H, OMe), 3.20 (s, 3 H, OMe), 3.27 (s, 3 H, OMe), 3.30–3.72 (14 H, H-3, H-4), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.50 (s, 6 H, OMe), 3.55 (s, 6 H, OMe), 3.60 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.65 (s, 9 H, OMe), 3.66 (s, 6 H, OMe), 3.81–3.42 (8 H, H-5$^{A,D\text{ or }B,E}$, H-5^{C,F,G}, H-6b^{C,F,G}), 4.30 (m, 2 H, H-5$^{B,E\text{ or }A,D}$), 4.95–5.05 (6 H, H-1), 5.22 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.7 Hz, H-1), 7.20–7.28 (6 H, *m*-H, *p*-H), 7.41–7.51 (4 H, *o*-H) ppm; ^{13}C{^{1}H} NMR (125.8 MHz C_6D_6, 25ºC): δ (assignment by HMQC) = 28.66 (d, $^{1}J_{C,P}$ = 15.4 Hz), 28.69 (d, $^{1}J_{C,P}$ = 16.2 Hz) (C-6$^{A,D\text{ or }B,E}$), 34.99 (d, $^{1}J_{C,P}$ = 19.1 Hz), 35.06 (d, $^{1}J_{C,P}$ = 19.7 Hz) (C-6$^{B,E\text{ or }A,D}$), 58.14 [×2], 58.20, 58.32, 58.71, 59.10, 59.14, 59.44, 59.68, 59.74, 61.77, 61.79, 61.90, 62.00, 62.05, 62.25 [×2] (OMe), 67.54 (d, $^{2}J_{C,P}$ = 11.7 Hz, C-5$^{A\text{ or }D}$), 67.57 (d, $^{2}J_{C,P}$ = 11.7 Hz, C-5$^{D\text{ or }A}$), 71.53 [×2], 71.80 (C-5^{C,F,G}), 72.13 (d, $^{TS}J_{C,P}$ = 2.6 Hz, C-6^{C}), 72.39 [×2] (C-6^{F,G}), 73.95 (d, $^{2}J_{C,P}$ = 14.3 Hz, C-5$^{B\text{ or }E}$), 74.26 (d, $^{2}J_{C,P}$ = 13.6 Hz, C-5$^{E\text{ or }B}$), 79.75, 82.22, 82.31, 82.37, 82.42, 82.97, 83.15, 83.23, 83.36 [×3], 83.42, 83.46, 83.58, 84.07, 84.55, 84.70 (C-2, C-3, C-4^{C,F,G}), 87.15 (d, $^{3}J_{C,P}$ = 8.0 Hz, C-4$^{B\text{ or }E}$), 87.32 (d, $^{3}J_{C,P}$ = 8.0 Hz, C-4$^{E\text{ or }B}$), 90.23 (d, $^{3}J_{C,P}$ = 2.7 Hz, C-4$^{A\text{ or }D}$), 90.38 (d, $^{3}J_{C,P}$ = 2.6 Hz, C-4$^{D\text{ or }A}$), 99.27, 99.32, 99.69, 99.90, 99.96 [×2], 101.19 (C-1), 128.96, 129.03 (*p*-C), 129.15 [×2] (overlapping d, $^{3}J_{C,P}$ = 4.8 Hz, *m*-C), 132.47 (d, $^{2}J_{C,P}$ = 18.7 Hz, *o*-C), 132.51 (d, $^{2}J_{C,P}$ = 18.7 Hz, *o*-C), 142.33 [×2] (d, $^{1}J_{C,P}$ = 11.7 Hz, *ipso*-C) ppm; ^{31}P{^{1}H} NMR (202.5 MHz C_6D_6, 25ºC): δ = –15.0 (s), –15.2 (s) ppm; elemental analysis (%) calcd for $C_{71}H_{110}O_{31}P_2 \cdot 0.5CH_2Cl_2$ (1521.56 + 42.47): C 54.91, H 7.15, found: C 54.82, H 7.35; MS (ESI-TOF): *m/z* (%): 1521.57 (100) $[M + H]^+$.

8: ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, –80ºC): δ = 40.6 and 31.6 (AB system, $^{2}J_{P1,P2}$ = 326 Hz), 38.0 and 33.8 (AB system, $^{2}J_{P1,P2}$ = 326 Hz), –144.3 (hept, $^{1}J_{P,F}$ = 716 Hz) ppm.

9: ^{31}P {^{1}H} NMR (121.5 MHz, CD_2Cl_2, –80ºC) = 21.7 and 11.4 (2 d, AB system, $^{2}J_{P1,P2}$ = 564 Hz), 17.7 and 5.6 (2 d, AB system, $^{2}J_{P1,P2}$ = 549 Hz) ppm.

10: ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25ºC): δ = 8.9 (br s with br Pt satellites, $^{1}J_{P,Pt} \approx$ 2500 Hz) ppm; ^{31}P {^{1}H} NMR (121.5 MHz, CD_2Cl_2, –80ºC) = 0.97 and 12.20 (2 d, AB system, $^{2}J_{P1,P2}$ = 476 Hz), 5.02 and 17.76 (2 d, AB system, $^{2}J_{P1,P2}$ = 492 Hz) ppm ($^{1}J_{Pt,P}$ poorly resolved); ^{31}P {^{1}H} NMR (202.5 MHz, $C_2D_2Cl_4$, +80ºC) = 7.04 and 7.35 (2 d with Pt satellites, ABX system, $^{1}J_{Pt,P1}$ = 2507 Hz, $^{1}J_{Pt,P2}$ = 2481 Hz, $^{2}J_{P1,P2}$ = 496 Hz) ppm.

11: $^{31}P\{^{1}H\}$ NMR (162.0 MHz, CD_2Cl_2, –80ºC) = 28.0 and 9.4 (2 dd, ABX system, $^{2}J_{P1,P2}$ = 354 Hz, $^{1}J_{P,Rh}$ = 118 and 118), 16.4 and 9.4 (2 dd, ABX system, $^{2}J_{P1,P2}$ = 354 Hz, $^{1}J_{P,Rh}$ = 118 and 118) ppm

Keywords: metallocavitands • cyclodextrins • trans chelating diphosphane • molecular dynamics • transition metal chemistry •

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[36] As expected, the isomeric phosphine-phosphine oxide, *i. e.* the one in which the phosphoryl group bridges the A and B glucose units, also forms. This ligand was isolated as a chelate complex (see SI).
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Graphical Abstract

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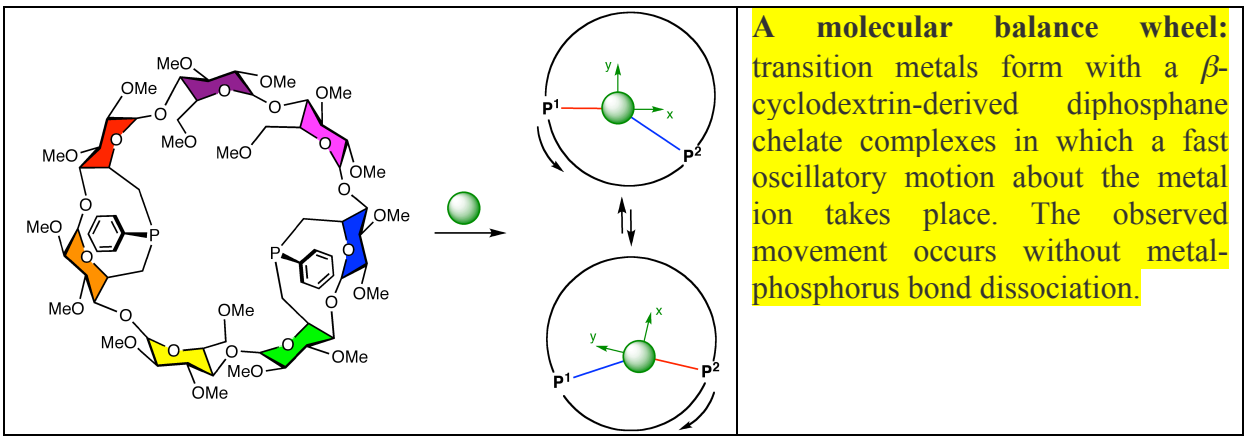

A molecular balance wheel: transition metals form with a *β*-cyclodextrin-derived diphosphane chelate complexes in which a fast oscillatory motion about the metal ion takes place. The observed movement occurs without metal-phosphorus bond dissociation.

Supporting Information

Angewandte Chemie

A cavity-shaped diphosphane displaying *os-chelating* behaviour

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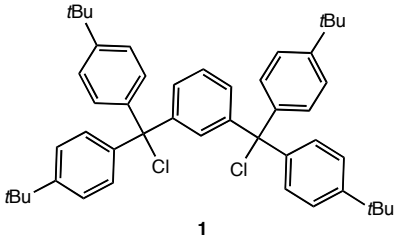
Content

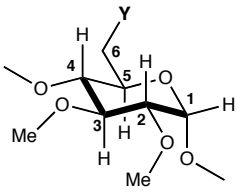
General Methods

All commercial reagents were used as supplied. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^1H, and $^{13}C\{^1H\}$ NMR spectra were recorded on FT Bruker AVANCE 300, AVANCE 400, AVANCE 500 and AVANCE 600 instruments. ^1H NMR spectral data were referenced to residual protiated solvents [7.26 ppm for $CDCl_3$, 7.16 ppm for C_6D_6 and 5.32 for CD_2Cl_2], ^{13}C chemical shifts are reported relative to deuterated solvents [77.0 ppm for $CDCl_3$, 128.06 ppm for C_6D_6 and for 54.00 CD_2Cl_2] and the ^{31}P NMR data are given relative to external H_3PO_4. Mass spectra were

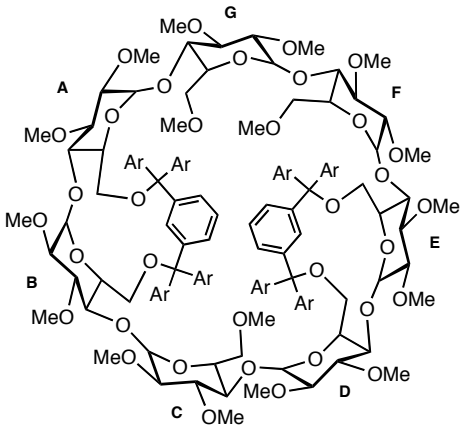
recorded either on a Maldi TOF spectrometer (MALDI-TOF) using α-cyano-4-hydroxycinnamic acid as matrix, or on a Bruker MicroTOF spectrometer (ESI-TOF) using CH_2Cl_2, MeCN or MeOH as the solvent. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (UMR 7177 CNRS), Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus. The dialkylating reagent **1**,[1] $PtCl_2(PhCN)_2$,[2] and $PdCl_2(PhCN)_2$[2] were prepared according to described procedures. Assignment of the stereochemistry of the P atoms 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 shown below.



1



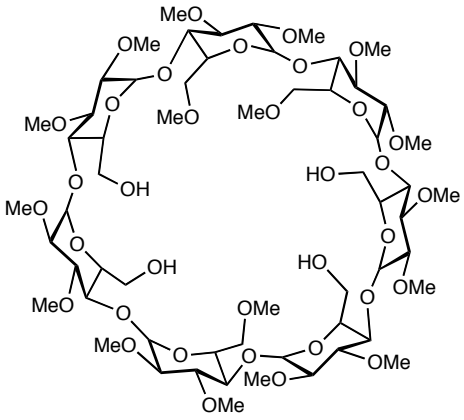
6^A,6^B,6^D,6^E-Tetra-*O*-6^A,6^B:6^D,6^E-bis{benzene-1,3-bis[bis(4-*tert*-butylphenyl)methyl]}-2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^C,6^F,6^G-heptadeca-*O*-methyl-*β*-cyclodextrin (2)



1,3-bis[bis(4-*tert*-butylphenyl)chloromethyl]benzene **1** (5.42 g, 7.7 mmol) was added to a solution of *β*-cyclodextrin (3.97 g, 3.5 mmol) and DMAP (0.51 g, 4.2 mmol) in pyridine (90 mL). The reaction mixture was stirred at 70ºC for 12 h before being cooled down to room temperature. Pyridine was then removed *in vacuo*. Addition of water (500 mL) to the residue produced a suspension that was filtrated. The cake was dried *in vacuo* at 50ºC for 12 h. The

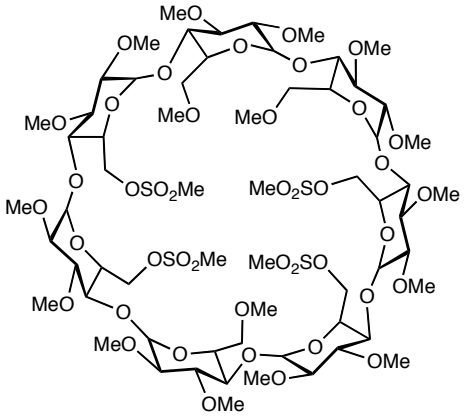
colourless solid was dissolved in DMF (150 mL) and NaH (5.88 g, 147 mmol) was added carefully followed by the addition of catalytic amounts of imidazole (0.010 g, 0.15 mmol). The reaction mixture was stirred at room temperature for 1 h before being cooled at 0ºC whereupon MeI (17.88 g, 7.8 mL, 126 mmol) was added dropwise at 0ºC. The yellow suspension was stirred for 12 h at room temperature. MeOH (50 mL) was then added slowly to quench excess NaH. The reaction mixture was poured into water (500 mL) under stirring before being extracted with Et_2O (3 × 300 mL). The organic exctract was dried ($MgSO_4$) and evaporated to dryness to afford a brown residue. The crude material was purified by column chromatography (SiO_2, petroleum ether/AcOEt, 80:20 to 65:35, *v*/*v*) to give the desired product **2** (4.63 g, 50%) as a colourless solid. R_f (SiO_2, petroleum ether/AcOEt, 60:40, *v*/*v*) = 0.60; m.p. dec.; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 1.17 (s, 6 H, *t*Bu), 1.18 (s, 6 H, *t*Bu), 1.20 (s, 6 H, *t*Bu), 1.24 (s, 6 H, *t*Bu), 1.27–1.29 (48 H, *t*Bu), 2.69 (d, 1 H, $^3J_{H\text{-}2,H\text{-}1}$ = 4.0 Hz, H-2), 2.72 (s, 3 H, OMe), 2.75 (d, 1 H, $^3J_{H\text{-}2,H\text{-}1}$ = 3.7 Hz, H-2), 3.06 (s, 3 H, OMe), 3.26 (s, 3 H, OMe), 3.33 (s, 3 H, OMe), 3.36 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.56 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 9 H, OMe), 3.64 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.20–4.05 (38 H, H-2, H-3, H-4, H-5, H-6a^{A,D}, H-6^{B,C,E,F,G}), 4.22–4.28 (3 H, H-1, H-6b^{A,D}), 4.50 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.5 Hz, H-1), 5.15 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, H-1), 5.37–5.39 (2 H, H-1), 5.49–5.51 (2 H, H-1), 6.99 (t, 2 H, $^3J_{H5\text{-}H4}$ = 6.5 Hz, H-5 of both bridging C_6H_4), 7.05–7.53 (36 H, aromatic H), 7.62 (s, 1 H, H-2 of bridging C_6H_4), 7.73 (s, 1 H, H-2 of bridging C_6H_4) ppm; ^{13}C{^{1}H} NMR (75.5 MHz $CDCl_3$, 25ºC): δ (assignment by HMQC) = 31.43 [×24] (Me of *t*Bu), 34.3 [×8] (C of *t*Bu), 57.80, 57.88, 58.06, 58.14, 58.25, 58.42, 58.80, 59.03, 59.51, 59.70, 60.60, 61.03, 61.52, 61.70, 61.75, 61.84, 61.98 (OMe), 61.68, 61.70, 62.73, 63.18 (C-6$^{A,B,D,E)}$, 71.09, 71.75, 72.54 (C-6^{C,F,G}), 70.46, 70.49, 70.61, 70.76, 71.20, 71.57, 71.65 (C-5), 77.21, 78.74, 80.19, 80.54, 80.98, 81.04, 81.19, 81.27, 81.64, 81.77 [×4], 82.13, 82.23, 82.26, 82.59 [×2], 82.74 [×2], 82.86 (C-2, C-3, C-4), 85.74, 86.11, 87.51, 87.85 [$OC(Ar)_3$], 97.74, 98.24, 98.51, 98.63, 98.77 [×3] (C-1), 124.11 [×5], 124.33, 124.43, 124.48 [×2], 124.59, 126.29, 126.44, 126.50, 126.83, 127.28, 127.46, 128.11, 128.14, 130.52, 131.00, 131.53, 131.88, 134.37, 134.95 (*o*-C and *m*-C), 140.09, 140.20, 140.41, 140.59, 140.94, 141.59, 141.92, 142.37, 142.83, 144.58, 144.96, 145.24, 148.46, 148.52, 148.54, 148.56, 148.60, 148.66 [×2], 148.92 (*ipso*-C) ppm; elemental analysis (%) calcd for $C_{155}H_{212}O_{35}\cdot CH_2Cl_2$ (2635.32 + 83.95): C 68.88, H 7.93, found: C 68.77, H 8.09; MS (ESI-TOF): *m/z* (%): 2657.38 (100) $[M + Na]^+$.

2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{F},6^{G}-Heptadeca-*O*-methyl-*β*-cyclodextrin (3)



HBF_4 (34 wt % aq, 7.5 g, 7.5 mL, 29 mmol) was added dropwise to a stirred solution of capped cyclodextrin **2** (2.55 g, 0.97 mmol) in MeCN (30 mL) at room temperature. After 30 min, NEt_3 (1.47 g, 2.0 mL) was added dropwise under stirring. Addition of water (100 mL) to the reaction mixture caused the carbinol to precipitate. The resulting suspension was filtrated and the filtrate extracted with $CHCl_3$ (3 × 50 mL). The combined organic extracts were washed with a saturated aqueous $NaHCO_3$ solution (100 mL) before being dried ($MgSO_4$). Removal of the solvent *in vacuo* gave tetrol **3** (1.32 g, 99%) as a colourless solid. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.18; m.p. 153°C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 2.61 (t, 1 H, $^3J_{OH\text{-}H\text{-}6}$ = 6.2 Hz, OH), 2.68 (t, 1 H, $^3J_{OH\text{-}H\text{-}6}$ = 5.9 Hz, OH), 2.78 (t, 1 H, $^3J_{OH\text{-}H\text{-}6}$ = 6.1 Hz, OH), 2.96 (t, 1 H, $^3J_{OH\text{-}H\text{-}6}$ = 5.8 Hz, OH), 3.17–3.22 (7 H, H-2), 3.30–4.00 (35 H, H-3, H-4, H-5, H-6) 3.37 (s, 9 H, OMe-6), 3.49 (s, 9 H, OMe), 3.51 (s, 6 H, OMe), 3.52 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.62 (s, 9 H, OMe), 3.63 (s, 3 H, OMe), 3.64 (s, 6 H, OMe), 3.65 (s, 3 H, OMe), 5.01–5.03 (2 H, H-1), 5.09 (d, 1 H, $^2J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, H-1), 5.10 (d, 1 H, $^2J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, H-1), 5.17 (d, 2 H, $^2J_{H\text{-}1,H\text{-}2}$ = 3.5 Hz, H-1), 5.23 (d, 1 H, $^2J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, H-1) ppm; ^{13}C{^{1}H} NMR (75.5 MHz $CDCl_3$, 25 ºC): δ (assignment by HMQC) = 58.25 [×3], 58.68, 58.77, 58.95, 59.00, 59.06, 59.19 [×2], 61.05, 61.09, 61.25, 61.28, 61.53, 61.63, 61.78 (OMe), 61.78, 61.97 [×2], 62.05 (C-$6^{A,B,D,E}$), 71.18, 71.32, 71.47 (C-$5^{C,F,G}$), 71.39, 71.54, 71.69 (C-$6^{C,F,G}$), 71.83, 72.03, 72.33, 72.53 (C-$5^{A,B,D,E}$), 78.29, 79.11 [×2] 79.96, 80.44, 80.69, 81.09, 81.24, 81.41, 81.45, 81.60 [×2], 81.73, 81.77 [×2], 81.98 [×4], 82.07, 82.14 (C-2, C-3, C-4), 98.37, 98.60, 98.70 [×2], 98.85 [×2], 98.92 (C-1) ppm; elemental analysis (%) calcd for $C_{59}H_{104}O_{35}$ (1373.44): C 51.60 , H 7.63 , found: C 51.68, H 7.57; MS (ESI-TOF): *m*/*z* (%): 1395.63 (100) $[M + Na]^+$.

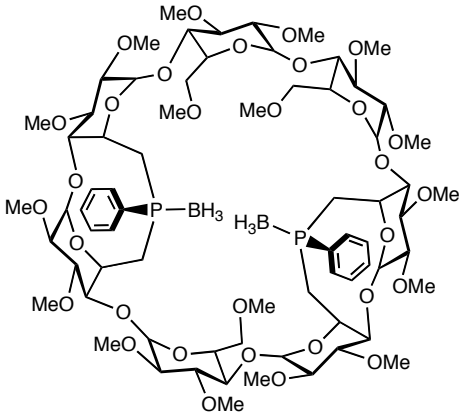
6^{A},6^{B},6^{D},6^{E}-*O*-Tetramethylsulfonyl-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{F},6^{G}-heptadeca-*O*-methyl-β-cyclodextrin (4)



Methanesulfonyl chloride (0.34 g, 0.23 mL, 2.94 mmol) was added to a solution of tetrol **3** (0.96 g, 0.70 mmol) and DMAP (0.35 g, 2.87 mmol) in dry pyridine (30 mL) at 0ºC. The reaction mixture was stirred at room temperature for 12 h before adding water (100 mL). The solution was extracted with AcOEt (3 × 50 mL). The combined organic extracts were washed sequentially with HCl 2 M (2 × 50 mL), NaOH 2 M (2 × 50 mL) and water (50 mL) before being dried ($MgSO_4$). Removal of the solvent *in vacuo* gave pure tetramesylate **4** (1.14 g, 97%) as a colourless solid. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.40; m.p. 201°C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 3.06 (s, 6 H, OSO_2Me), 3.07 (s, 3 H, OSO_2Me), 3.07 (s, 3 H, OSO_2Me), 3.14–3.21 (7 H, H-2), 3.37 (s, 3 H, OMe), 3.38 (s, 3 H, OMe), 3.39 (s, 3 H, OMe), 3.49 (s, 9 H, OMe), 3.50 (s, 6 H, OMe), 3.53 (s, 6 H, OMe), 3.60 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.62 (s, 6 H, OMe), 3.64 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.68 (s, 3 H, OMe), 3.40–4.05 (27 H, H-3, H-4, H-5, H-$6^{C,F,G}$), 4.32–4.34 (2 H, H-$6a^{A,D\text{ or }B,E}$), 4.53–4.70 (6 H, H-$6a^{B,E\text{ or }A,D}$,H-$6b^{A,B,D,E}$), 5.08–5.11 (4 H, H-1), 5.14 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, H-1), 5.20 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, H-1), 5.22 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, H-1) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz $CDCl_3$, 25ºC): δ (assignment by HMQC) = 37.17, 37.30 [×2], 37.50 (OSO_2Me), 58.26, 58.39 [×2], 58.46, 58.74, 59.10, 59.15 [×2], 59.36, 59.44, 61.11, 61.21, 61.62 [×3], 61.76, 61.80 (OMe), 69.32 [×2], 69.88 [×2] (C-$6^{A,B,D,E}$), 69.56 [×2], 69.67 [×2] (C-$5^{A,B,D,E}$), 70.87, 70.96 [×2] (C-$6^{C,F,G}$), 71.16 [×2], 71.32 (C-$5^{C,F,G}$), 78.10, 78.35, 80.13, 80.20, 80.63, 80.67 [×2], 81.01, 81.47, 81.61 [×5], 81.69, 81.75, 81.85 [×3], 81.95, 82.04 (C-2, C-3, C-4), 97.66, 98.41, 98.94 [×2], 99.12 [×2], 99.17 (C-1) ppm; elemental

analysis (%) calcd for $C_{63}H_{112}O_{43}S_4$ (1685.80): C 44.89, H 6.70, found: C 44.88 , H 6.65; MS (ESI-TOF): *m/z* (%): 1707.54 (100) $[M + Na]^+$.

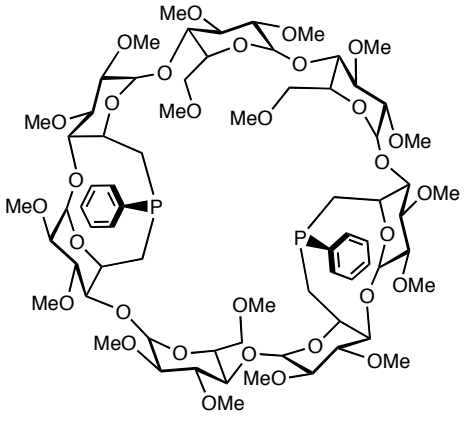
_P,P'_-{6^A,6^B,6^D,6^E-Tetradeoxy-6^A,6^B:6^D,6^E-bis[(*R*)-phenylphosphinidene]-2^A,2^B,2^C,2^D,2^E, 2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^C,6^F,6^G-heptadeca-*O*-methyl-β-cyclodextrin} diborane (5)



A solution of ^{n}BuLi in hexane (1.60 M, 1.22 mL, 1.96 mmol) was added dropwise to a stirred solution of H_2PPh (0.098 g, 0.89 mmol, 0.098 mL) in THF (16.5 mL) at –78 ºC. The yellow solution was allowed to rise to room temperature over 1 h whereupon the phosphide dianion precipitated. The resulting yellow suspension was cannulated slowly, within 1 h, into a stirred solution of tetramesylate **4** (0.300 g, 0.18 mmol) in THF (25 mL). The reaction mixture was stirred for 12 h at room temperature. The solvent was then removed *in vacuo* and excess of Li_2PPh was protonated with MeOH (15 mL). After removal of the solvent *in vacuo*, toluene (100 mL) was added and the resulting suspension filtered over celite. Evaporation of the solvent gave a colourless residue which was dissolved in THF (10 mL) before adding a solution of BH_3·THF in THF (1.00 M, 0.9 mL, 0.9 mmol) dropwise at 0ºC. After stirring for 12 h at room temperature, the solvent was removed *in vacuo* and the resulting colourless residue subjected to column chromatography (dried SiO_2, CH_2Cl_2/MeOH, 97:3, *v*/*v*) to afford pure **5** (0.120 g, 40%) as a colourless solid. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.35; m.p. 185ºC; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 0.89 (br s, 6 H, P-BH_3), 1.62–1.64 (4 H, H-6a^{A,B,D,E}), 2.89–2.91 (2 H, H-6b$^{A,D\text{ or }B,E}$), 3.17 (s, 3 H, OMe), 3.22 (s, 3 H, OMe), 3.27 (s, 3 H, OMe), 3.44 (s, 3 H, OMe), 3.45 (s, 6 H, OMe), 3.45 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.53, (s, 6 H, OMe), 3.57 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.64 (s, 6 H, OMe), 3.67 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.10–4.27 (34 H, H-2, H-3, H-4, H-5$^{B,E\text{ or }A,D}$, H-5^{C,F,G}, H-6b$^{B,E\text{ or }A,D}$, H-6^{C,F,G}), 4.60–4.62 (2 H, H-5$^{A,D\text{ or }B,E}$),

4.91 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, H-1), 4.94 (d, 2 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 4.97–5.00 (3 H, H-1), 5.11 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, H-1), 7.46–7.47 (6 H, *m*-H, *p*-H), 7.77–7.83 (4 H, *o*-H) ppm; $^{13}C\{^{1}H\}$ NMR (75.5 MHz $CDCl_3$, 25ºC): δ (assignment by HMQC) = 27.21 (d, $^{1}J_{C,P}$ = 35.3 Hz), 27.91 (d, $^{1}J_{C,P}$ = 34.4 Hz) (C-6$^{A,D\text{ or }B,E}$), 34.25 (d, $^{1}J_{C,P}$ = 30.0 Hz), 35.15 (d, $^{1}J_{C,P}$ = 30. Hz) (C-6$^{B,E\text{ or }A,D}$), 57.91 [×3], 58.00, 58.21, 58.45, 58.49, 58.66, 58.82, 58.90, 61.45, 61.57 [×2], 61.82, 61.91, 62.20, 62.22 (OMe), 64.52, 64.74 (C-5$^{A,D\text{ or }B,E}$), 68.67 (d, $^{2}J_{C,P}$ = 6.4 Hz), 68.99 (d, $^{2}J_{C,P}$ = 5.5 Hz) (C-5$^{B,E\text{ or }A,D}$), 70.86, 71.05, 71.44 (C-5^{C,F,G}), 70.57, 71.15, 71.42 (C-6^{C,F,G}), 80.06, 80.44, 80.48, 81.16, 81.28, 81.54, 81.80, 82.03, 82.26 [×5], 82.38, 82.46, 83.14, 83.30 (C-2, C-3, C-4^{C,F,G}), 86.73 (d, $^{3}J_{C,P}$ = 10.1 Hz), 86.98 (d, $^{3}J_{C,P}$ = 10.1 Hz) (C-4$^{A,D\text{ or }B,E}$), 89.09, 89.46 (C-4$^{B,E\text{ or }A,D}$), 98.46, 98.54, 99.55, 100.28, 100.45, 100.78, 101.18 (C-1), 128.73, 128.85 (*m*-C), 131.12, 131.19 (*p*-C), 131.55 (d, $^{2}J_{C\text{-}P}$ = 3.7 Hz), 131.67 (d, $^{2}J_{C\text{-}P}$ = 3.7 Hz) (*o*-C), 131.34 (d, $^{1}J_{C\text{-}P}$ = 11.4 Hz), 132.17 (d, $^{1}J_{C\text{-}P}$ = 11.4 Hz) (*ipso*-C) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz $CDCl_3$, 25ºC): δ = 17.8 (s), 18.4 (s) ppm; elemental analysis (%) calcd for $C_{71}H_{116}B_2O_{31}P_2\cdot$MeOH (1549.23 + 32.04): C 54.69, H 7.65, found: C 54.56, H 7.69; MS (ESI-TOF): *m/z* (%): 1571.71 (100) $[M + Na]^+$.

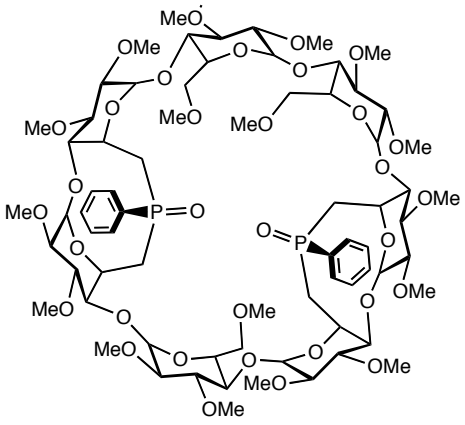
6^{A},6^{B},6^{D},6^{E}-Tetradeoxy-6^{A},6^{B}:6^{D},6^{E}-bis[(*R*)-phenylphosphinidene]-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{F},6^{G}-heptadeca-*O*-methyl-β-cyclodextrin (6)



A solution of **5** (80 mg, 0.52 mmol) in $HNEt_2$ (8 mL) was refluxed for 12 h. After cooling down to room temperature, the suspension was fitered over celite and the filtrate evaporated to dryness *in vacuo* to afford analytically pure **6** (0.80 mg, 99%). R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.40; m.p. 195ºC; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 1.73 (m, 2 H, H-6a$^{A,D\text{ or }B,E}$), 1.87 (m, 2 H, H-6a$^{B,E\text{ or }A,D}$), 2.81 (td, 2 H, $^{2}J_{H\text{-}6b,P}$ = $^{2}J_{H\text{-}6b,H\text{-}6a}$ =

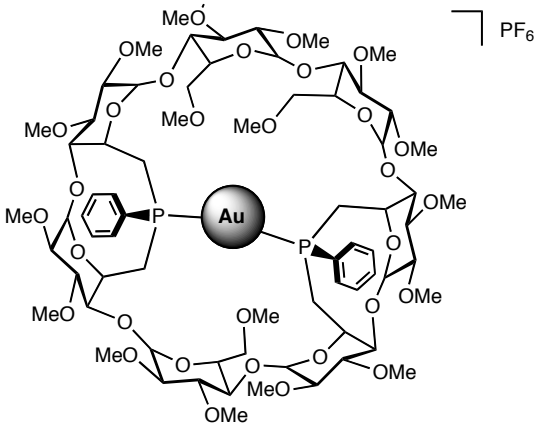
13.5 Hz, $^{3}J_{\text{H-6b,H-5}}$ = 3.9 Hz, H-6b$^{\text{A,D or B,E}}$), 3.05–3.29 (12 H, H-2, H-6a$^{\text{C,F,G}}$, H-6b$^{\text{B,E or A,D}}$), 3.11 (s, 3 H, OMe), 3.20 (s, 3 H, OMe), 3.27 (s, 3 H, OMe), 3.30–3.72 (14 H, H-3, H-4), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.50 (s, 6 H, OMe), 3.55 (s, 6 H, OMe), 3.60 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.65 (s, 9 H, OMe), 3.66 (s, 6 H, OMe), 3.81–3.42 (8 H, H-5$^{\text{A,D or B,E}}$, H-5$^{\text{C,F,G}}$, H-6b$^{\text{C,F,G}}$), 4.30 (m, 2 H, H-5$^{\text{B,E or A,D}}$), 4.95–5.05 (6 H, H-1), 5.22 (d, 1 H, $^{3}J_{\text{H-1,H-2}}$ = 3.7 Hz, H-1), 7.20–7.28 (6 H, *m*-H, *p*-H), 7.41–7.51 (4 H, *o*-H) ppm; ^{13}C{^{1}H} NMR (125.8 MHz C_6D_6, 25ºC): δ (assignment by HMQC) = 28.66 (d, $^{1}J_{\text{C,P}}$ = 15.4 Hz), 28.69 (d, $^{1}J_{\text{C,P}}$ = 16.2 Hz) (C-6$^{\text{A,D or B,E}}$), 34.99 (d, $^{1}J_{\text{C,P}}$ = 19.1 Hz), 35.06 (d, $^{1}J_{\text{C,P}}$ = 19.7 Hz) (C-6$^{\text{B,E or A,D}}$), 58.14 [×2], 58.20, 58.32, 58.71, 59.10, 59.14, 59.44, 59.68, 59.74, 61.77, 61.79, 61.90, 62.00, 62.05, 62.25 [×2] (OMe), 67.54 (d, $^{2}J_{\text{C,P}}$ = 11.7 Hz, C-5$^{\text{A or D}}$), 67.57 (d, $^{2}J_{\text{C,P}}$ = 11.7 Hz, C-5$^{\text{D or A}}$), 71.53 [×2], 71.80 (C-5$^{\text{C,F,G}}$), 72.13 (d, $^{\text{TS}}J_{\text{C,P}}$ = 2.6 Hz, C-6$^{\text{C}}$), 72.39 [×2] (C-6$^{\text{F,G}}$), 73.95 (d, $^{2}J_{\text{C,P}}$ = 14.3 Hz, C-5$^{\text{B or E}}$), 74.26 (d, $^{2}J_{\text{C,P}}$ = 13.6 Hz, C-5$^{\text{E or B}}$), 79.75, 82.22, 82.31, 82.37, 82.42, 82.97, 83.15, 83.23, 83.36 [×3], 83.42, 83.46, 83.58, 84.07, 84.55, 84.70 (C-2, C-3, C-4$^{\text{C,F,G}}$), 87.15 (d, $^{3}J_{\text{C,P}}$ = 8.0 Hz, C-4$^{\text{B or E}}$), 87.32 (d, $^{3}J_{\text{C,P}}$ = 8.0 Hz, C-4$^{\text{E or B}}$), 90.23 (d, $^{3}J_{\text{C,P}}$ = 2.7 Hz, C-4$^{\text{A or D}}$), 90.38 (d, $^{3}J_{\text{C,P}}$ = 2.6 Hz, C-4$^{\text{D or A}}$), 99.27, 99.32, 99.69, 99.90, 99.96 [×2], 101.19 (C-1), 128.96, 129.03 (*p*-C), 129.15 [×2] (overlapping d, $^{3}J_{\text{C,P}}$ = 4.8 Hz, *m*-C), 132.47 (d, $^{2}J_{\text{C,P}}$ = 18.7 Hz, *o*-C), 132.51 (d, $^{2}J_{\text{C,P}}$ = 18.7 Hz, *o*-C), 142.33 [×2] (d, $^{1}J_{\text{C,P}}$ = 11.7 Hz, *ipso*-C) ppm; ^{31}P{^{1}H} NMR (202.5 MHz C_6D_6, 25 ºC): δ = –15.0 (s), –15.2 (s) ppm; elemental analysis (%) calcd for $C_{71}H_{110}O_{31}P_2 \cdot 0.5CH_2Cl_2$ (1521.56 + 42.47): C 54.91, H 7.15, found: C 54.82, H 7.35; MS (ESI-TOF): *m/z* (%): 1521.57 (100) $[M + H]^+$.

6$^{\text{A}}$,6$^{\text{B}}$,6$^{\text{D}}$,6$^{\text{E}}$-Tetradeoxy-6$^{\text{A}}$,6$^{\text{B}}$:6$^{\text{D}}$,6$^{\text{E}}$-bis[(*S*)-phenyloxophosphinidene]-2$^{\text{A}}$,2$^{\text{B}}$,2$^{\text{C}}$,2$^{\text{D}}$,2$^{\text{E}}$,2$^{\text{F}}$, 2$^{\text{G}}$,3$^{\text{A}}$,3$^{\text{B}}$,3$^{\text{C}}$,3$^{\text{D}}$,3$^{\text{E}}$,3$^{\text{F}}$,3$^{\text{G}}$,6$^{\text{C}}$,6$^{\text{F}}$,6$^{\text{G}}$-heptadeca-*O*-methyl-β-cyclodextrin (7)



The bis(phosphane oxyde) **7** was quantitavely obtained by bubbling air through a solution of **6** in MeOH for 3 h at room temperature. Removal of the solvent *in vacuo* gave **7** as a white analytically pure product. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.30; m.p. 213ºC; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 1.91–1.93 (2 H, H-6a$^{A,D\text{ or }B,E}$), 2.21–2.23 (2 H, 6a$^{B,E\text{ or }A,D}$), 2.91–3.74 (28 H, H-2, H-3, H-4, H-6b^{A,B,D,E}, H-6a^{C,F,G}), 3.06 (s, 3 H, OMe), 3.08 (s, 3 H, OMe), 3.22 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 3.44 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.56 (s, 9 H, OMe), 3.60 (s, 6 H, OMe), 3.67 (s, 6 H, OMe), 3.68 (s, 3 H, OMe), 3.71 (s, 3 H, OMe), 3.86–4.08 (6 H, H-5^{C,F,G}, H-6b^{C,F,G}), 4.40–4.42 (2 H, H-5$^{A,D\text{ or }B,E}$), 4.62–4.64 (2 H, H-5$^{B,E\text{ or }A,D}$), 4.86 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 4.93 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 4.97 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 5.02 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 5.08 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 7.45–7.54 (6 H, *m*-H, *p*-H), 7.72–7.80 (4 H, *o*-H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz $CDCl_3$, 25ºC): δ (assignment by HMQC) = 33.41 (d, $^2J_{C,P}$ = 68.1 Hz), 33.50 (d, $^2J_{C,P}$ = 68.1 Hz) (C-6$^{A,D\text{ or }B,E}$), 37.82 (d, $^2J_{C,P}$ = 65.5 Hz), 37.87 (d, $^2J_{C,P}$ = 65.5 Hz) (C-6$^{B,E\text{ or }A,D}$), 57.89, 58.14, 58.17 [×2], 58.21, 58.25 [×2], 58.66, 58.73, 58.81, 61.48, 61.50, 61.62 [×2], 61.93, 62.10, 62.22 (OMe), 63.33 [×2] (C-5$^{A,D\text{ or }B,E}$), 66.22, 66.83 (C-5$^{B,E\text{ or }A,D}$), 70.30, 70.74, 70.83 (C-5^{C,F,G}), 70.89, 70.96, 71.04 (C-6^{C,F,G}), 80.31, 80.57, 81.25, 81.50 [×2], 81.67, 81.85 [×2], 82.04, 82.41 [×4], 82.65[×2], 83.37, 83.57 (C-2,C-3, C-4^{C,F,G}), 86.25 (d, $^3J_{C,P}$ = 11.8 Hz), 87.21 (d, $^3J_{C,P}$ = 11.8 Hz) (C-4$^{A,D\text{ or }B,E}$), 89.29 [×2] (C-4$^{B,E\text{ or }A,D}$), 98.81, 98.94, 99.73, 100.35 [×2], 100.65, 101.15 (C-1), 128.71 [×2] (d, $^2J_{C,P}$ = 11.8 Hz, *o*-C), 129.44 [×2] (d, $^3J_{C,P}$ = 9.3 Hz, *m*-C), 131.69 [×2] (*p*-C), 135.16 (d, $^1J_{C,P}$ = 98.1 Hz, *ipso*-C), 135.36 (d, $^1J_{C,P}$ = 98.1 Hz, *ipso*-C) ppm; ^{31}P{^{1}H} NMR (121.5 MHz $CDCl_3$, 25ºC): δ = 35.7 (s), 35.9 (s) ppm; elemental analysis (%) calcd for $C_{71}H_{110}O_{33}P_2$ (1553.56): C 54.89, H 7.14, found: C 54.82, H 7.53; MS (ESI-TOF): *m/z* (%): 1575.56 (100) $[M + Na]^+$.

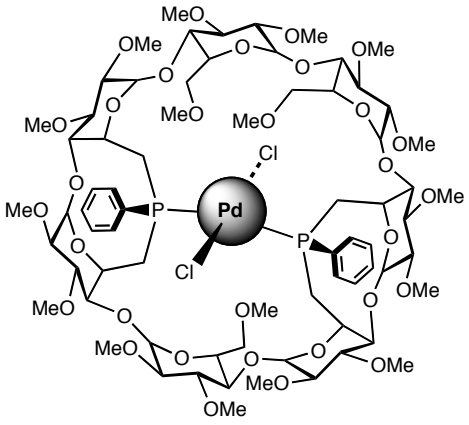
_P,P'_-{6^A,6^B,6^D,6^E-Tetradeoxy-6^A,6^B:6^D,6^E-bis[(*R*)-phenylphosphinidene]-2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^C,6^F,6^G-heptadeca-*O*-methyl-*β*-cyclodextrin}gold(I) hexafluorophosphate (8)



A solution of thallium hexafluorophosphate (0.020 g, 0.058 mmol) in THF (2 mL) was added to a solution of [AuCl(THT)] (THT = tetrathydrothiophene) (0.016 g, 0.053 mmol) in CH_2Cl_2 (10 mL). After stirring for 30 min, the solution was filtered through celite to eliminate thallium chloride, then added to a solution of **6** (0.080 g, 0.053 mmol) in CH_2Cl_2 (5 mL). After 30 min, the solution was filtered through celite and the filtered solution was concentrated to *ca.* 2 mL. Addition of pentane afforded complex **8** (0.099 g, 99%) as a pale brown precipitate. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.33; m.p. dec.; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 2.06 (dt, 1 H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 15.4 Hz, $^2J_{H\text{-}6a,P}$ = $^3J_{H\text{-}6a,H\text{-}65}$ = 5.7 Hz, H-6a$^{A \text{ or } D}$), 2.52 (m, 1 H, H-6a$^{D \text{ or } A}$), 2.65 (2 H, H-6a^{B,E}), 2.84 (s, 3 H, OMe), 2.95–3.70 (30 H, H-2, H-3, H-4$^{A,B,D,E \text{ and } C,F \text{ or } F,G \text{ or } C,G}$, H-5$^{C \text{ or } F \text{ or } G}$, H-6$^{C,F \text{ or } F,G \text{ or } C,G}$, H-6a$^{G \text{ or } C \text{ or } F}$, H-6b^{A,B,D,E}), 2.96 (s, 3 H, OMe), 3.30 (s, 3 H, OMe), 3.47 (s, 6 H, OMe), 3.50 (s, 6 H, OMe), 3.52 (s, 3 H, OMe), 3.54 (s, 3 H, OMe), 3.55 (s, 3 H, OMe), 3.56 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.61 (s, 6 H, OMe), 3.64 (s, 6 H, OMe), 3.67 (s, 3 H, OMe), 3.80–3.90 (2 H, H-4$^{G \text{ or } C \text{ or } F}$, H-6b$^{G \text{ or } C \text{ or } F}$), 4.21–4.43 (6 H, H-5$^{A,B,D,E \text{ and } F,G \text{ or } C,F \text{ or } C,G}$), 4.83 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1), 4.99 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.0 Hz, H-1), 5.06 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1), 5.07 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 5.10 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.5 Hz, H-1), 5.15 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 5.18 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, H-1), 7.42–7.47 (2 H, *m*-H), 7.55–7.67 (6 H, *m*-H, *p*-H, *o*-H), 7.73–7.79 (2 H, *o*-H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 28.27, 28.96 (C-6$^{B,E \text{ or } A,D}$), 36.23, 38.66 (C-6$^{A,D \text{ or } B,E}$), 57.77 [×2], 58.14 [×2], 58.22, 58.27, 58.50, 58.80, 59.09, 59.29, 59.51, 59.59, 60.04, 60.96, 60.97 [×2], 61.40 (OMe), 64.40, 65.05 (C-5$^{A,D \text{ or } B,E}$), 69.52, 70.43 [×2] (C-5$^{B,E \text{ or } A,D \text{ and } C \text{ or } F \text{ or } G}$), 72.64, 74.03 (C-5$^{F,G \text{ or } C,F \text{ or } C,G}$), 71.26, 71.95, 72.77 (C-6^{C,F,G}), 76.90, 77.07, 78.07 (C-4^{C,F,G}), 80.29, 80.67, 81.23, 81.28 [×2], 81.70, 81.79 [×3], 81.84, 82.36 [×2], 82.78, 83.91 (C-2, C-3), 88.61 [×2] (C-4$^{A,B \text{ or } D,E}$), 86.21 [×2] (C-4$^{D,E \text{ or } A,B}$), 95.20, 97.01, 97.44, 97.61, 98.73, 99.42, 99.54 (C-1), 129.59, 129.76 (*m*-C), 132.48 [×2] (*p*-C), 132.30, 132.69 (*o*-C), 137.75 [×2] (*ipso*-C)

ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25ºC): δ = 34.2 (br s), –144.3 (hept, $^{1}J_{P,F}$ = 716 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2, 25ºC): δ = 37.6 and 34.6 (AB system, $^{2}J_{P1,P2}$ = 326 Hz), –144.3 (hept, $^{1}J_{P,F}$ = 716 Hz) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2, –80ºC): δ = 40.6 and 31.6 (AB system, $^{2}J_{P1,P2}$ = 326 Hz), 38.0 and 33.8 (AB system, $^{2}J_{P1,P2}$ = 326 Hz), –144.3 (hept, $^{1}J_{P,F}$ = 716 Hz) ppm; elemental analysis (%) calcd for $C_{71}H_{110}AuF_6O_{31}P_3$ (1863.49): C 45.76, H 5.95, found: C 45.76, H 5.95; MS (ESI-TOF): *m/z* (%): 1717.62 (100) $[M - PF_6]^+$.

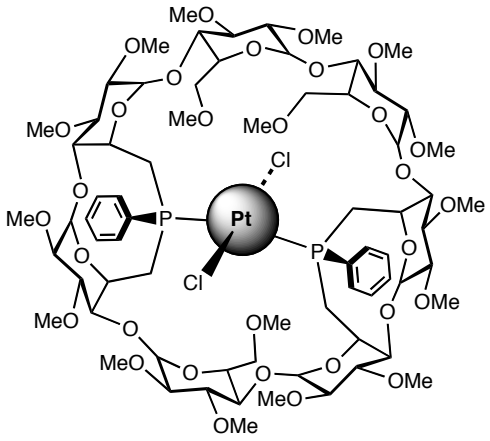
***trans-P,P'*-Dichlorido-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-6^{A},6^{B}:6^{D},6^{E}-bis[(*R*)-phenylphosphinidene]-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{F},6^{G}-heptadeca-*O*-methyl-*β*-cyclodextrin}palladium(II) (9)**



A solution of $[PdCl_2(PhCN)_2]$ (0.020 g, 0.053 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of diphosphine **6** (0.080 g, 0.053 mmol) in CH_2Cl_2 (10 mL) within 30 min at room temperature. After 30 min, the reaction mixture was evaporated to dryness and the residue subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 96:4, *v*/*v*) to give pure **9** (0.081 g, 90%) as a pale yellow powder. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.40; m.p. dec.; ^{1}H NMR (300.1 MHz, CD_2Cl_2, 25ºC): δ (assignment by COSY) = 2.0 (m, 1 H, H-6a$^{A\text{ or }D}$), 2.29 (m, 1 H, H-6a$^{D\text{ or }A}$), 2.55 (m, 1 H, H-6a$^{B\text{ or }E}$), 2.70 (m, 1 H, H-6a$^{E\text{ or }B}$), 2.78 (dd, 1 H, $^{3}J_{H\text{-}2,H\text{-}3}$ = 9.6 Hz, $^{3}J_{H\text{-}2,H\text{-}1}$ = 3.5 Hz, H-2), 2.98–3.14 (m, 8 H, H-2, H-4^{D,E}), 3.25–3.88 (m, 20 H, H-3, H-4^{A,B,C,F,G}, H-6a^{C,F,G}, H-6b$^{A,B,D,E\text{ and }C\text{ or }F\text{ or }G}$), 3.22 (s, 3 H, OMe), 3.24 (s, 3 H, OMe), 3.25 (s, 3 H, OMe), 3.35 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 3.44 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.54 (s, 6 H, OMe), 3.55 (s, 6 H, OMe), 3.57 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.73 (s, 3 H, OMe), 3.97–4.11 (m, 3H, H-5$^{C\text{ or }F\text{ or }G}$, H-6b$^{C,F\text{ or }C,G\text{ or }F,G}$), 4.20–4.33 (m, 4 H, H-5$^{A,B\text{ and }F,G\text{ or }C,F\text{ or }C,G}$), 4.36–4.41 (m, 1 H, H-5$^{E\text{ or }D}$), 4.44–4.90 (m, 1 H, H-5$^{D\text{ or }E}$), 4.81 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.6 Hz, H-

1), 4.91 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, H-1), 4.99 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1), 5.00 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 5.01 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1), 5.20 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 4.0 Hz, H-1), 5.40 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 4.4 Hz, H-1), 7.36–7.42 (m, 6 H, *m*-H, *p*-H), 7.95–8,01 (m, 4 H, *o*-H) ppm; $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2, 25ºC): δ (assignment by HMQC) = 22.86, 25.06 (C-$6^{A,D\text{ or }B,E}$), 31.51, 32.00 (C-$6^{B,E\text{ or }A,D}$), 54.74, 55.93, 55.88 [×2], 56.50, 56.56 [×2], 56.74, 57.64, 58.09, 58.37, 58.45, 58.86 [×2], 59.27 [×2], 59.45 (OMe), 61.71, 62.31 (C-$5^{A,D\text{ or }B,E}$), 66.18, 67.25 (C-$5^{B,E\text{ or }A,D}$), 68.58, 68.73, 68.87 (C-$5^{C,F,G}$), 69.07, 69.84, 70.03 (C-$6^{C,F,G}$), 75.71, 75.83 [×2] (C-$4^{C,F,G}$), 77.25, 77.45, 78.64, 79.08, 79.16, 79.33, 79.39, 79.47 [×2], 79.74, 80.12, 80.45, 80.96 [×2] (C-2, C-3), 82.50 [×2], 87.28 [×2] (C-$4^{A,B,D,E}$), 92.46, 92.84, 94.98, 95.99, 96.35, 96.79, 96.89 (C-1), 125.92 (virtual t, $|^{3}J_{C,P} + {}^{5}J_{C,P'}|$ = 9.8 Hz, *m*-C), 126.57 (virtual t, $|^{3}J_{C,P} + {}^{5}J_{C,P'}|$ = 9.5 Hz, *m*-C), 128.11, 128.33 (*p*-C), 130.97 (virtual t, $|^{2}J_{C,P} + {}^{4}J_{C,P'}|$ = 12.7 Hz, *o*-C), 131.37 (virtual t, $|^{2}J_{C,P} + {}^{4}J_{C,P'}|$ = 12.7 Hz, *o*-C), 132.87 [×2] (virtual t, $|^{2}J_{C,P} + {}^{4}J_{C,P'}|$ = 51.0 Hz, *ipso*-C) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25ºC): δ = 15.5 (br s) ppm; ^{31}P $\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2, –80ºC) = 21.7 and 11.4 (2 d, AB system, $^{2}J_{P1,P2}$ = 564 Hz), 17.7 and 5.6 (2 d, AB system, $^{2}J_{P1,P2}$ = 549 Hz) ppm; elemental analysis (%) calcd for $C_{71}H_{110}Cl_2O_{31}P_2Pd$ (1698.89): C 50.20, H 6.53, found: C 50.12, H 6.74; MS (ESI-TOF): *m/z* (%):1737.46 (19) $[M + K]^+$, 1721.47 (76) $[M + Na]^+$, 1661.51 (5) $[M - Cl]^+$.

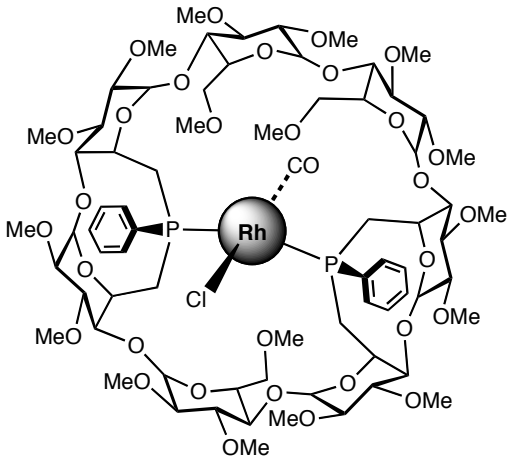
***trans-P,P'*-Dichlorido-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-6^{A},6^{B}:6^{D},6^{E}-bis[(*R*)-phenylphosphinidene]-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{F},6^{G}-heptadeca-*O*-methyl-*β*-cyclodextrin}platinum(II) (10)**



A solution of $[PtCl_2(PhCN)_2]$ (0.025 g, 0.053 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of diphosphine **6** (0.080 g, 0.053 mmol) in CH_2Cl_2 (10 mL) within 30 min at room

temperature. After 30 min, the reaction mixture was evaporated to dryness affording analytically pure **10** (0.089 g, 99%) as a pale yellow solid. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.40; m.p. dec.; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 2.12–2.21 (m, 1 H, H-6a$^{A\text{ or }D}$), 2.34 (dt, 1 H, $^3J_{H\text{-}6a,P}$ = 15.5 Hz, $^2J_{H\text{-}6a,H\text{-}6b}$ = 7.7 Hz, $^3J_{H\text{-}6a,H\text{-}5}$ = 7.7 Hz, , H-6a$^{D\text{ or }A}$), 2.68–2.76 (2 H, H-6a^{B,E}), 2.82 (dd, 1 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.2 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 3.1 Hz, H-2), 3.05–3.75 (22 H, H-2, H-3, H-4^{A,B,D,E}, H-6a^{C,F,G}, H-6b^{B,E}), 3.27 (s, 3 H, OMe), 3.30 (s, 3 H, OMe), 3.32 (s, 3 H, OMe), 3.38 (s, 3 H, OMe), 3.45 (s, 3 H, OMe) 3.48 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.59 (s, 6 H, OMe), 3.62 (s, 6 H, OMe), 3.63 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), 3.72 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 3.86–3.95 (6 H, H-4^{C,F,G}, H-6b$^{A,D\text{ and }C\text{ or }F\text{ or }G}$), 4.02–4.11 (4 H, H-5$^{F,G\text{ or }C,F\text{ or }C,G}$, H-6b$^{F,G\text{ or }C,F\text{ or }C,G}$), 4.25 (d, 1 H, $^3J_{H\text{-}5,H\text{-}6a}$ = 9.7 Hz, H-5$^{C\text{ or }F\text{ or }G}$), 4.33–4.39 (3 H, H-5$^{A\text{ or }D\text{ and }B,E}$), 4.55 (m, 1 H, H-5$^{D\text{ or }A}$), 4.80 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 4.91 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, H-1), 5.03 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.0 Hz, H-1), 5.06 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.3 Hz, H-1), 5.27 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.1 Hz, H-1), 5.54 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.7 Hz, H-1), 7.39–7.42 (6 H, *m*-H, *p*-H), 8.06–8.10 (4 H, *o*-H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 22.80, 26.50 (C-6$^{A,D\text{ or }B,E}$), 32.00, 33.00 (C-6$^{B,E\text{ or }A,D}$), 56.73, 57.74, 57.91, 58.15, 58.79, 58.84, 58.93, 59.02, 59.78, 60.42, 60.62, 60.96, 61.27, 61.40, 61.54, 61.72, 61.89 (OMe), 63.54, 64.29 (C-5$^{B,E\text{ or }A,D}$), 67.97, 69.10 (C-5$^{A,D\text{ or }B,E}$), 70.37, 70.45, 70.69 (C-5^{C,F,G}), 71.02, 71.89, 72.05 (C-6^{C,F,G}), 77.90 [×2], 78.07 (C-4^{C,F,G}), 79.02 [×2], 79.70 [×2], 80.54, 81.13 [×2], 81.37, 81.61, 82.11, 82.43, 82.95, 83.05, 83.44 (C-2, C-3), 84.50 [×2] (C-4$^{A,D\text{ or }B,E}$), 89.39 [×2] (C-4$^{B,E\text{ or }A,D}$), 94.64, 94.75, 96.97, 98.14, 98.26, 98.75, 99.25 (C-1), 127.95 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}|$ = 10.0 Hz, *m*-C), 128.52 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}|$ = 10.0 Hz, *m*-C), 130.28 [×2] (*p*-C), 133.25 (virtual t, $|^2J_{C,P} + {}^4J_{C,P'}|$ = 12.3 Hz, *o*-C), 133.69 (virtual t, $|^2J_{C,P} + {}^4J_{C,P'}|$ = 12.3 Hz, *o*-C), 135.57 [×2] (virtual t, $|^1J_{C,P} + {}^3J_{C,P'}|$ = 52.0 Hz, *ipso*-C) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25ºC): δ = 8.9 (br s with br Pt satellites, $^1J_{P,Pt} \approx$ 2500 Hz) ppm; ^{31}P {^{1}H} NMR (121.5 MHz, CD_2Cl_2, –80ºC) = 12.2 and 1.0 (2 d, AB system, $^2J_{P1,P2}$ = 476 Hz), 17.8 and 5.0 (2 d, AB system, $^2J_{P1,P2}$ = 492 Hz) ppm ($^1J_{Pt,P}$ poorly resolved); ^{31}P {^{1}H} NMR (202.5 MHz, $C_2D_2Cl_4$, 80ºC) = 7.35 and 7.0 (2 d with Pt satellites, ABX system, $^1J_{Pt,P1}$ = 2507 Hz, $^1J_{Pt,P2}$ = 2481 Hz, $^2J_{P1,P2}$ = 496 Hz) ppm. elemental analysis (%) calcd for $C_{71}H_{110}Cl_2O_{31}P_2Pt$ (1785.55): C 47.71, H 6.20, found: C 47.91, H 6.31; MS (ESI-TOF): *m/z* (%): 1792.45 (100) $[M + Li]^+$.

***trans-P,P'*-chlorido-carbonyl-{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},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{F},6^{G}-heptadeca-*O*-methyl-*β*-cyclodextrin}rhodium(I) (11)**



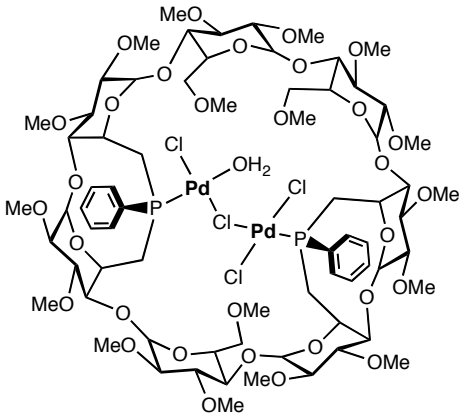
A solution of $[RhCl(CO)_2]_2$ (0.010 g, 0.026 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of diphosphine **6** (0.080 g, 0.053 mmol) in CH_2Cl_2 (10 mL) within 30 min at room temperature. After stirring for 30 min, the reaction mixture was evaporated to dryness affording analytically pure **10** (0.089 g, 99%) as an orange-yellow solid. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.40; m.p. dec.; IR (KBr) ν/cm^{-1}: 1970; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 2.25–2.38 (2 H, H-6a$^{A,D\text{ or }B,E}$), 2.55–2.65 (2 H, H-6a$^{B,E\text{ or }A,D}$), 2.78 (d, 1 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.0 Hz, H-2), 3.05–4.05 (32 H, H-2, H-3, H-4, H-5$^{C,F\text{ or }C,G\text{ or }F,G}$, H-6^{C,F,G}, H-6b^{A,B,D,E}), 3.27 (s, 3 H, OMe), 3.30 (s, 3 H, OMe), 3.33 (s, 3 H, OMe), 3.38 (s, 3 H, OMe), 3.46 (s, 3 H, OMe) 3.48 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.59 (s, 6 H, OMe), 3.60 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.64 (s, 6 H, OMe), 3.71 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 4.20 (d, 1 H, $^3J_{H\text{-}5,H\text{-}6a}$ = 9.4 Hz, H-5$^{G\text{ or }F\text{ or }C}$), 4.38–4.53 (4 H, H-5^{A,B,D,E}), 4.83 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, H-1), 4.91 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1), 5.06 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.1 Hz, H-1), 5.07 (d,1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.5 Hz, H-1), 5.11 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, H-1), 5.31 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.1 Hz, H-1), 5.48 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 4.5 Hz, H-1), 7.35–7.39 (6 H, *m*-H, *p*-H), 7.99–8.07 (4 H, *o*-H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 28.40 [×2] (virtual t, $|^1J_{C,P} + {}^3J_{C,P'}|$ = 9.9 Hz, C-6$^{A,D\text{ or }B,E}$), 30.19 [×2] (virtual t, $|^1J_{C,P} + {}^3J_{C,P'}|$ = 11.4 Hz, C-6$^{B,E\text{ or }A,D}$), 56.75, 57.89 [×2], 58.10, 58.72, 58.82, 58.92, 50.00, 59.44, 60.31, 60.57, 60.93 [×2], 61.06, 61.18, 61.69, 61.72 (OMe), 64.10, 64.79 (C-5$^{A,D\text{ or }B,E}$), 68.60, 69.63 (C-5$^{B,E\text{ or }A,D}$), 69.92, 70.41, 70.90 (C-5^{C,F,G}), 71.08, 71.69, 72.30 (C-6^{C,F,G}), 77.21 [×2], 77.64 (C-4^{C,F,G}), 79.57, 79.82, 80.34, 80.97,

81.24, 81.36 [×3], 82.38, 82.53, 83.08 [×2], 83.50, 84.42, (C-2, C-3), 84.95 [×2] (C-$4^{A,D\text{ or }B,E}$), 89.51 [×2] (C-$4^{B,E\text{ or }A,D}$), 94.36, 94.57, 97.01, 98.02, 98.34, 98.47, 99.08 (C-1), 127.68 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}| = 4.5$ Hz, *m*-C), 128.39 (virtual t, $|^3J_{C,P} + {}^5J_{C,P'}| = 4.5$ Hz, *m*-C), 129.72, 129.82 (*p*-C), 133.21 (virtual t, $|^2J_{C,P} + {}^4J_{C,P'}| = 6.3$ Hz, *o*-C), 133.58 (virtual t, $|^2J_{C,P} + {}^4J_{C,P'}| = 5.8$ Hz, *o*-C), 137.97 [×2] (virtual t, $|^1J_{C,P} + {}^3J_{C,P'}| = 22.5$ Hz, *ipso*-C) ppm; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 25ºC): $\delta = 18.7$ (br d, $^1J_{P,Rh} \approx 120$ Hz) ppm; $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, –80ºC) = 28.0 and 9.4 (2 dd, ABX system, $^2J_{P1,P2} = 354$ Hz, $^1J_{P,Rh} = 118$ and 118), 16.4 and 9.4 (2 dd, ABX system, $^2J_{P1,P2} = 354$ Hz, $^1J_{P,Rh} = 118$ and 118) ppm; elemental analysis (%) calcd for $C_{72}H_{110}ClO_{32}P_2Rh$ (1687.93): C 51.23, H 6.57, found: C 51.15, H 6.44; MS (ESI-TOF): *m/z* (%): 1725.48 (23) $[M + K]^+$, 1709.51 (58) $[M + Na]^+$, 1652.51 (16) $[M - Cl]^+$.

Reaction of $[PdCl_2(PhCN)_2]$ with 9 and formation of 12.

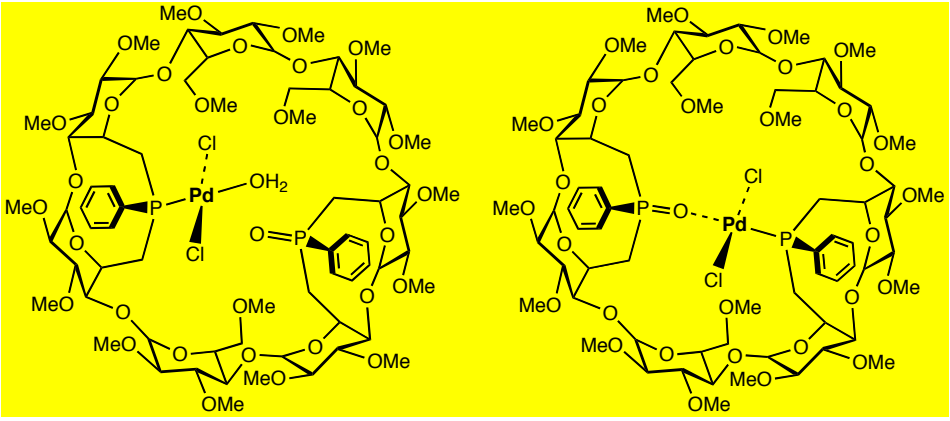
A solution of $[PdCl_2(PhCN)_2]$ (0.040 g, 0.106 mmol) in CH_2Cl_2 (5 mL) was added to a solution of diphosphine **6** (0.080 g, 0.053 mmol) in CH_2Cl_2 (10 mL) at room temperature. After 30 min, the reaction mixture was concentrated to *ca.* 2 mL and pentane (50 mL) was added. The suspension was then filtered over celite. Evaporation of pentane afforded a yellow powder (0.099 g, 99%) of formula $C_{71}H_{110}Cl_4O_{31}P_2Pd_2$ (**12'**), the exact structure of which is not known. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v/v*) = 0.35; m.p. dec.; ^1H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 1.71 (dt, 1 H, $^2J_{H\text{-}6a,P} = 13.9$ Hz, $^2J_{H\text{-}6a,H\text{-}6b} = {}^3J_{H\text{-}6a,H5} = 12.1$ Hz, H-$6a^{A\text{ or }D}$) 2.16 (dt, 1 H, $^2J_{H\text{-}6a,P} = 13.1$ Hz, $^2J_{H\text{-}6a,H\text{-}6b} = {}^3J_{H\text{-}6a,H\text{-}5} = 12.4$ Hz, H-$6a^{D\text{ or }A}$), 2.78–2.83 (2 H, H-$6^{B\text{ or }E}$), 2.98–3.03 (2H, H-$6^{E\text{ or }B}$), 3.07–3.34 (12 H, H-2, H-$4^{A,B,D,E}$, H-$6b^{A\text{ or }D}$), 3.48–3.88 (11 H, H-3, H-$4^{C,F,G}$, H-$6a^{C\text{ or }F\text{ or }G}$), 3.43 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.51 (s, 6 H, OMe), 3.51 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.54 (s, 3 H, OMe), 3.58 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.68 (s, 3 H, OMe), 3.70 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 4.05 (dd, 1 H, $^2J_{H\text{-}6b,H\text{-}6a} = 14.7$ Hz, $^3J_{H\text{-}6b,H\text{-}5} = 9.2$ Hz, H-$6b^{D\text{ or }A}$) 4.11–4.17 (2 H, H-$5^{C\text{ or }F\text{ or }G}$, H-$6b^{C\text{ or }F\text{ or }G}$), 4.27 (d, 1 H, $^2J_{H\text{-}6b,H\text{-}6a} = 10.9$ Hz, H-$6a^{F\text{ or }G\text{ or }C}$), 4.37 (d, 1 H, $^3J_{H\text{-}5,H\text{-}6a} = 10.0$ Hz, H-$5^{F\text{ or }G\text{ or }C}$), 4.47–4.58 (3 H, H-$5^{A\text{ or }D}$, H-$5^{G\text{ or }C\text{ or }F}$, H-$6a^{G\text{ or }C\text{ or }F}$), 4.75 (dd, 1 H, $^2J_{H\text{-}6b,H\text{-}6a} = 10.7$ Hz, $^3J_{H\text{-}6b,H\text{-}5} = 1.9$ Hz, H-$6b^{F\text{ or }G\text{ or }C}$), 4.82 (m, 1 H, H-$5^{D\text{ or }A}$), 4.90 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2} = 4.7$ Hz, H-1), 4.93 (dd, 1 H, $^2J_{H\text{-}6b,H\text{-}6a} = 11.1$ Hz, $^3J_{H\text{-}6b,H\text{-}5} = 1.8$ Hz, H-$6b^{G\text{ or }C\text{ or }F}$), 4.99 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2} = 4.4$ Hz, H-1), 5.00 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2} = 4.1$ Hz, H-1), 5.06 (m, 1 H, H-$5^{B\text{ or }E}$), 5.12 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2} = 4.4$ Hz, H-1), 5.14 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2} = 2.9$ Hz, H-1), 5.16 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2} = 3.6$ Hz, H-1), 5.21 (m, 1 H, H-$5^{E\text{ or }B}$), 5.28 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2} = 2.9$ Hz, H-1),

7.37–7.46 (6 H, *m*-H, *p*-H), 7.52–7.57 (2 H, *o*-H), 7.64–7.67 (2 H, *o*-H) ppm; $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 31.54 (d, $J_{C,P}$ = 31.8 Hz, C-$6^{D \text{ or } A}$), 31.12 (d, $J_{C,P}$ = 32.5 Hz, C-$6^{A \text{ or } D}$), 35.48(d, $J_{C,P}$ = 29.7 Hz, C-$6^{E \text{ or } B}$), 38.08 (d, $J_{C,P}$ = 23.1 Hz, C-$6^{B \text{ or } E}$), 57.40, 57.83, 58.01, 58.62, 58.66, 58.72, 59.32, 59.36, 59.68, 59.84, 61.31 [×2], 61.55, 61.71, 61.82, 61.86, 61.92 (OMe), 64.35 (C-$5^{D \text{ or } A}$), 64.59 (C-$5^{A \text{ or } D}$), 68.67 (C-$5^{E \text{ or } B}$), 69.49 (C-$5^{B \text{ or } E}$), 71.16, 71.45, 71.70 (C-$5^{C,F,G}$), 71.63, 72.78 [×2] (C-$6^{C,F,G}$), 79.98, 80.26, 80.49 [×2], 80.92, 81.31, 81.59 [×2], 82.04 [×2], 82.18 [×2], 82.73, 82.83, 82.96, 83.15 [×2] (C-2, C-3, C-$4^{C,F,G}$), 84.11 (d, $^{3}J_{C,P}$ = 11.4 Hz), 87.60 (d, $^{3}J_{C,P}$ = 11.4 Hz), 89.64, 89.83 (C-$4^{A,B,D,E}$), 97.55, 98.14, 98.26, 98.85, 99.79, 100.72, 102.07 (C-1), 128.55 (d, $^{3}J_{C,P}$ = 11.6 Hz, *m*-C), 128.70 (d, $^{3}J_{C,P}$ = 11.6 Hz, *m*-C), 131.02, 131.10 (*p*-C), 131.19, 131.29 (*o*-C), 130.7–131.94 [×2] (*ipso*-C) pmm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz $CDCl_3$, 25ºC): δ = 22.4 (br s), 27.3 (d, $^{4}J_{P,P'}$ = 4.4 Hz) ppm; elemental analysis (%) calcd for $C_{71}H_{110}Cl_4O_{31}P_2Pd_2$ (1876.21): C 45.45, H 5.91, found: C 45.39, H 6.09; MS (ESI-TOF): *m/z* (%): 1899.32 (75) $[M + Na]^+$, 1839.40 (25) $[M - Cl]^+$. Recristallisation of **12'** in CH_2Cl_2-pentane (undistilled) gave **12** (*vide infra*, X-ray analysis).



12

Dichlorido-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-6^{A},6^{B}[(*R*)-phenylphosphinidene]-6^{D},6^{E}-[(*S*)-phenyl oxophosphinidene]-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{F},6^{G}-heptadeca-*O*-methyl-*β*-cyclodextrin}palladium(II) (13) *and* dichloro-{6^{A},6^{B},6^{D},6^{E}-tetradeoxy-6^{A},6^{B}[(*S*)-phenyloxophosphinidene]-6^{D},6^{E}-[(*R*)-phenylphosphinidene]-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C}, 3^{D},3^{E},3^{F},3^{G},6^{C},6^{F},6^{G}-heptadeca-*O*-methyl-*β*-cyclodextrin}palladium(II) (14)



13 **14**

Air was bubbled through a solution of complex **9** (0.080 g, 0.047 mmol) in undistilled MeOH for 30 min. After refluxing the solution for 12 h, the solvent was removed *in vacuo* and the crude product was purified by column chromatography* (SiO_2, CH_2Cl_2/MeOH, 97:3, *v*/*v*) to give compound **13** (0.036 g, 45%) as a pale yellow solid. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.35; m.p. dec.; ^{1}H NMR (600.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 1.85 (m, 1 H, H-6a$^{D\text{ or }E}$), 1.91–1.96 (2 H, H-6a$^{A\text{ or B and E or D}}$), 2.80 (dd, 1 H, $^1J_{H\text{-}6a,P}$ = 18.6 Hz, $^2J_{H\text{-}6a,H\text{-}6b}$ = 15.8 Hz, H-6b$^{A\text{ or }B}$), 2.99–3.04 (2 H, H-6$^{B\text{ or }A}$), 3.07–3.80 (31 H, H-2, H-3, H-4, H-5^{D,E}, H-6^{C,F,G}, H-6b^{D,E}), 3.15 (s, 6 H, OMe), 3.35 (s, 3 H, OMe), 3,46 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.54 (s, 6 H, OMe), 3.59 (s, 3 H, OMe), 3.64 (s, 6 H, OMe), 3.67 (s, 3 H, OMe), 3.69 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 3.76 (s, 3 H, OMe), 3.96–4.02 (2 H, H-5$^{C,F\text{ or }C,G\text{ or }F,G}$), 4.25 (d, 1 H, $^3J_{H\text{-}5,H\text{-}6}$ = 10.4 Hz, H-5$^{G\text{ or }F\text{ or }C}$), 4.54 (m, 1 H, H-5$^{A\text{ or }B}$), 4.82 (m, 1 H, H-5$^{B\text{ or }A}$), 4.94 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.7 Hz, H-1), 4.99 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, H-1), 5.00 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, H-1), 5.03 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, H-1), 5.06 (m, 1 H, H-1), 5.09 (m, 1 H, H-1), 7.35 (td, 2 H, $^3J_{m\text{-}H,o\text{-}H}$ = $^3J_{m\text{-}H,p\text{-}H}$ = 7.9 Hz, $^4J_{m\text{-}H,P}$ = 0.5 Hz, *m*-H of (O)PPh), 7.41 (t, 1 H, $^3J_{p\text{-}H,m\text{-}H}$ = 7.9 Hz, *p*-H of (O)PPh), 7.57–7.59 (3 H, *m*-H and *p*-H of PdPPh), 7.86 (dd, 2 H, $^3J_{o\text{-}H,P}$ = 11.8 Hz, $^3J_{o\text{-}H,m\text{-}H}$ = 7.9 Hz, *o*-H of (O)PPh), 8.22 (m, 2 H, *o*-H of PdPPh) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 57.31, 57.87, 58.07, 58.54, 58.78, 58.83, 58.91, 59.12, 59.32, 59.55, 61.26, 61.38, 61.72 [×2], 61.83 [×2], 62.09 (OMe), 62.98 (C-5$^{A\text{ or }B}$), 66.38 (C-5$^{B\text{ or }A}$), 70.46 [×2] (C-6$^{C,F\text{ or }C,G\text{ or }F,G}$), 70.66 [×2] (C-5$^{C,F\text{ or }C,G\text{ or }F,G}$), 71.50 (C-6$^{G\text{ or }F\text{ or }C}$), 71.68 (C-5$^{G\text{ or }F\text{ or }C}$), 73.45 [×2] (C-5^{D,E}), 78.39 [×2], 80.79, 81.03 [×2], 81.13, 81.24, 81.71, 81.87, 81.96, 82.94 [×2], 83.04 [×2], 83.24, 83.58, 83.68 (C-2, C-3, C-4^{C,F,G}), 86.40, 86.93 (C-4^{D,E}), 89.36 [×2] (C-4^{A,B}), 95.33, 97.94, 98.86, 100.61, 100.65, 100.90, 101.23 (C-1), 128.16 (d, $^3J_{C,P}$ = 11.7 Hz, *m*-C of (O)PPh), 128.87 (d, $^3J_{C,P}$ = 11.4 Hz, *m*-C of PdPPh), 130.25 (d, $^2J_{C,P}$ = 10.2 Hz, *o*-C of PdPPh), 130.74 (*p*-C of (O)PPh), 132.11 (d, $^2J_{C,P}$ = 9.7 Hz,

o-C of (O)PPh), 132.48 (*p*-C of PdPPh) ppm (C-6^{A,B,D,E} and both *ipso*-C's could not be detected); $^{31}P\{^{1}H\}$ NMR (121.5 MHz $CDCl_3$, 25ºC): 33.0 (br s), 50.3 (br s) ppm; elemental analysis (%) calcd for $C_{71}H_{112}Cl_2O_{33}P_2Pd$ (1732.90): C 49.21, H 6.51, found: C 49.39, H 5.69; MS (ESI-TOF): *m/z* (%): 1737.52 (50) $[M + Li]^+$, 1735.48 (50) $[M - H_2O + Na]^+$.* During the purification, complex **14** (0.034 g, 43%) was also isolated. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.40; m.p. dec.; ^{1}H NMR (600.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 2.08 (m, 1 H, H-6a$^{A\text{ or }B}$), 2.17 (m, 1 H, H-6a$^{D\text{ or }E}$), 2.38 (m, 1 H, H-6a$^{E\text{ or }D}$), 2.52 (td, 1 H, $^{2}J_{H\text{-}6a,H\text{-}6b} = {}^{2}J_{H\text{-}6a,P} = 14.4$ Hz, $^{2}J_{H\text{-}6a,H\text{-}5} = 5.7$ Hz, H-6a$^{B\text{ or }A}$), 2.75 (t, 1 H, $^{2}J_{H\text{-}6b,H\text{-}6a} = {}^{2}J_{H\text{-}6b,P} = 15.2$ Hz, H-6b$^{B\text{ or }A}$), 2.80 (dd, 1 H, $^{2}J_{H\text{-}6b,H\text{-}6ba} = 16.4$ Hz, $^{3}J_{H\text{-}6b,H\text{-}5} = 7.3$ Hz, H-6b$^{D\text{ or }E}$), 3.01–3.82 (25 H, H-2, H-3, H-4, H-6a^{C,F,G}, H-6b^{E}), 3.24 (s, 3 H, OMe), 3.31 (s, 3 H, OMe), 3,32 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.49 (s, 6 H, OMe), 3.59 (s, 6 H, OMe), 3.60 (s, 3 H, OMe), 3.62 (s, 6 H, OMe), 3.64 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 3.85 (s, 3 H, OMe), 3.95 (dd, 1 H, $^{2}J_{H\text{-}6b,H\text{-}6a} = 11.5$ Hz, $^{3}J_{H\text{-}6b,H\text{-}5} = 1.5$ Hz, H-6b$^{C\text{ or }F\text{ or }G}$), 4.05 (d, 1 H, $^{2}J_{H\text{-}6b,H\text{-}6a} = 11.7$ Hz, $^{3}J_{H\text{-}6b,H\text{-}5} = 1.9$ Hz, H-6b$^{F\text{ or }G\text{ or }C}$), 4.11 (d, 1 H, $^{2}J_{H\text{-}6b,H\text{-}6a} = 9.8$ Hz, H-6b$^{A\text{ or }B}$), 4.14 (m, 1 H, H-5$^{C\text{ or }F\text{ or }G}$), 4.15 (dd, 1 H, $^{2}J_{H\text{-}6b,H\text{-}6a} = 10.9$ Hz, $^{3}J_{H\text{-}6b,H\text{-}5} = 2.4$ Hz, H-6b$^{G\text{ or }C\text{ or }F}$), 4.48 (m, 1 H, H-5$^{A\text{ or }B}$), 4.35 (m, 1 H, H-5$^{G\text{ or }C\text{ or }F}$), 4.42 (2 H, H-5$^{B\text{ or }A\text{ and }F\text{ or }G\text{ or }C}$), 4.49 (2 H, H-5^{D,E}), 4.84 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2} = 3.3$ Hz, H-1), 4.97 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2} = 4.3$ Hz, H-1), 4.99 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2} = 4.3$ Hz, H-1), 5.06 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2} = 3.8$ Hz, H-1), 5.07 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2} = 4.5$ Hz, H-1), 5.23 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2} = 4.2$ Hz, H-1), 5.26 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2} = 4.3$ Hz, H-1), 7.42–7.45 (td, 2 H, $^{3}J_{m\text{-}H,o\text{-}H} = {}^{3}J_{m\text{-}H,p\text{-}H} = 7.9$ Hz, $^{4}J_{m\text{-}H,P} = 2.0$ Hz, *m*-H of (O)PPh), 7.47 (m, 1 H, *p*-H of (O)PPh), 7.58 (td, 2 H, $^{3}J_{m\text{-}H,o\text{-}H} = {}^{3}J_{m\text{-}H,p\text{-}H} = 7.6$ Hz, $^{4}J_{m\text{-}H,P} = 2.6$ Hz, *m*-H of PdPPh), 7.62 (m, 1 H, *p*-H of PdPPh), 8.05–8.10 (4 H, *o*-H) ppm; $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 31.77 (d, $^{1}J_{C,P} = 26.8$ Hz, C-6$^{A\text{ or }B}$), 32.12 ((d, $^{1}J_{C,P} = 59.4$ Hz, C-6$^{E\text{ or }D}$), 37.61 (d, $^{1}J_{C,P} = 31.9$ Hz, C-6$^{B\text{ or }A}$), 42.14 (d, $^{1}J_{C,P} = 72.4$ Hz, C-6$^{D\text{ or }E}$), 59.84, 56.96, 57.84, 58.10, 58.79, 58.85 [×2], 58.92, 60.29, 60.39, 60.61, 60.93, 61.70, 61.73 [×2], 61.94 [×2] (OMe), 61.98 (C-5$^{E\text{ or }D}$), 63.21 (d, $^{2}J_{C,P} = 4.0$ Hz, C-5$^{A\text{ or }B}$), 66.06 (C-5$^{D\text{ or }E}$), 68.27 (d, $^{2}J_{C,P} = 3.5$ Hz, C-5$^{B\text{ or }A}$), 70.42 [×2], 70.09 (C-5^{C,F,G}), 71.20, 71.57, 72.22 (C-6^{C,F,G}), 77.29, 80.27, 80.36, 80.47, 80.54, 81.00, 81.14, 81.17, 81.68, 81.75, 81.84, 81.90, 82.06, 82.08, 82.43, 82.82, 82.93, 83.45, 83.81, 84.26 (C-2, C-3, C-4$^{A\text{ or }B\text{ and }C,D,E,F,G}$), 89.31 (d, $^{3}J_{C,P} = 12.8$ Hz, C-4$^{B\text{ or }A}$), 94.20, 97.42, 98.11, 98.90, 99.49, 99.64, 99.78 (C-1), 128.66 (d, $^{3}J_{C,P} = 5.9$ Hz, *m*-C), 128.73 (d, $^{3}J_{C,P} = 6.2$ Hz, *m*-C), 130.11 (d, $^{2}J_{C,P} = 9.1$ Hz, *o*-C of (O)PPh), 131.03 (*p*-C of (O)PPh), 132.13 (*p*-C of PdPPh), 132.74 (d, $^{2}J_{C,P} = 9.1$ Hz, *o*-C of PdPPh), 133.72 (d, $^{1}J_{C,P} = 6.7$ Hz, *ipso*-C of (O)PPh), 134.24 (d, $^{1}J_{C,P} = 6.7$ Hz, *ipso*-C of PdPPh) ppm; $^{31}P\{^{1}H\}$ NMR (121.5

MHz $CDCl_3$, 25ºC): 33.8 (d, $^2J_{P,P}$ = 4.4 Hz), 54.5 (d, $^2J_{P,P}$ = 4.4 Hz) ppm; elemental analysis (%) calcd for $C_{71}H_{110}Cl_2O_{32}P_2Pd$ (1714.89): C 49.73, H 6.47, found: C 49.60, H 6.55; MS (ESI-TOF): *m/z* (%): 1753.47 (30) $[M + K]^+$, 1737.49 (70) $[M + Na]^+$.

Crystal structure of 7•0.5 CH_2Cl_2•0.5 C_5H_{12}: *M*r = 2163.56, orthorhombic, $P2_12_12_1$, *a* = 15.1479(3), *b* = 15.6542(3), *c* = 36.0599(9) Å, *V* = 8550.8(3) Å^3, *Z* = 4, D_X = 1.268 mg m^{-3}, λ(MoKα) = 0.71073Å, μ = 0.163 mm^{-1}, *F*(000) = 3488, *T* = 150(1) K. Data were collected on an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite MoKα radiation, λ = 0.71073 Å). The structure was solved with SIR-97[3] which revealed the non hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier Difference. The whole structure was refined with SHELXL97[4] by the full-matrix least-square techniques (use of *F* square magnitude; x, y, z, β_{ij} for Pd, P, Cl, C and O atoms, x, y, z in riding mode for H atoms; 988 variables and 18635 observations with $I > 2.0\ \sigma(I)$; calc $w = 1/[\sigma^2\ (Fo^2) + (0.0985P)^2 + 0.0000P]$ where $P = (Fo^2 + 2\ Fc^2)/3$. R = 0.071, R_W = 0.190 and S_W = 0.791, $\Delta\rho < 0.645$ eÅ^{-3}. The alerts level A in the checkcif are mainly due to disordered MeO groups and solvents molecules. CCDC 756653 contains the supplementary crystallographic data for this paper. Crystallographic data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 11EZ, UK; ax: (internat.) 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal structure of 12•0.5C_5H_{12}: *M*r = 1930.22, monoclinic, $P2_12_12_1$, *a* = 13.6733(3), *b* = 24.1680(5), *c* = 14.1445(3) Å, β = 109.022(2)°, *V* = 4418.9(2) Å^3, *Z* = 2, D_X = 1.451 mg m^{-3}, λ(MoKα) = 0.71073Å, μ = 0.643 mm^{-1}, *F*(000) = 2010, *T* = 130(1) K. Data were collected on an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite MoKα radiation, λ = 0.71073 Å). The structure was solved with SIR-97[3] which revealed the non hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier Difference. The whole structure was refined with SHELXL97[4] by the full-matrix least-square techniques (use of *F* square magnitude; x, y, z, β_{ij} for Pd, P, Cl, C and O atoms, x, y, z in riding mode for H atoms; 1010 variables and 19198 observations with $I > 2.0\ \sigma(I)$; calc $w = 1/[\sigma^2\ (Fo^2) + (0.0815P)^2 + 0.0000P]$ where $P = (Fo^2 + 2\ Fc^2)/3$. R = 0.057, R_W = 0.143 and S_W = 0.851, $\Delta\rho < 3.11$ eÅ^{-3}. CCDC 758028 contains the supplementary

crystallographic data for this paper. Crystallographic data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 11EZ, UK; ax: (internat.) 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal structure of 13•C_5H_{12}: *M*r = 1804.99, orthorhombic, $P2_12_12_1$, a = 17.6384(7), b = 19.4659(5), c = 27.2535(8) Å, V = 9357.4(5) Å^3, Z = 4, D_X = 1.281 mg m^{-3}, λ(MoKα) = 0.71073Å, μ = 0.366 mm^{-1}, F(000) = 3816, T = 100(1) K. Data were collected on an Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite MoKα radiation, λ = 0.71073 Å). The structure was solved with SIR-97[3] which revealed the non hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier Difference. The whole structure was refined with SHELXL97[4] by the full-matrix least-square techniques (use of F square magnitude; x, y, z, β_{ij} for Pd, P, Cl, C and O atoms, x, y, z in riding mode for H atoms; 1002 variables and 20360 observations with $I > 2.0\ \sigma(I)$; calc $w = 1/[\sigma^2\ (Fo^2) + (0.0600P)^2 + 0.0000P]$ where $P = (Fo^2 + 2\ Fc^2)/3$. R = 0.055, R_W = 0.131 and S_W = 0.770, $\Delta\rho$ < 1.608 eÅ^{-3}. CCDC 770728 contains the supplementary crystallographic data for this paper. Crystallographic data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 11EZ, UK; ax: (internat.) 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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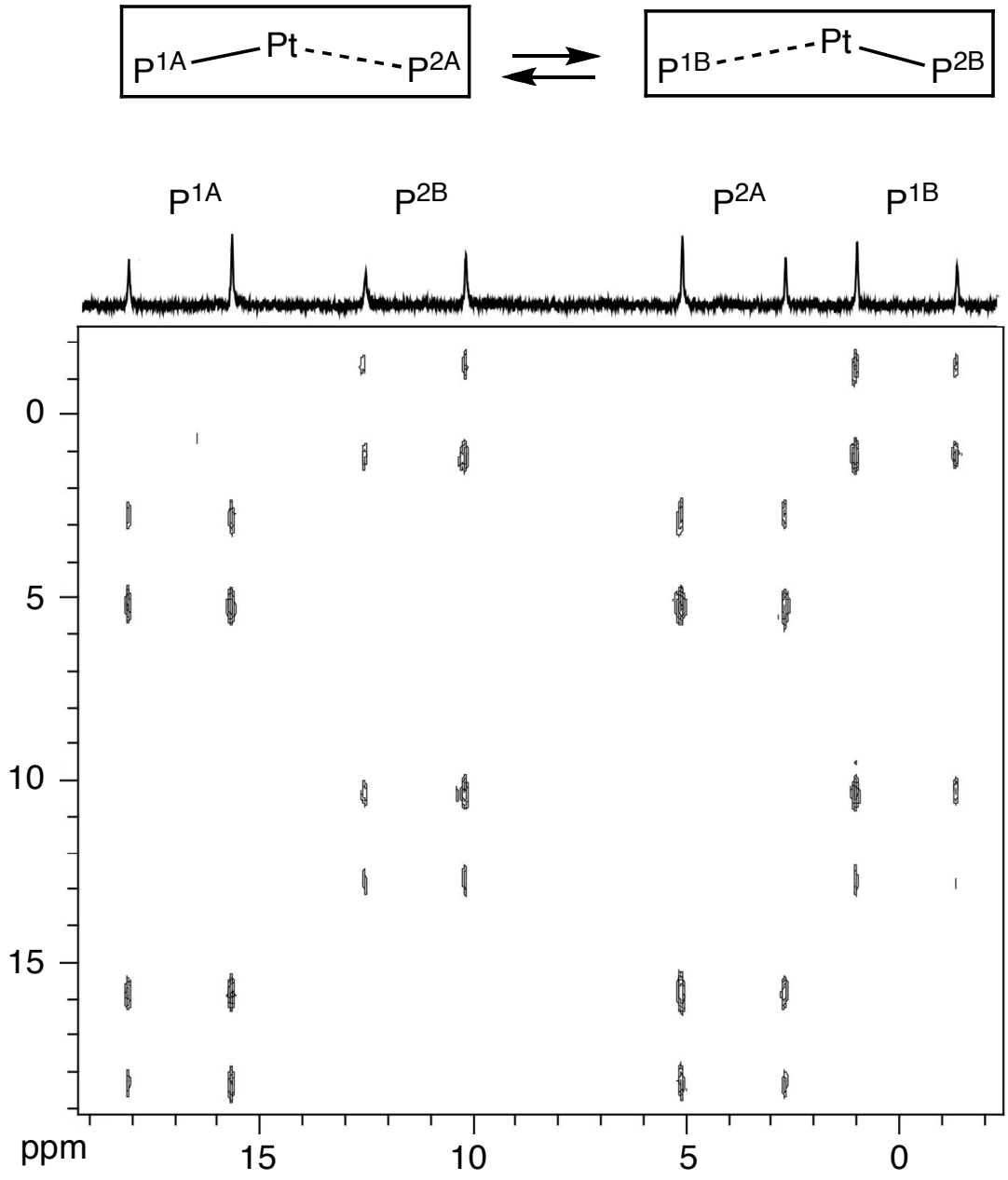

Figure SI-1. $^{31}P\{^{1}H\}$ NMR spectrum and $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ COSY 2D NMR spectrum of complex **10** at –80ºC recorded in CD_2Cl_2 at 202.5 MHz

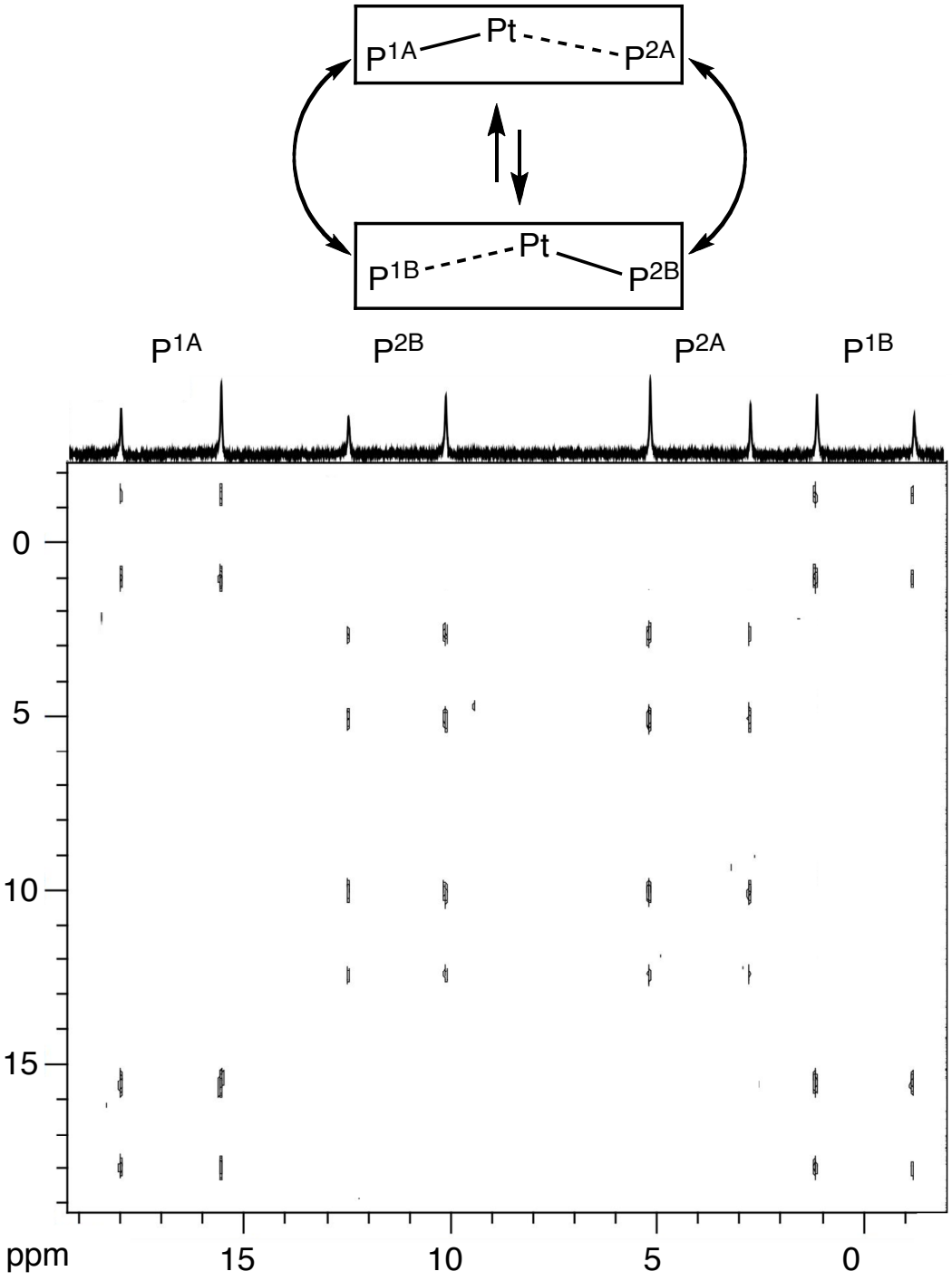

Figure SI-2. $^{31}P\{^{1}H\}$ NMR spectrum and off resonance $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ ROESY NMR spectrum of complex **10** at –60ºC recorded in CD_2Cl_2 at 202.5 MHz.

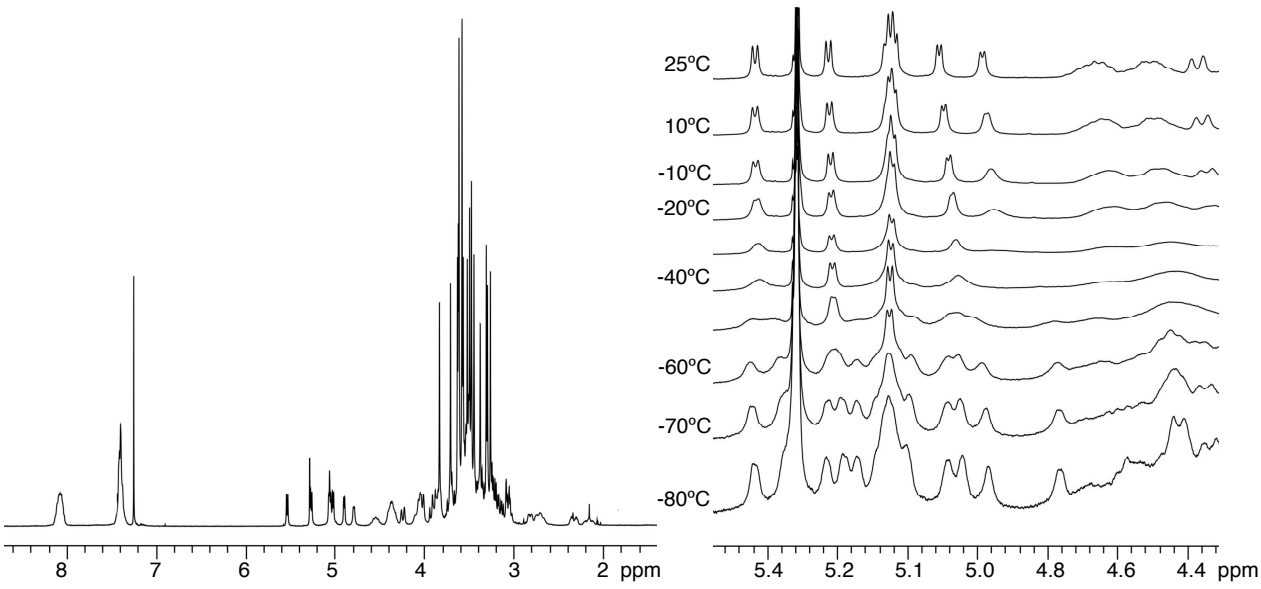

Figure SI-3. ^{1}H NMR spectrum recorded in $CDCl_3$ at 25ºC at 300.1 MHz (left) and ^{1}H NMR spectra showing the anomeric protons zone in the range –80 / 25ºC recorded in CD_2Cl_2 at 500.1 MHz (left) of complex **10**.

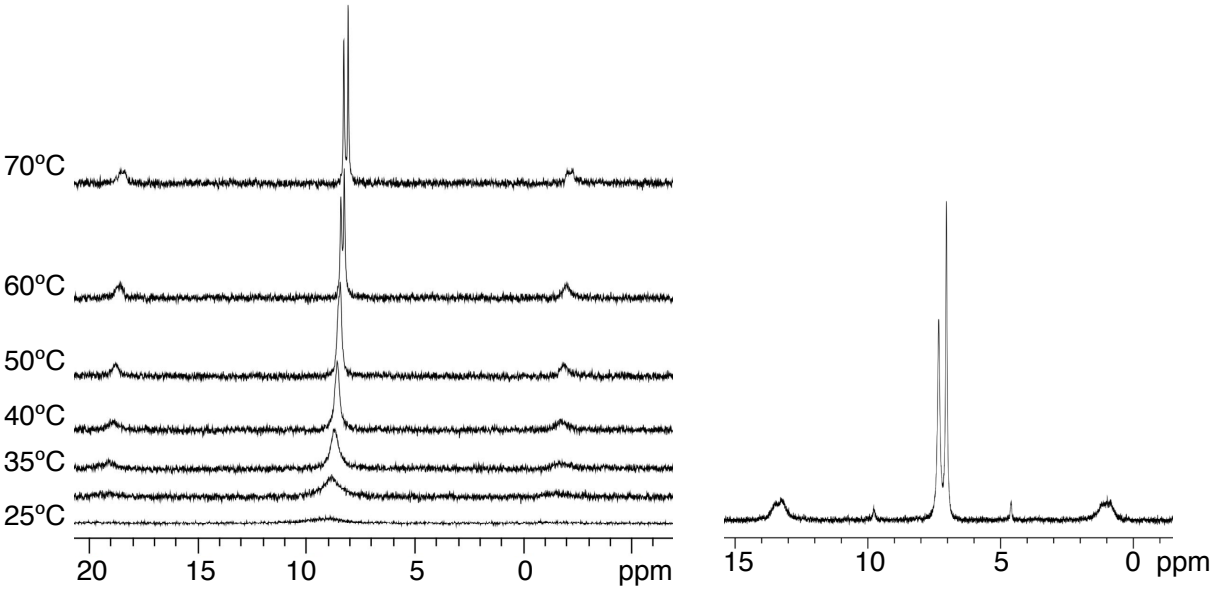

Figure SI-4. ^{31}P{^{1}H} NMR spectra in the range 25ºC – 70ºC at 121.5 MHz (left) and ^{31}P{^{1}H} NMR spectrum at 80ºC at 202.5 MHz (right) recorded in $C_2D_2Cl_4$ of complex **10**.