Molecular Recognition Between a Water-Soluble Organometallic Complex and a β-Cyclodextrin: First Example of Second-Sphere Coordination Adducts Possessing a Catalytic Activity

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Abstract: Formation of stable second-sphere adducts between a water-soluble organometallic complex and a cyclodextrin (CD) is possible by finely designing the structure of the water-soluble phosphane. The key point to obtain such adducts was the synthesis of a water-soluble phosphane which possesses a *tert*-butylphenyl group recognized by the CD and separated from the phosphorus atom by a phenyl ring to avoid phosphane decoordination during the molecular recognition process between the organometallic complex and the CD. These adducts are able to catalyze the cleavage of water-insoluble carbonate in a biphasic system.

Keywords: Biphasic catalysis; cyclodextrins; molecular recognition; palladium; phosphane ligands

Cyclodextrins (CDs) are cyclic oligosaccharides composed of six, seven, or eight D-glucopyranose units that are well-known to form inclusion complexes with numerous compounds including organometallic complexes.[1] When a CD includes a part of an organometallic complex into its internal hydrophobic cavity, the CD behaves as a second-sphere ligand, binding non-covalently the first-sphere ligands of the metal center.[2] The effect of such second-sphere ligands on the chemical, electrochemical, and photochemical properties of organometallic compounds, as well as on their geometries in solution and in the solid state, has been intensively investigated and it has been demonstrated that second-sphere coordination can induce unusual behaviors.[3]

Although second-sphere coordination adducts of a trimethylphosphane/platinum complex with CDs have been fully characterized,[4] the involvement of CDs as hosts in the second-sphere of transition metals has not been exploited in aqueous organometallic catalysis. This stems from the poor ability of CD to solubilize classical highly hydrophobic organometallic complexes in water and from the strong destabilizing effect of CDs on water-soluble organometallic compounds. For instance, addition of CD to stable water-soluble hydride-rhodium complex $[RhH(CO)L_3]$ (L = water-soluble phosphane ligand) resulted in ligand dissociation and formation of phosphane low-coordinated rhodium species.[5] This phenomenon was attributed to the complexation of the phosphane ligand by the CD. In particular, it was assumed that the phosphorus donor atom located near the CD cavity is not available for coordination to a metal center due to steric crowding.

In this paper, we describe the first example of catalytically-active adducts formed between a water-soluble organometallic catalyst and a CD. The key point of our strategy to obtain such adducts was the synthesis of a water-soluble phosphane which possesses a fragment recognized by the CD and distant from the metal center to avoid phosphane decoordination during the molecular recognition process between the organometallic complex and the CD. A triphenylphosphine bearing sulfonate groups and a *tert*-butylphenyl group on phenyl rings was sought to fulfill the above requirement. Indeed, it is well-known that sulfonate groups are highly hydrophilic groups allowing immobilization of numerous phosphanes in water[6] and that the *tert*-butylphenyl group fits tightly into the cavity of a CD.[7] Moreover, the presence of a phenyl group between the phosphorus atom and the *tert*-butylphenyl group should be sufficient to keep the phosphorus atom away from the CD. This last point is crucial to preserve the coordinating ability of the phosphorus atom.

Such a ligand was synthesized in three steps from commercially available products. Thus, Friedel–Crafts alkylation of 1-bromo-4-phenylbenzene with *tert*-butyl chloride, followed by the reaction of the corresponding Grignard reagent with $ClP(Ph)_2$ and a sulfonation in oleum afforded the new targeted phosphane bis(3-sodium sulfonatophenyl)-[4-(4-*tert*-butylphenyl)phenyl]-phosphine (**1**) (Scheme 1).

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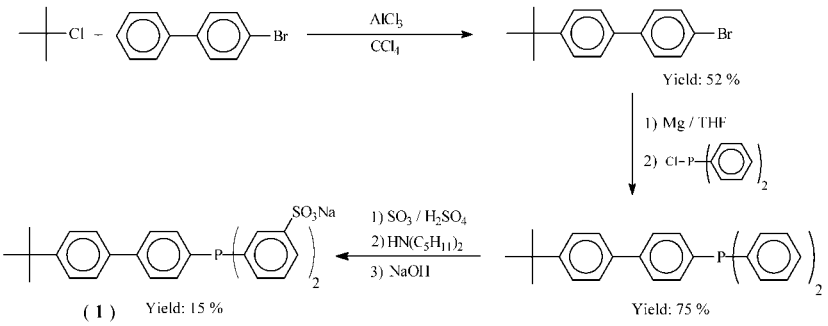

Scheme 1. Synthesis of bis(3-sodium sulfonatophenyl)-[4-(4-*tert*-butylphenyl)phenyl]phosphine (**1**).

Although the yield of the last step was very low (15%) due to the formation of large amounts of phosphine oxide and unknown products during the sulfonation process, this reaction route allowed us to obtain **1** on a multigram scale.

The stoichiometry of the inclusion process between **1** and native β-CD or methylated β-CD was determined by Job's method.[8] For the β-CD and the methylated β-CD, a series of samples containing variable ratios (from 0 to 1) of CD and **1** was prepared keeping the total concentration of the species constant (1 mM in this present case). The differences of chemical shift in the ^{1}H NMR spectra for the proton H-1′ (*tert*-butyl group) were measured as a function of the molar ratio. The Job's plot for the β-CD/**1** system is displayed in Figure 1.

For β-CD and methylated β-CD, Job's plots derived from the ^{1}H NMR spectra showed a maximum at r = 0.5 and symmetrical shapes, indicating unambiguously the formation of a 1:1 inclusion complex.

The association constants of each inclusion complex were evaluated by a titration method from ^{1}H NMR and UV-VIS spectroscopic data. The association constant values for β-CD/**1** and methylated β-CD/**1** inclusion complexes were found to be 27500 M^{-1} and 38600 M^{-1} at 298 K, respectively. The structures of these 1:1 inclusion complexes were determined from two-dimensional T-ROESY experiments.[9] The partial T-ROESY spectra of a solution containing β-CD and **1** are shown in Figure 2.

The strong interactions observed between the H-5 and H-3 protons of the β-CD and the protons of the (*t*-BuC_6H_4)C_6H_4 group confirm that this group is included into the β-CD host cavity. Moreover, the absence of cross-peaks between H-6 proton of β-CD and the *tert*-butyl group of **1** strongly suggests that **1** penetrated into the β-CD cavity from the primary OH group side. Interestingly, the lack of cross-peaks between the sulfonated rings of **1** and the β-CD proves that these rings are distant from the β-CD. A computer generated illustrative view of this 1:1 inclusion complex is presented in Figure 3.

A similar structure was found for the 1:1 inclusion complex between **1** and methylated β-CD. Finally, it must be pointed out that the triphenylphosphine part

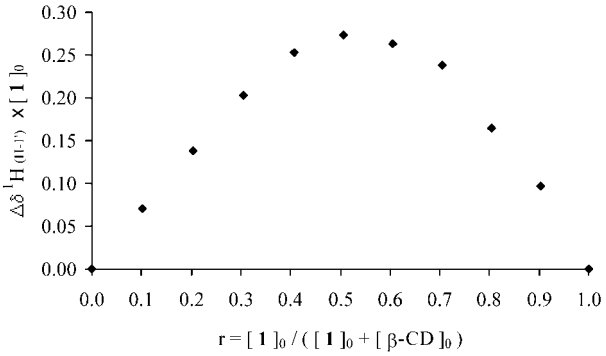

Figure 1. Job's plot for the β-CD/**1** system. The continuous variation plot was derived from differences of chemical shift in the ^{1}H NMR spectra for the proton H-1′ (*tert*-butyl group) at 298 K in D_2O.

of the phosphane **1** lies entirely in the bulk aqueous phase in these illustrative views. Consequently, it is quite reasonable to suppose that the electronic and steric properties of the phosphane **1** should not be greatly modified by the presence of the cyclodextrin.

The formation of second-sphere adducts between methylated β-CD and a water-soluble organometallic complex containing **1** as hydrosoluble ligand was investigated by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy using the [Pd(**1**)$_3$] species as organometallic complex model. The spectra of the [Pd(**1**)$_3$] complex in the presence of increasing amounts of methylated β-CD are presented in Figure 4.

Except for the narrowing of the ^{31}P{^{1}H} NMR signal of the [Pd(**1**)$_3$] species (δ = 24.2 ppm), the ^{31}P{^{1}H} NMR spectra obtained in the presence of 1 or 4 equivalents of methylated β-CD were substantially similar to that obtained without methylated β-CD. More interestingly is the fact that the peak at −9.3 ppm corresponding to the uncoordinated phosphane **1** complexed by the methylated β-CD did not increase when the equivalent number of methylated β-CD varied from 1 to 4, indicating that the methyl β-CD did not modify the percentage of the palladium species involved in the different equilibria depicted in Equation (1).

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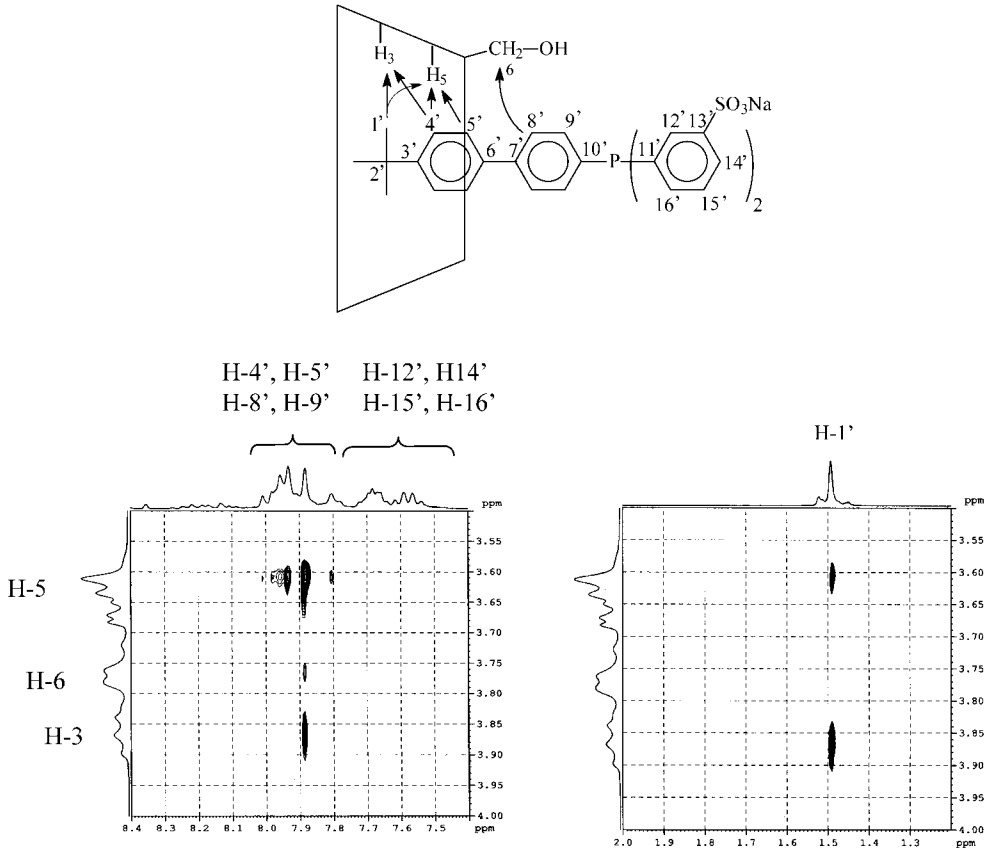

Figure 2. Partial contour plots of the T-ROESY spectrum of a solution containing β-CD (10 mM) and **1** (10 mM) in D_2O at 298 K (300 MHz, mixing period: 500 ms) The main interactions observed in the T-ROESY spectrum are indicated on the schematic representation of the 1:1 inclusion complex.

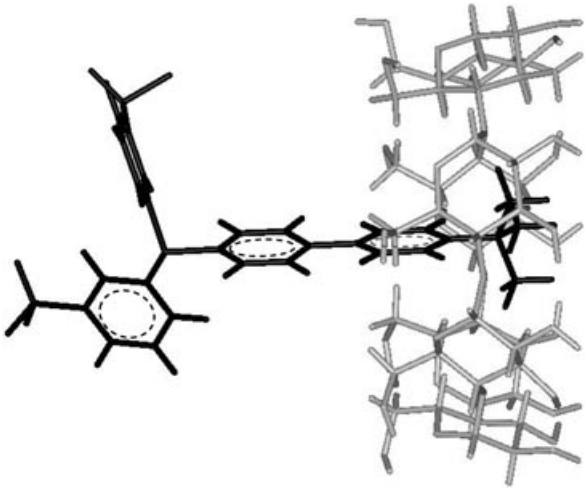

Figure 3. Computer generated illustrative view of the 1:1 inclusion complex between **1** and β-CD.

$$\mathrm{Pd}(\mathbf{1})_3 \overset{-\mathbf{1}}{\rightleftharpoons} \mathrm{Pd}(\mathbf{1})_2 \overset{-\mathbf{1}}{\rightleftharpoons} \mathrm{Pd}(\mathbf{1}) \qquad (1)$$

In particular, no shift of equilibria towards phosphane low-coordinated palladium species and uncoordinated phosphane **1** occurred. In fact, it seems that only the exchange rate between the [Pd(**1**)$_3$] species and **1** was affected as a narrowing of $^{31}P\{^1H\}$ NMR signal of the [Pd(**1**)$_3$] species was observed when increasing amounts of methylated β-CD were added.[10] So, from the $^{31}P\{^1H\}$ NMR study, it can be concluded that addition of methylated β-CD to [Pd(**1**)$_3$] species does not promote the dissociation of the ligand and, consequently, the formation of phosphane low-coordinated palladium species as previously observed with transition metals coordinated by classical water-soluble phosphanes such as the sodium salt of trisulfonated triphenylphosphine.[5] The proof of the formation of second-sphere adducts was then furnished by the ^1H NMR study. Indeed, the shift of the signal of the *tert*-butyl group to lower fields and the modification of the aromatic and CD protons patterns observed in the ^1H NMR spectrum indicate unambiguously that the *tert*-butylphenyl group of the coordinated phosphane **1** is included in the CD cavity, suggesting the formation of a stable second-sphere coordination adduct: [Pd(**1**)$_3$(methylated β-CD)$_3$]. The ability of the methylated β-CD/**1** inclusion complex to bind to zerovalent palladium was also demonstrated by mixing an aqueous phase containing this inclusion complex

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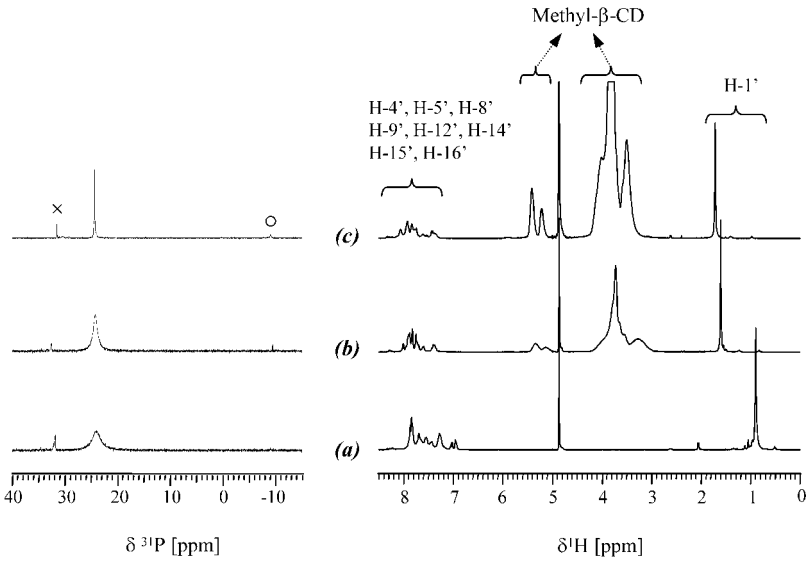

Figure 4. ***(a)*** $^{31}P\{^1H\}$ and ^1H NMR spectra of [Pd(**1**)$_3$] species alone; ***(b)*** $^{31}P\{^1H\}$ and ^1H NMR spectra of [Pd(**1**)$_3$] species in the presence of 1 equivalent of methyl β-CD with regard to **1**; ***(c)*** $^{31}P\{^1H\}$ and ^1H NMR spectra of [Pd(**1**)$_3$] species in the presence of 4 equivalents of methyl β-CD with regard to **1**; (×): phosphane **1** oxide; (○): 5% of phosphane **1** was initially present in the solution containing the [Pd(**1**)$_3$] species.

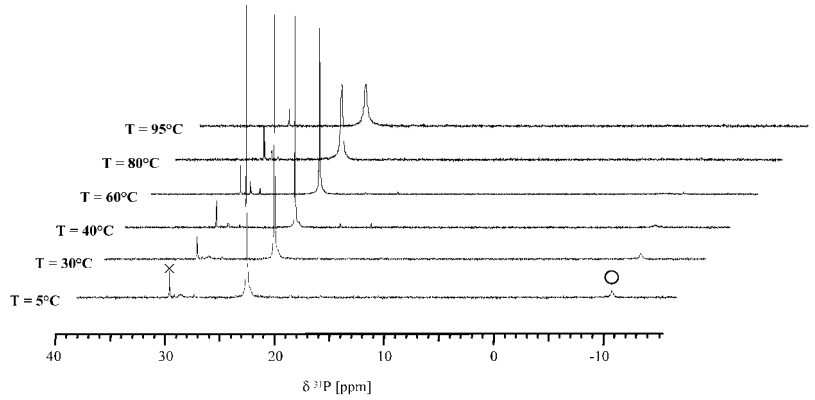

Figure 5. $^{31}P\{^1H\}$ NMR spectra of [Pd(**1**)$_3$] species in the presence of 4 equivalents of methyl-β-CD recorded at different temperatures in D_2O. (×): Phosphane **1** oxide; (○): 5% of phosphane **1** was initially present in the solution containing the [Pd(**1**)$_3$] species.

with a toluene solution containing the [Pd(PPh$_3$)$_4$] complex. In a few minutes, the aqueous and organic solutions became red and colorless, respectively, indicating transfer of palladium metal from the organic to the aqueous phase. $^{31}P\{^1H\}$ and ^1H NMR spectra confirm also the formation of a second-sphere adduct. Indeed, the $^{31}P\{^1H\}$ NMR signal of the methylated β-CD/**1** inclusion complex shifted from −9.3 ppm to 24.2 ppm after contact with the organic phase, whereas the ^1H NMR spectra was not affected. Outstandingly, the adduct is also stable at high temperatures. Indeed, the peak corresponding to the free phosphane complexed by the methyl β-CD at −9.3 ppm did not seem to increase when the solution containing 4 equivalents of methylated β-CD was heated up to 95 °C (Figure 5).

The significant broadening of the NMR signal at 24.2 ppm during the heating was probably due to an increase in the exchange rate between the second-sphere coordination adduct [Pd(**1**)$_3$(methylated β-CD)$_3$] and the uncoordinated phosphane **1** complexed by the methylated β-CD.

The palladium-catalyzed cleavage of water-insoluble allyl undecyl carbonate in an aqueous-organic two-phase system was chosen to evaluate the catalytic behavior of the adduct formed between the [Pd(**1**)$_3$] complex and the methylated β-CD.[11,12] The cleavage rates obtained in the presence of increasing amounts of methylated β-CD are presented in Figure 6.

Without methylated β-CD, the cleavage rate of allyl undecyl carbonate was surprisingly high for a substrate

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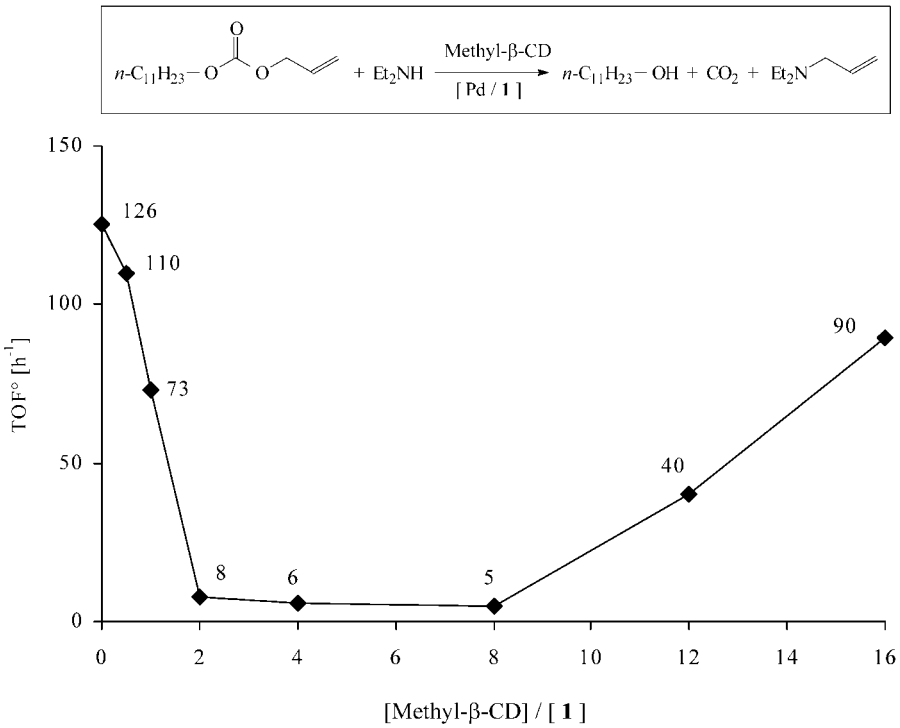

Figure 6. TOF° *vs.* [methyl-β-CD]/ phosphane **1** ratio. TOF° = initial turn over frequency = (μmol of allyl undecyl carbonate initially converted) (μmol Pd)$^{-1}$ h^{-1}. Experimental conditions: $Pd(OAc)_2$ (4.46 μmol), phosphane **1** (40.2 μmol), allyl undecyl carbonate (446 μmol), diethylamine (892 μmoL), water (4 g) and heptane (4 g).

insoluble in water. This high activity was due to the surface active properties of **1**. Indeed, formation of an emulsion was clearly observed during this experiment and surface tension measurements indicate that **1** has a surfactant behavior (cmc = 1.8 mM; γ_{cmc} = 40.6 mNm^{-1} at 298 K). When methylated β-CD was added to the catalytic solution, the reaction rate dropped up to a methylated β-CD/**1** ratio of 8. Above this ratio, the reaction rate increased progressively with the methylated β-CD/**1** ratio to reach an activity close to that obtained initially without CD. The drastic rate decrease observed at low methylated β-CD/**1** ratios (<2) was ascribed to the loss of the surface active properties of **1**, due to binding between **1** and methylated β-CD. Indeed, formation of an inclusion complex between these two compounds allowed us to mask the hydrophobic part of the phosphane. This assumption was fully supported by the absence of an emulsion for a methylated β-CD/**1** ratio higher than 2. Furthermore, control experiments with methyl α-D-glucopyranoside (a compound which has the same subunit as the methylated β-CD but which do not possess a lipophilic host cavity) confirm that the disappearance of the emulsion is not due to a modification of physical and chemical characteristics of medium by the methyl-β-CD (ionic strength, polarity, viscosity...). Indeed, formation of an emulsion was also observed in the presence of 0.435 g (2.24 mmol) of methyl α-D-glucopyranoside, an amount corresponding to a methyl-β-CD/phosphane ratio of 8.

For a methylated β-CD/**1** ratio lower than 1–2, the nature of the active species in the medium cannot be clearly discussed. Indeed, [Pd(**1**)$_3$] species complexed by one, two or three methylated β-CDs can coexist in the medium as the amount of methylated β-CDs is too low to complex all the phosphane. However, for a methylated β-CD/**1** ratio higher than 2, **1** is totally bound to the methylated β-CD and the reaction rates observed at ratio between 2 and 8 could be considered as the *intrinsic catalytic activity* of [Pd(**1**)$_x$(methylated β-CD)$_x$] second-sphere adducts under severe mass transfer limitation conditions. The rate increase observed for higher methylated β-CD concentrations (>8) is attributed to the beneficial effect of a methylated β-CD excess on the mass transfer, and shows that these adducts have a catalytic activity similar to that observed with a catalytic system composed of palladium(0) and trisulfonated triphenylphosphine under similar conditions.[10,12] The fact that the catalytic activity is comparable to that observed with the classical catalytic system suggests strongly that the metal center is electronically or sterically not influenced by presence of the cyclodextrin in the coordination sphere. This interesting property could be advantageously used to anchor, without alteration of the catalytic behavior, water-soluble organometallic complexes on water-insoluble material or membrane-containing CDs and, consequently, could lead to important developments in homogeneous catalyst separation technology.

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In conclusion, we have demonstrated that formation of catalytically active second-sphere adducts between water-soluble organometallic complex and CD is possible by finely designing the structure of the water-soluble phosphane. Studies are currently in progress to immobilize supramolecular water-soluble homogeneous catalysts on supports containing CDs.

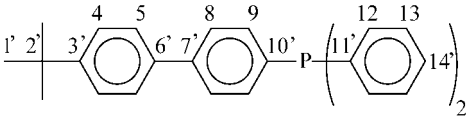
Experimental Section

General Remarks

The ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded at 300.13, 121.49 and 75.46 MHz, respectively, on a Bruker Avance 300 DPX instrument. IR spectra were recorded on a Vector 22 Bruker spectrometer. Elemental analyses were performed by the department of Micro-Analyses at the University of Artois using an EA 1110 CHNS Thermoquest instrument. Gas chromatographic analyses were carried out on a Shimadzu GC-17A gas chromatograph equipped with a methyl silicone capillary column (25 m × 0.25 mm) and a flame ionization detector (GC:FID). Palladium acetate, β-CD and methylated β-CD were purchased from Aldrich. The methylated β-CD was a native β-CD partially *O*-methylated with statistically 1.8 OH groups modified per glucopyranose unit. 1-Bromo-4-(4-*tert*-butylphenyl)benzene was synthesized as reported in the literature.[13]

[4-(4-*tert*-Butylphenyl)phenyl]diphenylphosphine

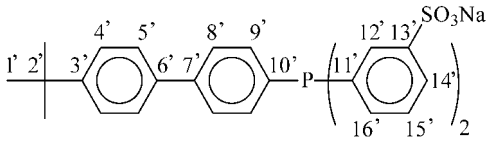
This was obtained on a multigram scale by a modified published procedure.[14] To a suspension of magnesium (1.84 g, 76 mmol, 1.1 equivs.) in 50 mL of anhydrous THF was introduced under nitrogen 1-bromo-4-(4-*tert*-butylphenyl)benzene (6.67 g, 23 mmol, 0.33 equivs.). After a few minutes, the reaction began and 13.34 g (46 mmol, 0.66 equivs.) of 1-bromo-4-(4-*tert*-butylphenyl)benzene in THF (20 mL) were added dropwise. The reaction mixture was then heated under reflux for 1 hour. After cooling, chlorodiphenylphosphine (12.93 g, 58.65 mmol, 0.85 equivs.) in THF (10 mL) was added dropwise and then heated under reflux for 1 hour. Once the reaction was complete, the mixture was poured into a mixture of ice (*ca* 100 g) and HCl (100 mL, 1 N). The aqueous phase was extracted twice with toluene (3 × 35 mL) and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The resulting oil was recrystallized from ethanol to give white crystals. Yield: 17.3 g (75%). The notation used in NMR assignments of phosphine is indicated below:



^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K): δ = 1.38 (s, 9H, H1′), 7.3–7.5 (m, 18H, H4′,5′,8′,9′,12′,13′,14′); $^{13}C\{^{1}H\}$ NMR (75.47, MHz, $CDCl_3$, 298 K): δ = 31.7 (s, C1′), 34.7 (s, C2′), 126.3 (s, C4′), 127.2 (s, C5′), 127.5 (d, $^{3}J_{P\text{-}C}$ = 5 Hz, C8′), 129.0 (d, $^{3}J_{P\text{-}C}$ = 6 Hz, C13′), 129.3 (s, C14′), 134.2 (d, $^{2}J_{P\text{-}C}$ = 19 Hz, C12′), 134.6 (d, $^{2}J_{P\text{-}C}$ = 20 Hz, C9′), 136.1 (d, $^{1}J_{P\text{-}C}$ = 20 Hz, C10′), 137.8 (d, $^{1}J_{P\text{-}C}$ = 11 Hz, C11′), 138.1 (s, C6′), 141.8 (s, C7′), 151.1 (s, C3′); $^{31}P\{^{1}H\}$ NMR (121.49 MHz, $CDCl_3$, 298 K): δ = −6.07 (s); anal. (%): calcd. for $C_{28}H_{27}P$ (M = 394 g·mol^{-1}): C 85.28, H 6.85; found: C 84.90, H 6.64.

Bis(3-sodium sulfonatophenyl)-[4-(4-*tert*-butylphenyl)phenyl]phosphine (1)

[*p*-(*p*-*t*-BuC_6H_4)Ph]P(Ph)$_2$ (8 g, 20.3 mmol) was dissolved in 11.6 mL of 100% concentrated sulfuric acid obtained by mixture of 9.2 mL of concentrated sulfuric acid (18 N, 96%) and 2.4 mL of oleum (65%). After cooling to 5 °C, the oleum (65%, 16.5 mL) was added slowly under vigorous stirring and keeping the temperature below 10 °C. The reaction mixture was then kept at room temperature for 20 hours under a nitrogen atmosphere. Excess of oleum was neutralized by addition of 12 mL of degassed water. The mixture was poured into a mixture of ice and water (300 g/300 mL), and dipentylamine (6.38 g, 40.62 mmol) was then added. The ammonium salt of the sulfonated phosphine was recovered from the acidic aqueous layer by addition of ethyl acetate (4 × 50 mL). The organic phase was washed with water up to neutral pH, dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The resulting solid was then dissolved in isoamyl alcohol and extracted 20 times with 20 mL of an NaOH solution (0.07 N). Each fraction was analyzed by $^{31}P\{^{1}H\}$ NMR spectroscopy. The fractions where a unique signal at −4.72 ppm was observed were concentrated under vacuum and a white solid was obtained. This solid was recrystallized from methanol to give white crystals. Yield: 1.8 g (15%). The notation used in NMR assignments of **1** is indicated below:



^{1}H NMR (300.13 MHz, D_2O, 298 K): δ = 0.88 (s, 9H, H1′), 6.95 (t, $^{3}J_{H\text{-}H} \sim {}^{3}J_{P\text{-}H}$ = 7.5 Hz, 2H, H9′), 7.05 (t, $^{3}J_{H\text{-}H} \sim {}^{3}J_{P\text{-}H}$ = 7.5 Hz, 2H, H16′), 7.11 (d, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 2H, H5′), 7.2–7.3 (m, 6H, H4′,8′,15′), 7.62 (d, $^{3}J_{H\text{-}H} \sim {}^{3}J_{P\text{-}H}$ = 7.8 Hz, 2H, H12′), 7.67 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, H14′); $^{13}C\{^{1}H\}$ NMR (75.47, MHz, D_2O, 298 K): δ = 30.6 (s, C1′), 35.2 (s, C2′), 122.0 (d, $^{3}J_{P\text{-}C}$ = 8 Hz, C8′), 126.4 (s, C14′), 128.0 (s, C7′), 130.0 (d, $^{3}J_{P\text{-}C}$ = 7 Hz, C15′), 130.7 (d, $^{2}J_{P\text{-}C}$ = 28 Hz, C12′), 132.0 (d, $^{1}J_{P\text{-}C}$ = 6 Hz, C10′), 132.2 (s, C4′), 136.1 (d, $^{2}J_{P\text{-}C}$ = 20 Hz, C16′), 136.2 (s, C6′), 136.4 (s, C5′), 137.2 (d, $^{2}J_{P\text{-}C}$ = 18 Hz, C9′), 139.3 (d, $^{1}J_{P\text{-}C}$ = 7 Hz, C11′), 143.9 (d, $^{3}J_{P\text{-}C}$ = 7 Hz, C13′), 155.9 (s, C3′); $^{31}P\{^{1}H\}$ NMR (121.49 MHz, D_2O, 298 K): δ = −4.72 (s); FT-IR: (KBr): ν = 2962 (m), 1460 (w), 1304 (m), 1221 (s), 1195 (s), 1079 (w), 1040 (m), 1001 (w), 787 (m), 719 (w), 676 (w), 624 (w), 520 cm^{-1} (w); anal. (%): calcd. for $C_{28}H_{25}Na_2O_6PS_2 \cdot 4\,H_2O$ (M = 670 g·mol^{-1}): C 50.15, H 4.92; found: C 49.74, H 4.31.

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Determination of the Association Constant

The protons of the *tert*-butyl group were chosen for evaluating the association constant by ^{1}H NMR spectroscopy. Assuming a 1:1 inclusion mechanism, the observed chemical shift of the protons the *tert*-butyl group (δ_{OBS}) and the complex concentration [COMP] are described as follows:

$$\delta_{OBS} = (\delta_{Phos.}\ [Phos.] + \delta_{COMP}\ [COMP])/[Phos.]_T \quad (2)$$

$$[COMP] = -1/2\ [(1/K + [CD]_T + [Phos.]_T)^2 - 4\ [CD]_T\ [Phos.]_T]^{1/2} + 1/2\ (1/K + [CD]_T + [Phos.]_T) \quad (3)$$

where K, T, and $\delta_{Phos.}$ stand for formation constant, total, and chemical shift of the protons of the *tert*-butyl group in the absence of CD, respectively. For a given value of K, [COMP] is known and δ_{COMP} may be calculated from (2) for each $[CD]_T$. Standard deviation over δ_{COMP} has then to be minimized relative to K.

An algorithmic treatment similar to the one described above was used to calculate the association constant from UV-VIS data (recorded in the range 200–350 nm). The algorithmic treatment was applied to derivatives of the UV spectra, so that no effect from the refractive index relative to the β-CD was observed.[15]

The values calculated by assuming a 1:1 inclusion for the β-CD/**1** complex were found to be 28300 M^{-1} and 26750 M^{-1} from ^{1}H NMR and UV-VIS data, respectively. The value reported in the text is an average of these two values (27500 M^{-1}). In the case of the methylated β-CD/**1** inclusion complex, the values found from ^{1}H NMR and UV-VIS data were higher: 39900 M^{-1} and 37300 M^{-1}, respectively. The value reported in the text is also an average of these two values (38600 M^{-1}). The very low discrepancy observed between the association constant values derived by the two techniques proves the reliability of the corresponding measures.

Computer Generated Illustrative View of the 1:1 Inclusion Complex between 1 and β-CD

The steric complementarity between β-CD and phosphane **1** has been illustrated by means of computed three-dimensional models. The β-CD structure corresponds to a non-distorted conformation with C_7 symmetry, while phosphane **1** has been constructed by the use of PC Spartan Pro version 1.0.8., and minimized on the basis of AM1 Hamiltonian. Then, the phosphane **1** has been manually docked into the cavity of β-cyclodextrin, so that the induced spatial proximity approximately corresponds to the cross-peaks observed in the T-ROESY spectra. The absence of steric hindrance has been checked for each atom of the inclusion compound.

NMR Study on the [Pd(1)$_3$] Complex

This complex was synthesized according to a modified literature procedure:[16] $Pd(PPh_3)_4$ (412 mg, 0.36 mmol) was dissolved in 8 g of degassed toluene under nitrogen. Phosphane **1** (320 mg, 0.53 mmol) was dissolved in D_2O (8 g) and cannulated onto the palladium solution. The mixture was stirred for 30 min at room temperature. After decantation, the aqueous phase was recovered. This solution contained the expected palladium complex [Pd(**1**)$_3$] and an excess of about 5% of free phosphane **1** (with regard to the initial amount of phosphane **1**). The study in the presence of methylated β-CD was conducted as follows: to 1 mL of the above [Pd(**1**)$_3$] solution was introduced under nitrogen the required amount of methylated β-CD. After 15 min of stirring, the solution was transferred *via* cannula into a nitrogen pressurized 5 mm NMR tube.

Catalytic Experiments

$Pd(OAc)_2$ (4.46 μmol, 1 mg), phosphane **1** (40.2 μmol) and the required amount of methylated β-CD were introduced under a nitrogen atmosphere into a Schlenk tube containing water (4 g). After stirring with a magnetic bar for 1 h, the yellow solution was transferred into a mixture of allyl undecyl carbonate (446 μmol), diethylamine (892 μmol) and heptane (4 g). The medium was stirred at 1000 rpm at room temperature and the reaction was monitored by quantitative gas chromatographic analysis of the organic layer

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