Host–Guest Systems

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Self-Assembled Supramolecular Bidentate Ligands for Aqueous Organometallic Catalysis**

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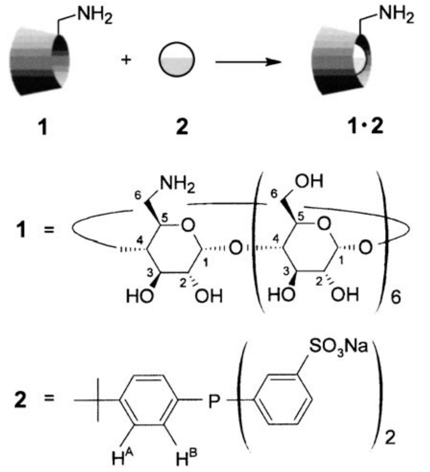
Supramolecular chemistry is one of the fastest growing areas of chemistry and greatly contributes to the development of numerous new innovative concepts. This is especially true in the field of organometallic catalysis where host–guest interactions have proved to be a powerful tool to elaborate new strategies aimed at improving the performances of catalytic entities.[1] Among them, the design of supramolecular bidentate ligands appeared as an elegant approach to stabilize organometallic complexes under catalytic conditions and constitutes a possible way to access a library of ligands.[2] For that purpose, chelating ligands with an appropriate bite angle[3] have been elaborated by the self-assembly of monophosphanes or monophosphites. These assemblies were found to be efficient as supramolecular bidentate ligands in numerous reactions.[4] However, all these reactions were performed in organic media that did not constitute an ecological alternative in the context of green chemistry. Our experience with cyclodextrins (CDs) and their use in aqueous solutions[5] led us to design a water-soluble supramolecular bidentate ligand starting from a well-chosen β-cyclodextrin/sulfonated phosphane couple.[6] Our approach relies on the self-assembly of the 6^{I}-amino-6^{I}-deoxycyclomaltoheptaose (**1**)[7] and the disodium bis(3-sulfonatophenyl)(4-*tert*-butylphenyl)phosphane (**2**)[8] (Scheme 1).

Indeed, we postulated that the inclusion of **2** in the cavity of **1** by the NH_2-containing face would result in the formation of a rigid chelating bidentate ligand, with the nitrogen and the phosphorus atoms on the same side of the supramolecular edifice. Herein, we report the results of our investigations on the host–guest interaction between **1** and **2** and the ability of the resulting supramolecular complex to coordinate platinum complexes. The efficiency of the obtained organoplatinum complexes was demonstrated in a hydrogenation reaction of a water-soluble allylic alcohol.



Scheme 1. Formation of the supramolecular bidentate ligand (**1·2**) from 6^{I}-amino-6^{I}-deoxycyclomaltoheptaose (**1**) and disodium bis(3-sulfonatophenyl)(4-*tert*-butylphenyl)phosphane (**2**).

The formation of inclusion complexes between **1** and **2** was confirmed by NMR spectroscopy measurements. A 1:1 stoichiometry was revealed by the NMR continuous-variation method, and the association constant between **1** and **2** was found to be $40\,000\,\text{M}^{-1}$ at 25 °C (see Supporting Information).

The geometry of the supramolecular entity was deduced from 2D T-ROESY NMR experiments with an equimolar mixture of **1** and **2**. The absence of strong correlation between hydrogen atoms H^A or H^B and H3 and the presence of a correlation between H^B and H6 unambiguously proved the inclusion of **2** by the primary face of **1**. Moreover, cross-peaks between the *t*Bu protons of **2** and the inner protons H3 and H5 of **1** confirmed the penetration of the aromatic cycle of **2** in the cavity of **1**. Thus, the obtained supramolecular chelating complex reveals the expected structural features to coordinate a metal as the phosphorus and nitrogen atoms are spatially close.

More interestingly, subsequent addition of $K_2[PtCl_4]$ (1 equiv) to the supramolecular complex **1·2** (1 equiv) gave three different complexes (**3**, **4**, and **5**; Scheme 2), whose structures were elucidated by analyzing the $^{31}P\{^{1}H\}$ NMR spectrum depicted in Figure 1.

The two doublets at $\delta = 16.42$ and 6.29 ppm were indicative of two coupled phosphanes ($^{2}J_{P,P} = 19.36$ Hz) coordinated to the same platinum ion (complex **3**). Their coupling constants $^{1}J_{P,Pt}$ with ^{195}Pt (33.7 % natural abundance) were deduced from their satellite peaks (3884 Hz and 3250 Hz, respectively).[9] The magnitude of $^{1}J_{P,Pt}$ was typical of two inequivalent phosphorus atoms located *cis* to each other,[10] with one of them (a) situated *trans* to chloride ($^{1}J_{P,Pt} = 3884$ Hz)[11] and the other (b) lying *trans* to a nitrogen center ($^{1}J_{P,Pt} = 3250$ Hz).[12]

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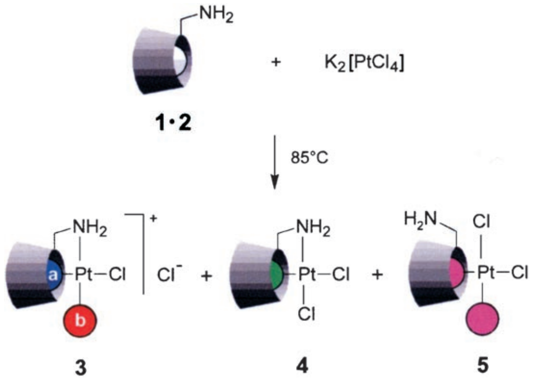


Scheme 2. Synthesis of the platinum complexes **3**, **4**, and **5**: 1) **1** (1 equiv), **2** (1 equiv), D_2O, room temperature, 5 min; 2) $K_2[PtCl_4]$ (1 equiv) dissolved in D_2O, 85 °C, 90 min. For an easier understanding of the NMR spectra, phosphanes **2** in a different chemical environment has been colored blue, complex **3** red, complex **4** green, and complex **5** pink.

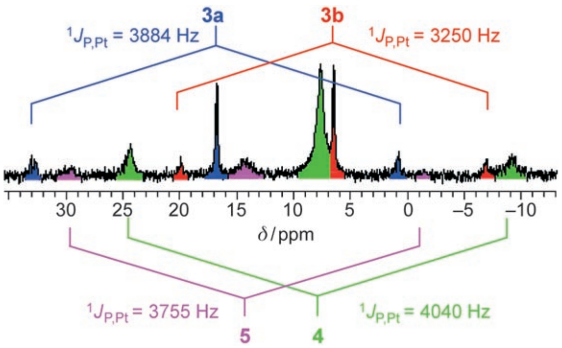


Figure 1. ^{31}P NMR spectrum (recorded at 85 °C) of an equimolar mixture of $K_2[PtCl_4]$ and the **1·2** supramolecular complex in D_2O after heating the sample for 90 min at 85 °C.

The structure of **3** was established by changing the amounts and the order of addition of the reactants in the NMR tube. Thus, when $K_2[PtCl_4]$, **2**, and **1** (1:2:1 ratio) were successively dissolved in D_2O, **3** was exclusively formed after 15 min heating at 60 °C (Figure 2).

The coordination of the nitrogen center was unambiguously demonstrated by analysis of the DEPT 135 spectrum, which clearly revealed a downfield shift (from $\delta = 41$ to 45 ppm) of the resonance of the carbon center adjacent to the NH_2 group and a strong splitting of the other resonances as well (see Supporting Information). Two singlets ($\delta = 1.32$ and 0.97 ppm) were detected in the *t*Bu region of the ^{1}H NMR spectrum and were further evidence of inequivalence of the phosphanes. The definitive attribution of these ^{1}H resonances was revealed by the T-ROESY spectrum (Figure 3). Indeed, intense correlation peaks were detected between the inner protons of **1** and the *t*Bu group of **2** at $\delta = 1.32$ ppm, suggesting an inclusion of this phosphane (**3a**) inside the cavity of **1**. Note that, once coordinated to a platinum atom, **1** appeared to be a first- and second-sphere ligand owing to its direct coordination of the nitrogen atom to the metal and the inclusion of a first-sphere ligand (**2**) in its cavity.[13] As no other cross-peak was detected in the spectrum, the *t*Bu group at $\delta = 0.97$ ppm therefore corresponded to a non-included phosphane (**3b**).

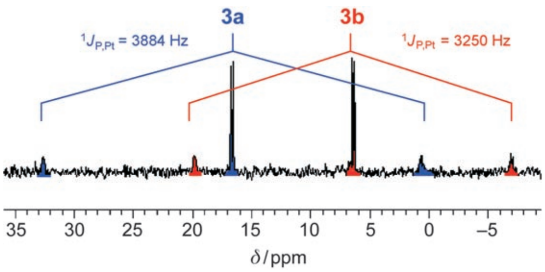


Figure 2. ^{31}P NMR spectrum (recorded at room temperature) of a 1:2:1 mixture of $K_2[PtCl_4]$, **1**, and **2** in D_2O after heating the sample for 15 min at 60 °C.

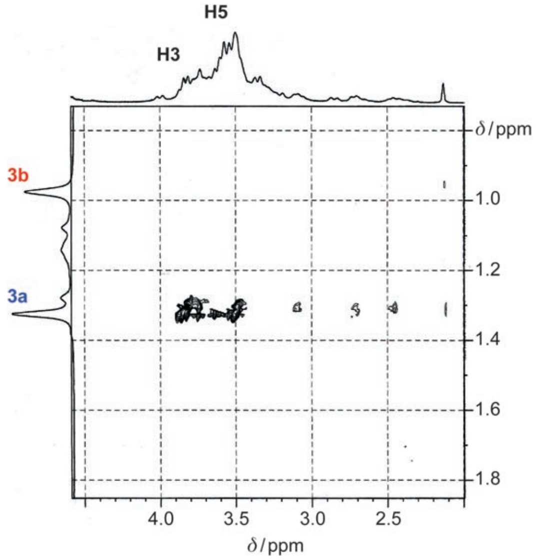


Figure 3. 2D T-ROESY partial spectrum at room temperature of **3** (10 mм) showing cross-peaks indicative of inclusion of **2** in **1**.

The resonance centered at $\delta = 8.17$ ppm (Figure 1, green peak) was attributed to the phosphane low-coordinated species **4**. Indeed, the two satellites ($\delta = 24.76$ and -8.43 ppm) of this signal revealed a $^{1}J_{P,Pt}$ coupling constant of 4040 Hz, characteristic of a phosphane located *cis* to a nitrogen center.[11] To confirm this attribution, **4** was precipitated from the initial mixture of **3**, **4**, and **5** (Scheme 2, Figure 1) by addition of methanol and analyzed by ^{31}P NMR spectroscopy (Figure 4). The resonance characteristic of the **1·2** supramolecular ligand that binds the platinum in a P,N bidentate mode was clearly identified.

It was also noticed that the ^{31}P NMR signals of **4** were shifted upfield compared to well-known previously described cationic complexes $[L_nPtCl]^+Cl^-$ ($L = PR_3$, $n = 2$ or 3), thus confirming a phosphane low-coordinated structure.[9] Similar trends have been reported previously and were attributed to the coordination of a nitrogen atom to the platinum.[14] Moreover, the presence of intense cross-peaks on the T-ROESY spectrum between *t*Bu protons and the inner protons of **1** confirmed the existence of the **1·2** supramolecular chelate assembly.

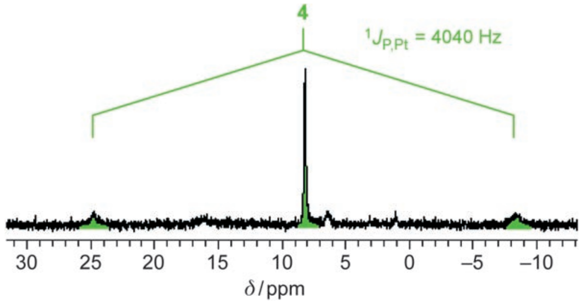
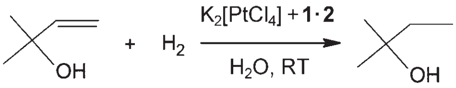


Figure 4. ^{31}P NMR spectrum (recorded at room temperature in D_2O) of the brown precipitate resulting from the addition of methanol to the initial mixture of **3**, **4**,and **5**.

The broad signal at $\delta = 14$ ppm (line width >200 Hz) in Figure 1 (violet peak) was attributed to **5** by comparison with previous data (see Supporting Information).[9] The $^1J_{P,Pt}$ coupling constant of 3755 Hz was characteristic of two phosphanes oriented *cis* to each other. One of the platinum-coordinated phosphanes was included in **1**, which consequently acted as a second-sphere ligand.[13] The broadening of the peak at $\delta = 14$ ppm is a consequence of the dynamic inclusion of **2** in the cavity of **1**[14] and also arises from chemical exchange of Cl^- for H_2O.[16]

Experiments were performed to evaluate the efficiency of the above-described coordination complexes as catalysts in the hydrogenation reaction of 2-methyl-3-buten-2-ol (Scheme 3). This substrate was chosen to avoid mass-transfer limitations and double-bond isomerization. First, ^1H NMR measurements were carried out to check that the reactant and the product of the hydrogenation reaction were unable to displace the phosphane from the CD cavity. Indeed, in the reverse case, the **1·2** supramolecular bidentate structure would be destroyed and the concept would be unusable. Thus, 2-methyl-3-buten-2-ol or 2-methylbutan-2-ol was successively mixed with aqueous solutions of **1·2** or a mixture of **3**, **4**, and **5**. As no variation in chemical shift could be detected, this clearly showed that the reactant and the product were unable to interact with those species and that the **1·2** supramolecular complex remained stable under the experimental conditions. Then, hydrogenation reactions were performed with various amounts of **2**. When **2** (2 equiv) was mixed with **1** (1 equiv) and $K_2[PtCl_4]$ (1 equiv), no reaction occurred (initial activity $<10\ h^{-1}$) regardless of the order in which the components were added. Conversely, when the brown precipitate that contained predominantly **4** was dissolved in water and used as a catalyst an initial activity of $2600\ h^{-1}$ was measured.



Scheme 3. Platinum-catalyzed hydrogenation of 2-methyl-3-buten-2-ol in water at room temperature with $K_2[PtCl_4]$ and **1·2** as catalyst.

In summary, the cyclodextrin–phosphane assembly constitutes a new class of supramolecular bidentate ligands. To our knowledge, the **1·2** supramolecular entity is the first water-soluble self-assembled P,N mixed donor described. Its chelating properties have been demonstrated on platinum and lead to three different coordination complexes. On the basis of these encouraging results, we are currently compiling a library of heterobidentate ligands to evaluate their performances in biphasic organometallic catalysis.

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