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Supramolecular Trapping of Phosphanes by Cyclodextrins: A General Approach to Generate Phosphane Coordinatively Unsaturated Organometallic Complexes

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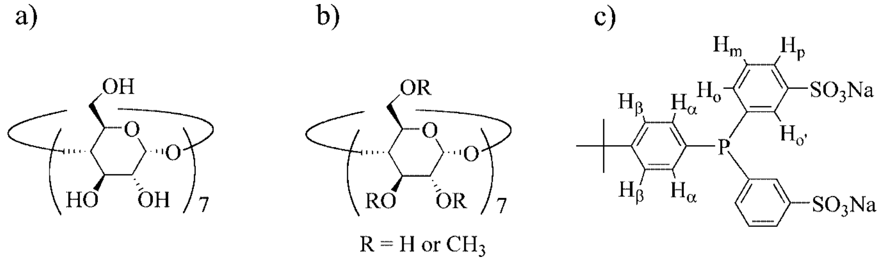
As shown by $^{31}P\{^1H\}$ NMR spectroscopy, addition of the native β-cyclodextrin or randomly methylated β-cyclodextrin to an aqueous solution of $Cl[Pt\{(p\text{-}tBuC_6H_4)P(m\text{-}C_6H_4SO_3Na)_2\}_3Cl]$ or $[Pd\{(p\text{-}tBuC_6H_4)P(m\text{-}C_6H_4SO_3Na)_2\}_3]$ allows us to generate the phosphane coordinatively unsaturated $[Pt\{(p\text{-}tBuC_6H_4)P(m\text{-}C_6H_4SO_3Na)_2\}_2Cl_2]$ or $[Pd\{(p\text{-}tBuC_6H_4)P(m\text{-}C_6H_4SO_3Na)_2\}_2]$ complexes, respectively. The existence of second-sphere coordination adducts between the organometallic complex and the cyclodextrin, in which the local bulkiness around the metallic centre is high, appears to be the essential prerequisite for the dissociation of one $(p\text{-}tBuC_6H_4)P(m\text{-}C_6H_4SO_3Na)_2$ phosphane ligand from the metal centre.

Introduction

One of the most challenging aspects of organometallic catalysis is to generate phosphane unsaturated species. Indeed, these complexes are generally accepted as the catalytically active species in numerous transition-metal-catalysed reactions.[1] An efficient strategy that favours the formation of such compounds consists of using hindered phosphanes. Actually, because of the bulkiness generated around the metallic centre, coordination of numerous ligands to the metal is prohibited and low-coordinated species are obtained. Thus, the use of hindered phosphane has proved to be efficient in generating coordinatively unsaturated complexes that are well known as active catalysts in hydroformylation[2] and carbon–carbon or carbon–heteroatom bond formation.[3] Unfortunately, these catalytic entities have often remained experimentally inaccessible in large amounts because of their low stability, and have required the synthesis of elaborate phosphanes.

We have recently put forward the remarkable properties of cyclodextrins to form inclusion complexes with water-soluble phosphane ligands used to dissolve the organometallic catalyst in water.[4] In particular, the native β-cyclodextrin (β-CD, Scheme 1) and the randomly methylated β-cyclodextrin (RAME-β-CD, Scheme 1) have proved to strongly interact with the disodium bis(3-sulfonatophenyl)(4-*tert*-butylphenyl)phosphane $[(p\text{-}tBuC_6H_4)P(m\text{-}C_6H_4SO_3Na)_2$ (**1**)] (Scheme 1) as a result of the well-known ability of the *tert*-butylphenyl group to fit tightly into the β-CD cavity.[5] Thus, the association constants for the β-



Scheme 1. (a) Native β-cyclodextrin (β-CD), (b) randomly methylated β-cyclodextrin (RAME-β-CD), (c) disodium bis(3-sulfonatophenyl)(4-*tert*-butylphenyl)phosphane $[(p\text{-}tBuC_6H_4)P(m\text{-}C_6H_4SO_3Na)_2]$ (**1**).

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CD/**1** and RAME-β-CD/**1** inclusion complexes were found to be notably higher than those measured for the inclusion complexes formed with trisulfonated triphenylphosphane (TPPTS); a phosphane currently used in aqueous organometallic catalysis (400000 and 250000 M^{-1} at 25 °C for β-CD/**1** and RAME-β-CD/**1** inclusion complexes, respectively; 1200 and 1000 M^{-1} at 25 °C for β-CD/TPPTS and RAME-β-CD/TPPTS inclusion complexes, respectively).

Interestingly, the strong interaction between **1** and CD derivatives can be used to generate phosphane low-coordinated rhodium species.[5] Indeed, we have demonstrated that [HRh(CO)(**1**)$_3$] can be partially converted in the presence of β-CD or RAME-β-CD into the hydroxy complex [HORh(CO)(**1**)$_2$] under nitrogen, or into the hydrido complex [HRh(CO)$_2$(**1**)$_2$] under carbon monoxide.

In this paper, we would like to demonstrate that the use of a hydrosoluble phosphane, very strongly interacting with CDs such as **1**, could be a general approach to generate phosphane coordinatively unsaturated complexes under mild conditions. The feasibility of our approach was exam-

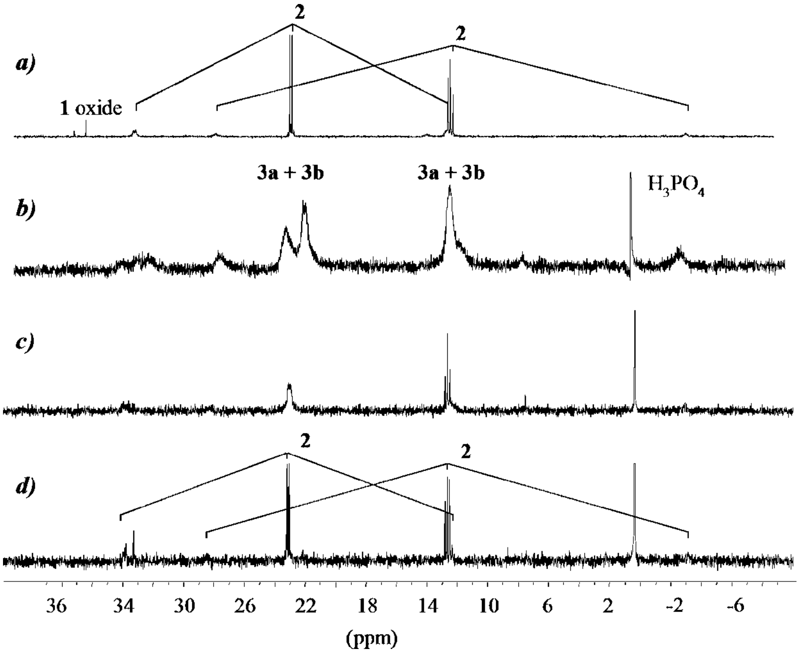


Figure 1. $^{31}P\{^1H\}$ NMR spectra of the platinum complex Cl[ClPt((*p*-*t*BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$)$_3$] (**2**) (10 mM) in D$_2$O (a) without cyclodextrin at 25 °C; after addition of 1 equiv. β-CD with respect to the platinum at (b) 25 °C; (c) 60 °C; (d) 85 °C.

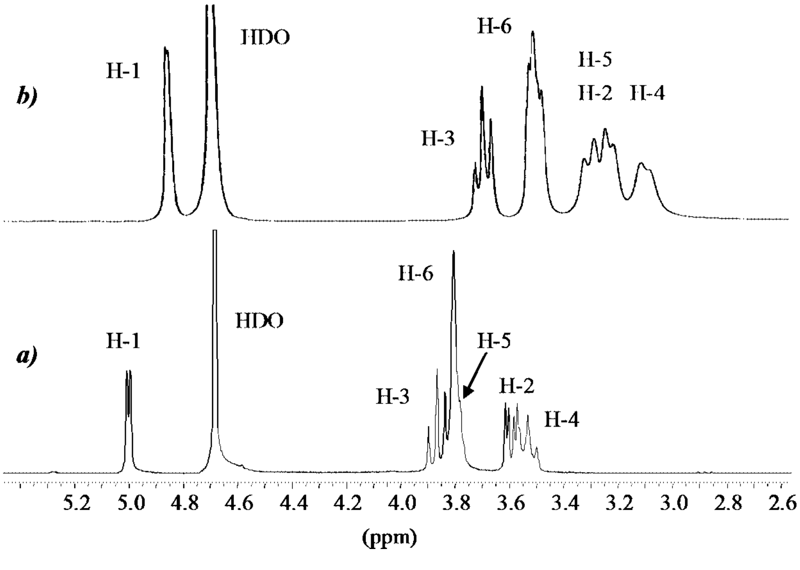


Figure 2. ^1H NMR spectra at 25 °C in D$_2$O of (a) β-CD alone (10 mM); (b) β-CD after addition of 1 equiv. Cl[ClPt((*p*-*t*BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$)$_3$] (2) (10 mM).

ined using platinum or palladium complexes of **1** and β-CD or RAME-β-CD as phosphane trapping agents.

Results and Discussion

Initial experiments were performed using β-CD whose well-defined ^{1}H NMR signals are easier to read than the signals of RAME-β-CD, where the overlapped resonances are often noninterpretable. The Cl[Pt(**1**)$_3$Cl] platinum complex (**2**) was prepared by mixing K_2PtCl_4 with 3 equiv. of **1** according to a procedure previously described in the literature for the synthesis of the analogous complex Cl[Pt(TPPTS)$_3$Cl].[6] Figure 1 shows the ^{31}P{^{1}H} NMR spectra relative to **2** without β-CD (Figure 1, a) and in the presence of 1 equiv. of β-CD at 25 °C (Figure 1, b), 60 °C (Figure 1, c) and 85 °C (Figure 1, d).

Since only one third of the platinum (^{195}Pt) has a spin of 1/2, the phosphorus of the square-planar structure of **2** exhibits a 1:4:1 triplet of doublets centred at δ = 23.0 ppm ($^1J_{\mathrm{P}cis\text{–}\mathrm{Pt}}$ = 2494 Hz; $^2J_{\mathrm{P}cis\text{–}\mathrm{P}trans}$ = 18.6 Hz) corresponding to the two phosphorus atoms *cis* to the chloride and a 1:4:1 triplet of triplets centred at δ = 12.4 ppm ($^1J_{\mathrm{P}trans\text{–}\mathrm{Pt}}$ = 3718 Hz; $^2J_{\mathrm{P}cis\text{–}\mathrm{P}trans}$ = 18.6 Hz) corresponding to the phosphorus atom *trans* to the chloride (Figure 1, a). At 25 °C, addition of β-CD leads to the appearance of new resonances and a broadening of all signals (Figure 1, b). No peak is detected in the chemical shift region of the free or CD-included phosphane (from 0 ppm to –12 ppm). This can be explained by assuming that β-CD interacts with **2** without inducing the dissociation of phosphane **1** from the metal. The nature of the interactions between both species **1** and **2** with β-CD has been established by ^{1}H NMR spectroscopic measurements. Figure 2 shows the ^{1}H NMR spectra of β-CD, both alone and also as a stoichiometric β-CD/**2** mixture (Figure 2).

Upon addition of **2** to the β-CD solution, strong upfield chemical shifts are observed for the internal 3-H and 5-H CD protons suggesting the formation of inclusion complexes between **2** and β-CD. It should be noted that the other protons of the CD are also shielded upfield by the presence of **2**, indicating that they are also affected by the inclusion process. The formation of inclusion complexes between **2** and β-CD was unambiguously demonstrated by a 2D NMR T-ROESY spectrum of a 1:1 mixture of **2** and β-CD, which revealed intense cross-peaks between the *t*Bu group of the phosphane and the internal CD protons 3-H, 5-H and 6-H (Figure 3).

Nevertheless, the absence of correlations between the 3-H, 5-H or 6-H protons and H$_\alpha$ shows that the penetration of the phosphane into the CD cavity was not deep (Scheme 2).

This observation is opposite to what has previously been established for the β-CD/**1** inclusion complex. Indeed, a detailed study has clearly demonstrated that phosphane **1** was

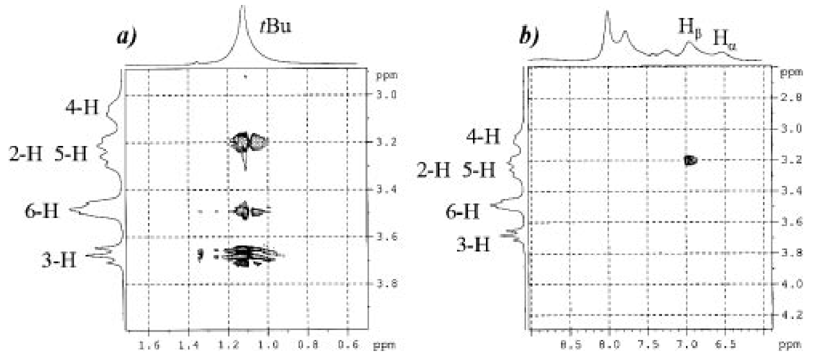
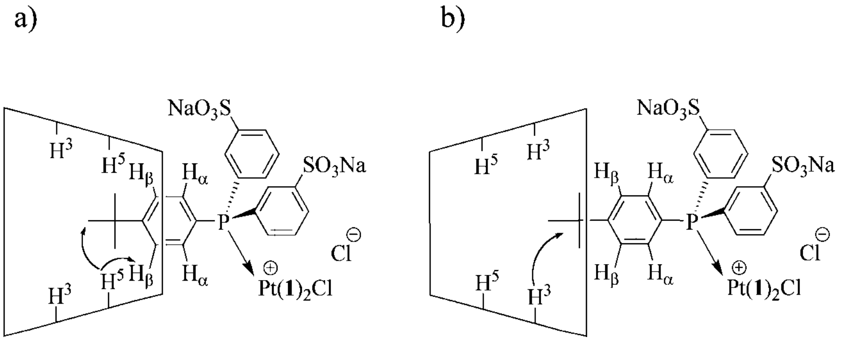
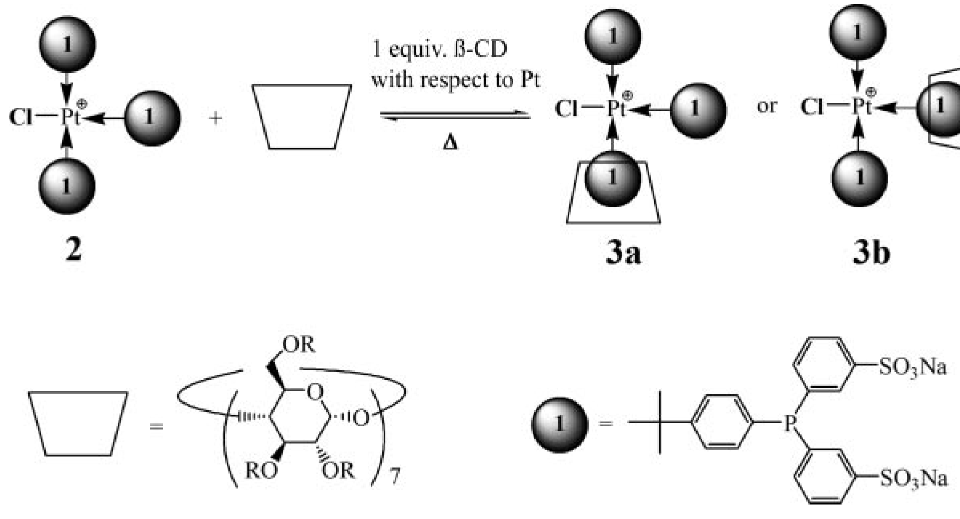


Figure 3. Partial contour plot of the T-ROESY spectrum of a solution containing β-CD (10 mM) and **2** (10 mM) in D_2O at 25 °C with a 300 ms mixing time. (a) Cross-peaks between the β-CD protons and protons of the *tert*-butyl group. (b) Cross-peaks between the β-CD protons and the aromatic protons of phosphane **1**.



Scheme 2. Second-sphere coordination adducts between β-CD and **2** with a recognition process (a) at the primary face and (b) at the secondary face. The interactions observed in the T-ROESY spectrum between the different protons and the deduced orientation of the phosphane **1** in the CD cavity are also shown.



Scheme 3. Equilibrium between the platinum complexes of **1** in the presence of 1 equiv. β-CD (inclusion of **1** at the secondary face is also possible).

deeply included in the β-CD cavity at the primary face (intense cross-peaks between H_α and 5-H or 6-H, see Supporting Information). Therefore, **1** interacted very differently with β-CD when free in solution and when coordinated to the platinum complex. Furthermore, the presence of intense cross-peaks between the *t*Bu group of the phosphane and the 3-H, 5-H and 6-H CD protons strongly suggests that inclusion occurred at the primary face (Scheme 2, a) but also at the secondary face of the β-CD (Scheme 2, b). Indeed, a low-deep inclusion of **2** at the primary face of the β-CD cannot rationalise the intense cross-peak observed between the *t*Bu and 3-H proton. Finally, it must be pointed out that the inclusion of the phosphane **1** into the cavity at the secondary face was so small that no contact was detected between the 3-H and H_β (or a fortiori H_α) protons.

Knowing that **2** and β-CD were supramolecularly interacting, the splitting and broadening of the peaks of Figure 1 (b) are attributed to the existence of two possible inclusions of **2** in β-CD (Scheme 3), either by one of the two ligands **1** *cis* to the chloride (species **3a**) or by the ligand **1** *trans* to the chloride (species **3b**). Although inclusion of **2** at the secondary face also occurred, only the structures obtained with an inclusion at the primary face have been represented for clarity in Scheme 3.

Interestingly, the splitting of the signal at $\delta = 23.0$ ppm, corresponding to the two phosphorus atoms *cis* to the chloride, into two broad signals in the 25–20 ppm region in the presence of β-CD (see parts a and b in Figure 1) indicates that the coordinated *cis* phosphanes **1** become inequivalent when β-CD binds to complex **2**. As only 1 equiv. of β-CD was added to a solution of **2**, this phenomenon probably finds its origin in the fact that when one of the two *cis* phosphanes **1** is included into the β-CD cavity, the other remains nonincluded. Finally, the important and unusual upfield shifts observed in the ^{1}H NMR spectrum for the external protons of the CD (1-H, 2-H and 4-H) might be explained by the closeness in species **3** of nonincluded coordinated ligands **1** with the edges of a β-CD bound to a coordinated ligand **1**, suggesting an overcrowded environment at the periphery of the CD.

Consequently, at room temperature, it appears that β-CD acts as a host for a ligand that was directly coordinated to the platinum. Although the formation of second-sphere coordination adducts between CD derivatives and organometallic complexes is a well-known phenomenon,[7] it is worth mentioning that the formation of such adducts between CD and organometallic complexes bearing phosphane ligands has rarely been observed. Indeed, to the best

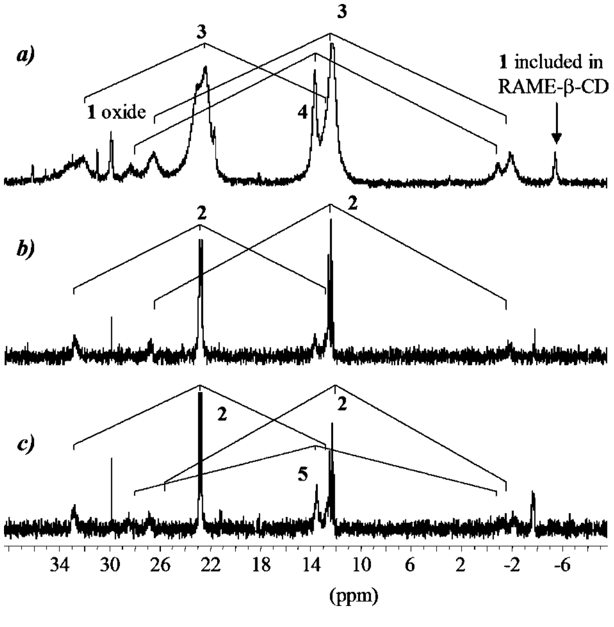
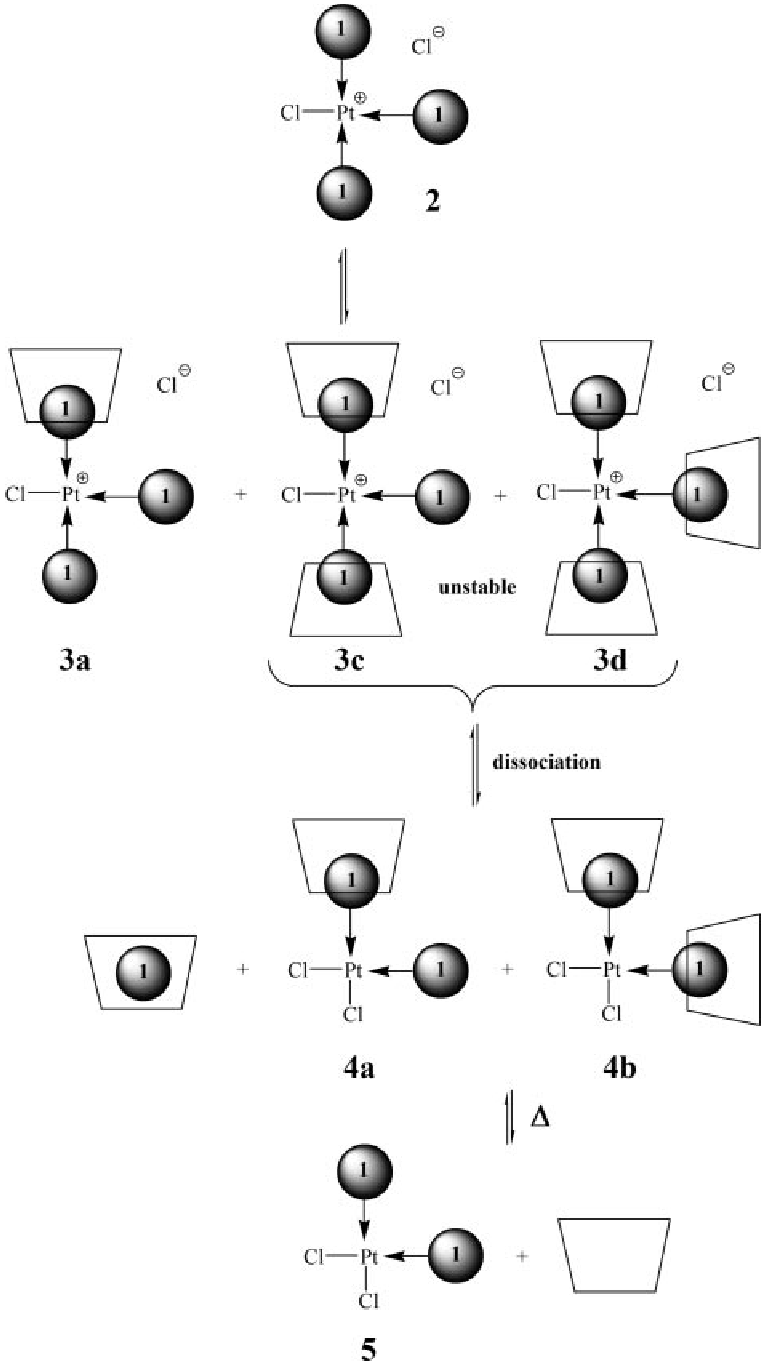


Figure 4. $^{31}P\{^1H\}$ NMR spectra of the platinum complex $Cl[ClPt((p\text{-}tBuC_6H_4)P(m\text{-}C_6H_4SO_3Na)_2)_3]$ (**2**) (10 mM) in D_2O with 12 equiv. RAME-β-CD with respect to the platinum at (a) 25 °C; (b) 60 °C; (c) 85 °C.

of our knowledge, there are only four reports in the literature on the formation of such adducts in organic or aqueous media.[8]

Information concerning the thermal stability of second-sphere coordination adducts **3** was obtained by carefully examining the $^{31}P\{^1H\}$ NMR spectra recorded at various temperatures. Increasing the temperature to 60 and 85 °C gave more resolved spectra (see parts c and d in Figure 1). In particular, the $^{31}P\{^1H\}$ NMR spectrum recorded at 85 °C (Figure 1, d) strongly resembles that recorded at 25 °C (Figure 1, a), indicating that the second-sphere coordination adducts **3a** and **3b** disappeared when the temperature was increased. Actually, an increase in the temperature decreased the association constant between β-CD and **1**, which found expression in a dissociation of β-CD from the organometallic complex. Interestingly, the spectrum recorded at 60 °C suggests that the β-CD interacted more strongly with the *cis* ligands than with the *trans* ligand. Indeed, the signal at δ = 12.4 ppm corresponding to the *trans* phosphane is well resolved whereas the signal corresponding to the *cis* phosphanes remains broad at 60 °C. This result can easily be rationalised by considering that the steric



Scheme 4. Equilibria between the platinum complexes of **1** in the presence of 12 equiv. RAME-β-CD (inclusion of **1** at the secondary face is also possible). Some second-sphere coordination adducts are not represented for clarity.

congestion around the *trans* ligand is more important than it is around the *cis* ligand.

The stability of the second-sphere adducts in the presence of various amounts of β-CD or RAME-β-CD was also investigated. Similar results were obtained with 3 equiv. β-CD and with 1 or 3 equiv. RAME-β-CD. However, the results were very different when 12 equiv. RAME-β-CD was used. Indeed, along with the numerous changes already observed above, the $^{31}P\{^1H\}$ NMR spectrum also revealed a broad 1:4:1 triplet centred at δ = 13.8 ppm ($^1J_{P,Pt}$ = 3700 Hz) assigned to a new platinum species (**4**) and a resonance characteristic of an inclusion complex between **1** and the RAME-β-CD at δ = –5.5 ppm (Figure 4, a).

This new platinum species **4** was identified by comparing its chemical shift and platinum-phosphorus coupling constant values with those for the known water-soluble platinum complexes and by integration of the ^{31}P NMR signals. Actually, we found that the spectroscopic data of **4** are very similar to those of [*cis*-Pt(TPPTS)$_2$Cl$_2$][6] and that the intensity of the ^{31}P NMR signal of the species **4** was twice as high as the intensity of the signal relative to the RAME-β-CD/**1** inclusion complex. These two findings led us to assume that the new platinum species **4** corresponds to second-sphere coordination adducts between [Pt(**1**)$_2$Cl$_2$] and the RAME-β-CD obtained by dissociation of **1** from adducts **3** according to Scheme 4.

As previously observed with adducts **3** (vide infra), dissociation of RAME-β-CD from platinum species **4** occurred at high temperatures, leading to nonincluded [Pt(**1**)$_2$Cl$_2$] (**5**). Indeed, increasing the temperature led to the destabilisation of the second-sphere coordination adducts (well-defined peaks at 60 and 85 °C) and additionally to a larger proportion of the signal corresponding to free phosphane **1** in interaction with RAME-β-CD (Figure 4, parts b and c) (Scheme 4). As the intensity of the signal relative to the RAME-β-CD/**1** inclusion complex is directly proportional to the ^{31}P NMR signal of the new species **4** and **5**, the percentage (**4** and **5**) could be determined starting from the integration of the peak assigned to the free phosphane **1** that is included into RAME-β-CD (see Supporting Information). At 85 °C, an amount of 22% (**4** and **5**) was calculated.

In order to confirm that the formation of the phosphane coordinatively unsaturated platinum complexes **4** and **5** was a result of the RAME-β-CD similar experiments have been performed with methyl-α-D-glucopyranoside, which constitutes the monomeric "building block" of RAME-β-CD. No modification of the spectra could be observed in this case, proving that the molecular recognition ability of RAME-β-CD plays a fundamental role in the formation of **4** and **5**.

Throughout these experiments, it was clear that an excess of RAME-β-CD was necessary to generate the phosphane coordinatively unsaturated platinum complexes. The explanation of such a phenomenon not only lies in the strength of the RAME-β-CD/**2** interaction, but also in the steric hindrance generated by the presence of RAME-β-CD on the first-sphere ligands. Indeed, below 3 equiv. of RAME-β-CD with respect to the amount of platinum, it is reasonable to assume that the equilibrium between the nonincluded and included **2** remained possible as the steric hindrance around the metallic centre should not be very important when one CD is bound to a coordinated phosphane **1** (Scheme 3). By contrast, when a large amount of RAME-β-CD was added, the equilibrium was displaced towards the second-sphere coordination adducts containing two and three CDs. The local bulkiness around the metallic centre of the obtained supramolecular adducts probably became too high and a steric decongestion by dissociation of the phosphane/CD inclusion complex from the platinum occurred leading to phosphane low-coordinated complexes **4** or **5**, depending on the temperature (Scheme 4). These observations are perfectly consistent with those already made above with β-CD for which a hindered structure for the β-CD/**2** complex has been thought of (vide infra). So, the existence of second-sphere coordination adducts in which the local bulkiness around the metallic centre is high appears to be an intermediate step in the formation of phosphane coordinatively unsaturated complexes.

The NMR study has been widened to the palladium complex [Pd{(p-tBuC$_6$H$_4$)P(m-C$_6$H$_4$SO$_3$Na)$_2$}$_3$] (**6**) whose $^{31}P\{^1H\}$ NMR spectrum is depicted in Figure 5 (a).

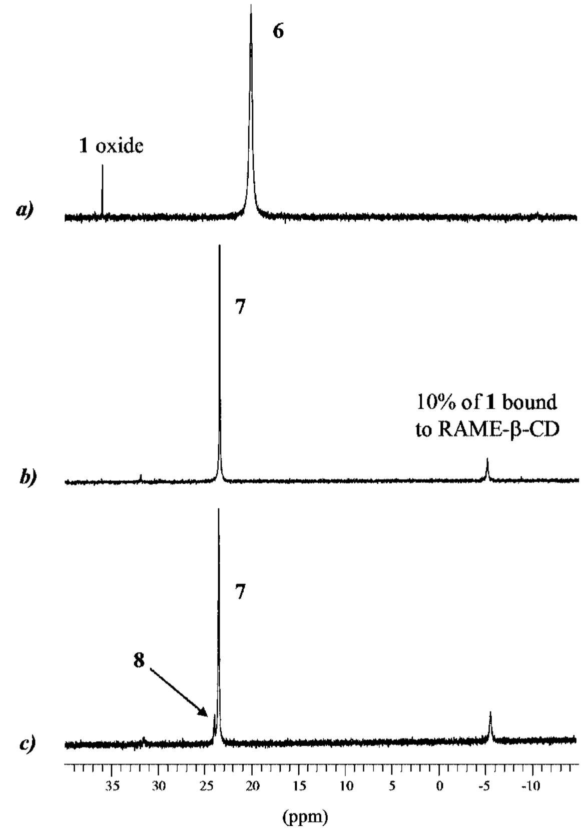
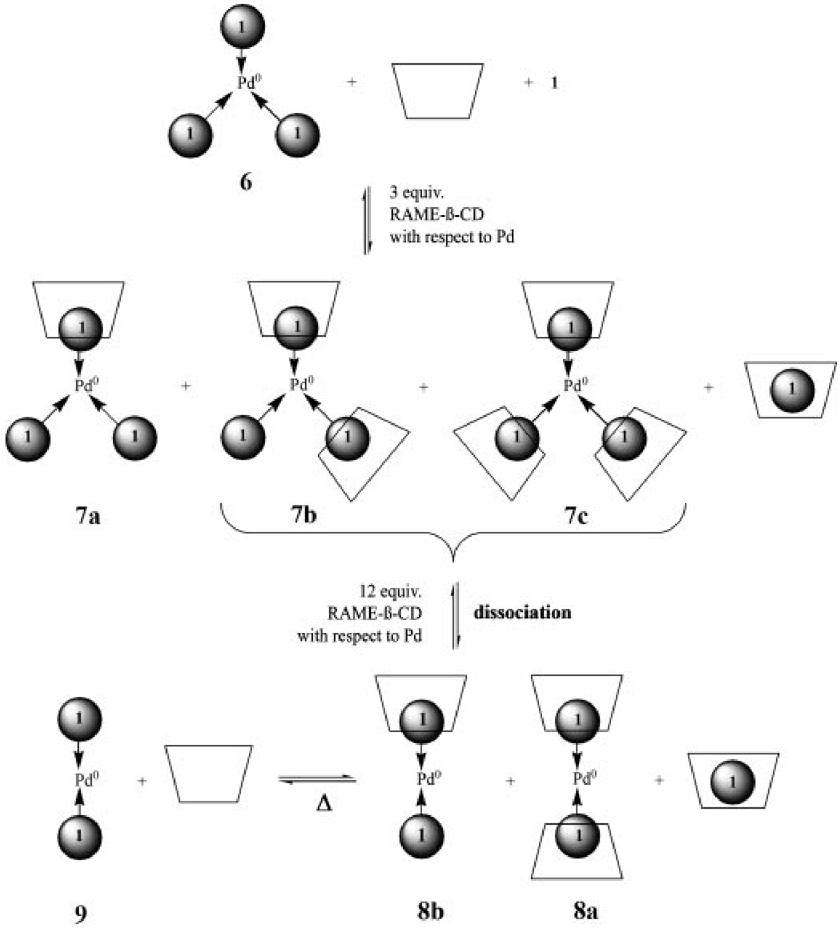


Figure 5. $^{31}P\{^1H\}$ NMR spectra of palladium complex [Pd((p-tBuC$_6$H$_4$)P(m-C$_6$H$_4$SO$_3$Na)$_2$)$_3$] (**6**) (20 mM) in D$_2$O at 25 °C (a) without cyclodextrin; (b) after addition of 3 equiv. RAME-β-CD with respect to palladium; (c) after addition of 12 equiv. RAME-β-CD with respect to palladium.

Besides the minor resonance of the phosphane oxide impurity (δ = 36 ppm), a broad signal was detected at δ =



Scheme 5. Equilibria between the palladium complexes of **1** in the presence of various amounts of RAME-β-CD (inclusion of **1** at the secondary face is also possible).

20.1 ppm. As an excess of phosphane **1** was present in the medium (10%, see Exp. Sect.), this broad peak is an average signal resulting from the fast equilibrium between free phosphane **1** and the palladium complex **6**.[9] By addition of 3 equiv. of RAME-β-CD with respect to **6**, two distinct signals are observed at δ = 24 and δ = –5.5 ppm (Figure 5, b). Integration of the ^{31}P NMR signals at δ = –5.5 ppm shows that the amount of noncoordinated **1** is 10%, which corresponds to the excess of phosphane **1** initially present in the medium. This last result indicates that 3 equiv. of RAME-β-CD were insufficient to induce the formation of the phosphane coordinatively unsaturated species. Consequently, the signal at δ = 24 ppm has been assigned to the second-sphere coordination adducts of the palladium complex **6** with the RAME-β-CD (species **7**) and the signal at δ = –5.5 ppm to the phosphane **1** in interaction with RAME-β-CD (Scheme 5). Moreover, it can be concluded that RAME-β-CD decreased the exchange rate between phosphane **1** and the palladium species since the excess of the phosphane **1** complex is visible.

Much more interesting were the results obtained when 12 equiv. of RAME-β-CD, with respect to the palladium complex, were added to an aqueous solution of **6** (Figure 5, c). Indeed, a new species at δ = 24.5 ppm (**8**) was observed and the amount of phosphane **1** bound to RAME-β-CD was higher than the previous one (16% compared with 10%). Furthermore, calculations showed that the intensity of the ^{31}P NMR signal of the new species **8** was twice as high as the intensity of the phosphane **1** signal that appeared. By analogy with the platinum complexes, this outstanding result led us to assume that **8** was the palladium species [(**1**)$_2$Pd^0] containing two phosphane ligands included in the RAME-β-CD cavities. As observed for platinum species **4** and **5**, the steric hindrance generated by two or three CDs around the metallic centre of **6** could be invoked to explain the formation of the phosphane low-coordinated palladium species **8** (Scheme 5).

Here again, the amounts of included phosphane **1** and complex **8** were found to be dependent on the temperature. Indeed, when the solution containing 12 equiv. of RAME-β-CD with respect to **6** was heated at 40 °C (Figure 6, b) and 60 °C (Figure 6, c), the signals corresponding to the palladium complex **8** and phosphane **1** included into RAME-β-CD notably increased. Although no evidence has been obtained contrary to that for the platinum species, it is reasonable to think that, at higher temperatures, dissociation of the second-sphere adducts **8** could lead to the formation of species [(**1**)$_2$Pd^0] (species **9**, Scheme 5).

Calculations revealed that the amount of phosphane **1** that appeared was directly connected to the amount of spe-

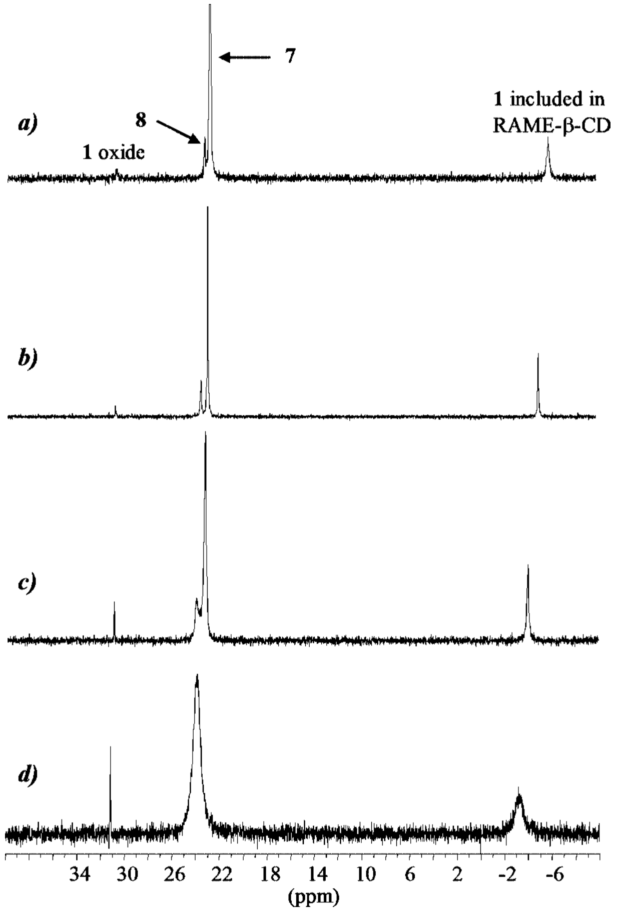


Figure 6. $^{31}P\{^1H\}$ NMR spectra of a mixture of [Pd((*p*-*t*BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$)$_3$] (**6**) (20 mM) and RAME-β-CD (240 mM) in D$_2$O at various temperatures: (a) 25 °C; (b) 40 °C; (c) 60 °C; (d) 85 °C.

cies **8** and **9** (see Supporting information). The percentage of **8** and **9** relative to the total amount of palladium could reach 40% at 85 °C (Figure 7).

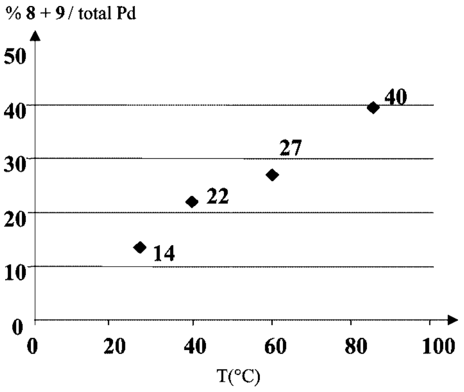


Figure 7. Percentage of palladium species (**8** and **9**) relative to the total palladium amount [% complex (**8** and **9**)/total Pd] as a function of the temperature [Pd((*p*-*t*BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$)$_3$ (20 mM) and RAME-β-CD (240 mM)].

Finally, it must be pointed out that the above phenomena were reversible since a new $^{31}P\{^1H\}$ NMR spectrum recorded at 27 °C, after the heating period, was identical to that observed before heating the sample.

To confirm that the formation of the phosphane coordinatively unsaturated palladium complexes **8** and **9** was due to RAME-β-CD, similar experiments were also performed with methyl-α-D-glucopyranoside. As previously reported with the platinum species, no modification of the spectra could be observed in this case, proving that the molecular recognition ability of RAME-β-CD plays a fundamental role in the formation of **8** and **9**.

Conclusion

This work has clearly demonstrated that the strong interaction between RAME-β-CD and the especially designed phosphane **1** can be used for generating phosphane coordinatively unsaturated platinum and palladium complexes, which are spectroscopically evidenced by ^{31}P NMR measurements. This constitutes the first example of the existence of low-coordinated palladium species in water. The existence of second-sphere coordination adducts in which the local bulkiness around the metallic centre is high appeared to be the essential prerequisite leading to the dissociation of the sulfonated ligand from the metal. Studies are currently underway in our laboratory to examine the catalytic activity of these supramolecularly generated species.

Experimental Section

General Remarks: The ^{1}H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker Avance 300 DPX instrument at 300.13 and 75.46 MHz, respectively. The 2D T-ROESY experiments were run using the software supplied by Bruker. Mixing times for T-ROESY experiments were set at 300 ms. The data matrix for the T-ROESY was made from 512 free induction decays, 1 K points each, resulting from the coaddition of 32 scans. The real resolution was 1.5–6.0 Hz/point in the F2 and F1 dimensions. They were transformed in the nonphase, sensitive mode after QSINE window processing. Palladium acetate, potassium chloro-platinate and randomly methylated β-cyclodextrin (RAME-β-CD) were purchased from Aldrich. RAME-β-CD was a native β-CD partially methylated; statistically 1.8 OH groups per glucopyranose unit were modified. The synthesis of the disodium bis(3-sulfonatophenyl)(4-*tert*-butylphenyl)phosphane [(*p*-*t*BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$ (**1**)] was described in one of our previous publications.[10]

$^{31}P\{^1H\}$ NMR Study on the Complex Cl[Pt{(*p*-*t*BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$}$_3$Cl] (2): K$_2$Pt$_2$Cl$_4$ (21 mg, 0.05 mmol) was dissolved in degassed deuterated water (5 mL). Three equiv. of **1** (7.9 mg, 0.15 mmol) were added to the solution, which was then stirred for 30 min at room temperature under nitrogen. Complex **2** was quantitatively obtained. Studies in the presence of β-CD or RAME-β-CD were conducted as follows: the required amount of cyclodextrin was introduced into 1 mL of the above solution. After 15 min. of stirring the solution was transferred into a 5 mm NMR tube.

$^{31}P\{^1H\}$ NMR Study on the Complex [Pd{(*p*-*t*BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$}$_3$] (4): [Pd{(*p*-*t*BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$}$_3$] in a D$_2$O solution was synthesized according to a modified literature procedure.[9a] Pd(PPh$_3$)$_4$ (412 mg, 0.36 mmol) was dissolved in degassed toluene (8 g) in a Schlenk tube under nitrogen. (*p*-*t*BuC$_6$H$_4$)-

$P(m\text{-}C_6H_4SO_3Na)_2$ (277 mg, 0.53 mmol) was dissolved in D_2O (8 g) and cannulated into the palladium solution. The mixture was stirred for 30 min at room temperature. After decantation, the aqueous phase was recovered. The obtained $[Pd\{(p\text{-}t\text{Bu}C_6H_4)P(m\text{-}C_6H_4SO_3Na)_2\}_3]$ solution was then used for the $^{31}P\{^1H\}$ NMR spectroscopic study. This solution contained the expected palladium complex $[Pd\{(p\text{-}t\text{Bu}C_6H_4)P(m\text{-}C_6H_4SO_3Na)_2\}_3]$ and an excess of about 10% of free $(p\text{-}t\text{Bu}C_6H_4)P(m\text{-}C_6H_4SO_3Na)_2$ {with regard to the initial amount of $(p\text{-}t\text{Bu}C_6H_4)P(m\text{-}C_6H_4SO_3Na)_2$}. A study in the presence of RAME-β-CD was conducted as follows: the required amount of RAME-β-CD was introduced, under nitrogen, to 1 mL of the above $[Pd\{(p\text{-}t\text{Bu}C_6H_4)P(m\text{-}C_6H_4SO_3Na)_2\}_3]$ solution. After 15 min. of stirring, the solution was transferred via a cannula into a nitrogen pressurized 5 mm NMR tube.

Supporting Information (for details see the footnote on the first page of this article): Spectroscopic study of the β-CD/**1** complex. Determination of the percentage of platinum complex $[Cl_2PtL_2]$ relative to the total platinum amount. Determination of the percentage of palladium complex $[PdL_2]$ relative to the total palladium amount.

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