

## Cyclodextrins as Supramolecular Hosts for Organometallic Complexes

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### 1. Introduction to Cyclodextrins as Supramolecular Hosts

Native cyclodextrins are oligosaccharides composed of six or more D-glucopyranose residues attached by  $\alpha$ -1,4-linkages in a cyclic array. The most current cyclodextrins contain six, seven, or eight glucose residues and are named  $\alpha$ -cyclodextrin ( $\alpha$ -CD),  $\beta$ -cyclodextrin ( $\beta$ -CD), and  $\gamma$ -cyclodextrin ( $\gamma$ -CD), respectively (Figure 1).<sup>1</sup> The specific coupling of the glucose monomers gives a rigid conical molecular structure with a hollow interior of a specific volume (Table 1). This internal cavity, which is highly hydrophobic, can accommodate a wide range of guest molecules, ranging from polar compounds such as alcohols, acids, amines, and small inorganic anions to apolar compounds such as aliphatic and

aromatic hydrocarbons.<sup>2</sup> In all cases, the guest is bound at least partially, within the cavity of the CD. The driving forces for the inclusion complexation of CD with substrates are attributed to several factors such as van der Waals forces, hydrophobic interactions, electronic effects, and steric factors.<sup>3</sup>

The ability of CDs to include a part of an organometallic complex in their internal hydrophobic cavities has also been demonstrated by numerous researchers.<sup>4–11</sup> The inclusion generally modifies the chemical, electrochemical, and photochemical properties of organometallic compounds.

When the organometallic complex interacts with the CD, four types of adduct can be observed:

(i) The CD behaves as a second-sphere ligand, binding noncovalently the first-sphere ligands of the metal center as schematically represented in Figure 2a.

(ii) The CD acts simultaneously as a first- and second-sphere ligand. In fact, the CD is attached covalently to a ligand of the organometallic complex and includes another ligand of the complex into its cavity as depicted in Figure 2b.

(iii) The CD acts simultaneously as a first-sphere ligand and as a transient second-sphere ligand. In this case, the CD is covalently connected to a ligand of the organometallic complex and includes temporarily in its cavity a substrate that reacts with the organometallic complex (Figure 2c). This type of adduct is observed in catalytic processes conducted in one-phase or two-phase systems.

(iv) The CD can be considered as a transient second-sphere ligand when a hydrophobic substrate included into the CD cavity binds temporarily to a water-soluble organometallic catalyst (Figure 2d). Contrary to the above case, these adducts form only in catalytic processes conducted in an aqueous organic two-phase medium. Indeed, the presence of water is required to force inclusion of the substrate into the CD cavity.

The characteristics and the properties of these four types of adducts will be separately discussed. We shall restrict ourselves to studies in which at least one direct metal–carbon bond is formed in organometallic supramolecular systems that have been well-identified or are strongly suspected of

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Sébastien Tilloy was born in 1972 in Douai (North, France). He received his Ph.D. degree in 1998 from the University of Artois under the supervision of Professor Monflier. In 2000, he became Maître de Conférences at the University of Artois, where he completed his Habilitation in 2004. In 2005, he spent six months in a postdoctoral position at the University of Amsterdam (Netherlands) with Professor Piet van Leeuwen and Dr. Joost Reek. His research interests are centered on the cyclodextrins and more specifically on their implications in the fields of water-soluble organometallic catalysis and targeted delivery of drugs.

existing. We will discuss neither situations where the cyclodextrins were used more as a scaffold than as true hosts nor metalocyclodextrins where the metal was coordinated by heteroatoms (atoms different from carbon and hydrogen). For more information about these topics, the reader should refer to previous reviews.<sup>12–15</sup> Moreover, much attention will be devoted to the applications of these supramolecular materials.

## 2. Cyclodextrins as Second-Sphere Ligands

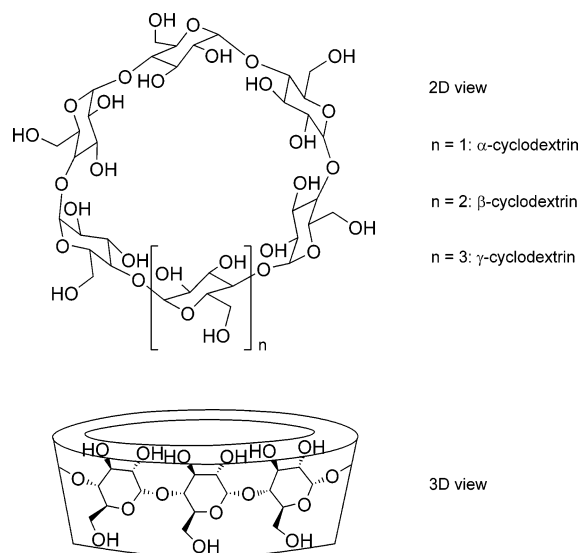
### 2.1. Organometallic Complexes Bearing Cyclopentadienyl and/or $\eta^6$ -Arene Ligands

#### 2.1.1. Adducts with Sandwich Complexes

**2.1.1.1. Ferrocenyl Derivatives.** *2.1.1.1.1. Structures Determination.* The first examples of second-sphere coord-



Eric Monflier was born in Boulogne sur Mer (France) in 1966. He graduated from Ecole Nationale Supérieure de Chimie de Lille (ENSCL) and received his Ph.D. degree from the University of Lille in 1992 under the supervision of Professor F. Petit in the field of organometallic chemistry and homogeneous catalysis. In 1992, he became Maître de Conférences at the University of Artois, where he set up an independent research group working on aqueous phase organometallic catalysis. In 1995, he received his Habilitation, and he was promoted Professor in 1996. His current research interests are mainly in the field of supramolecular catalysis and catalysis in multiphase systems. He has played a key role in the development of efficient supramolecular mass transfer promoters for aqueous organometallic catalysis.



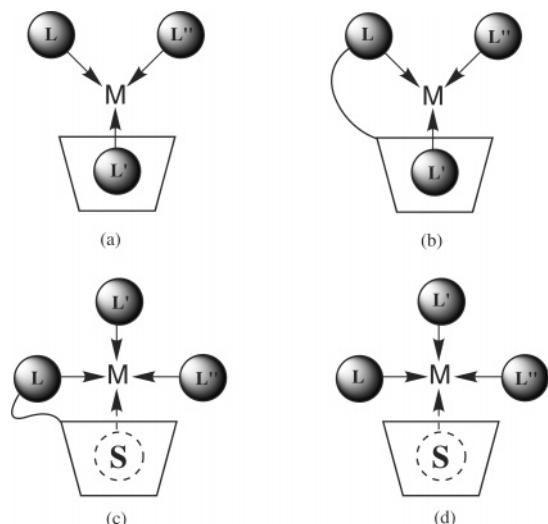
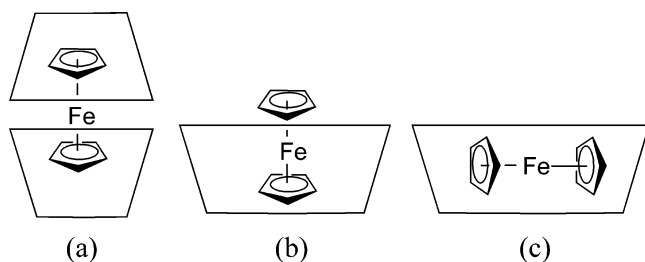
**Figure 1.**

dination adducts between a CD and organometallic complexes were observed with ferrocene (Fc) and its derivatives. Thus, Breslow was the first to report in 1975 that Fc forms a 1:1 adduct with  $\beta$ -CD in both *N,N*-dimethylformamide and dimethyl sulfoxide.<sup>16</sup> Nevertheless, the first crystalline inclusion complexes of Fc and its derivatives were prepared by Harada and Takahashi in 1984.<sup>17</sup> The inclusion complexes were obtained by direct addition of crystals of Fc or its derivatives into aqueous solutions of CD.

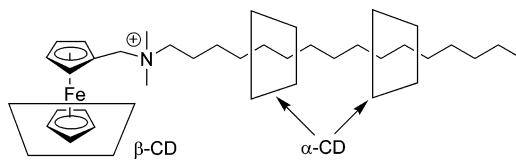
The second-sphere coordination adducts between native or chemically modified CD and Fc or its derivatives have been the subject of numerous studies using a wide range of techniques, among which induced circular dichroism was the first to establish the stoichiometry of the inclusion complexes.<sup>18–21</sup> Three structures were proposed for these adducts as shown in Figure 3.<sup>22–24</sup> The stoichiometry of the Fc–CD complexes was found to be dependent on the sizes of the CDs.  $\beta$ -CD and  $\gamma$ -CD formed 1:1 stoichiometric inclusion

**Table 1. Parameters of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Cyclodextrins (CDs)**

	$\alpha$ -CD	$\beta$ -CD	$\gamma$ -CD
glucose residues	6	7	8
molecular weight	973	1135	1297
cavity diameter (Å)	4.7–5.3	6–6.6	7.5–8.3
cavity height (Å)	7.9	7.9	7.9
cavity volume (mL/mol)	174	262	472

**Figure 2.****Figure 3.**

complexes whereas  $\alpha$ -CD formed a 2:1 (CD–guest) complex with Fc. Even if other studies on complexes of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD with acylferrocenes ( $C_5H_5FeC_5H_4-COR$ ,  $R = H, CH_3, CF_3$ ;  $XC_5H_4FeC_5H_4Y$ ,  $X = Y = COCH_3$ ,  $X, Y = COCH_2-CH_2, COCH_2CO$ ) showed that the signs of the Cotton effect exhibited no simple correlation with the proposed geometry,<sup>25</sup> the orientation of Fc in the CD cavity was definitely confirmed by comparing the induced circular dichroism spectrum of a hindered Fc derivative (1,4,7,10,13-pentaoxa-[13]ferrocenophane) for which an equatorial inclusion is only possible in the presence of  $\beta$ -CD with that of Fc in  $\beta$ -CD or  $\gamma$ -CD.<sup>26</sup> Indeed, it has been unambiguously demonstrated that the orientation of Fc in  $\beta$ -CD is considered to be nearly parallel to the molecular axis of  $\beta$ -CD while that of Fc appears to be close to normal to the molecular axis of the  $\gamma$ -CD.<sup>27</sup> However, it should be noticed that calculations on the  $\beta$ -CD–Fc adduct indicate that Fc can adopt both axial and equatorial orientations in the  $\beta$ -CD cavity.<sup>28</sup> Both <sup>13</sup>C spin–lattice relaxation time ( $T_1$ ) measurements and polarimetry studies evidenced a change in conformation of  $\beta$ -CD by inclusion of Fc.<sup>29</sup> Strong interactions of Fc and its derivatives with  $\beta$ -CD and  $\gamma$ -CD have been observed whereas  $\alpha$ -CD complexes were much more dissociated in solution, as proved by the addition of chromium(III) tris-(2,4-pentanedionate), which caused the  $T_1$  to fall dramatically due to the domination of paramagnetic relaxation over the

**Figure 4.**

dipole–dipole mode.

Cyclic voltammetry was also the technique of choice for studies on Fc–CD interactions.<sup>30–37</sup> As an example, a bimodal CD complexation of Fc derivatives containing  $n$ -alkyl chains of varying length has been evidenced by cyclic voltammetry and <sup>1</sup>H NMR spectroscopy.<sup>38</sup> The results suggest that  $\beta$ -CD and  $\gamma$ -CD interact with the Fc subunit, while  $\alpha$ -CD binds long alkyl chains containing guests by threading their aliphatic moieties through its cavity. Thanks to this dual mode of CD binding, a mixture of ferrocenylammonium derivatives containing 16 methylene groups,  $\alpha$ -CD, and  $\beta$ -CD resulted in the isolation of a quaternary complex exhibiting the stoichiometric ratio 1:2:1 (Figure 4). These results were confirmed by calorimetric results which clearly indicate that the complexation of several alkyldimethyl(ferrocenylmethyl)ammonium cations by the hosts  $\alpha$ - and  $\beta$ -CD in aqueous media is enthalpically driven.<sup>39</sup> Interestingly, the presence of urea considerably diminishes the enthalpic stabilization of the trimethyl(ferrocenylmethyl)ammonium cation– $\beta$ -CD complex by improving solvation of the aromatic surfaces of the guest in a similar way to that urea exerted on proteins. The existence of specific interactions between urea molecules and aromatic surfaces resulted from a balance between opposing enthalpic and entropic contributions, as evidenced by flow calorimetry measurements in aqueous media on a series of carboxylate and quaternary ammonium Fc derivatives in the presence and in the absence of large concentrations of urea.<sup>40</sup> Note that 1:1 complexes of Fc and several Fc derivatives containing  $n$ -alkyl chains of varying length with  $\alpha$ -CDs and  $\beta$ -CDs have also been characterized by electrospray mass spectroscopy.<sup>41</sup>

Cyclic voltammetry also helped characterize a 2:1 inclusion complex formed by a tetracarbonyl molybdenum complex bearing the diimine ligand  $N,N'$ -bis(ferrocenylmethylene)ethylenediamine immobilized in permethylated  $\beta$ -CD by addition of the guest to a solution of the host in dichloromethane. Upon encapsulation, strong interactions between the CD host and the Fc subunit occur, leading to a decrease in the influence of the  $M(CO)_4$  fragment on the overall Fc properties.<sup>42</sup>

The association constant of Fc with  $\beta$ -CD was determined in various solvents and was found to be  $60 M^{-1}$  in DMSO by cyclic voltammetry,<sup>43</sup>  $320 M^{-1}$  in 20% aqueous DMSO by the same technique,<sup>43</sup> and  $1.65 \times 10^4 M^{-1}$  in water by solubility measurements.<sup>44</sup> Thermogravimetric measurements demonstrated that complexes of  $\alpha$ - and  $\beta$ -CD with Fc are thermally stable and do not liberate Fc on heating at 100 °C in vacuo.<sup>24,45</sup> Nevertheless, Teixeira-Dias et al. reported on an instable 2:1 (host to guest) complex between  $\beta$ -CD and (1,1'-ferrocenediyl)dimethylsilane that rapidly evolved to a complex in which a  $\beta$ -CD is covalently grafted with the ferrocenyl moiety as shown in Figure 5.<sup>46</sup> The formation of the  $\beta$ -CD bearing a ferrocenyl group was explained by a nucleophilic attack of one of the  $\beta$ -CD hydroxyl groups on the strained C–Si–C bridge of the organometallic complex. By contrast, no reaction with the  $\beta$ -CD occurred for the unstrained diferrocenyldimethylsilane Fc–SiMe<sub>2</sub>–Fc. A 2:1



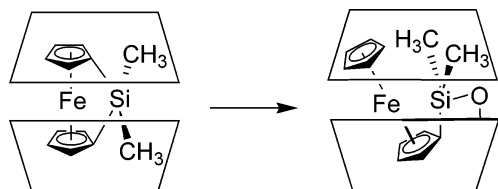


Figure 5.

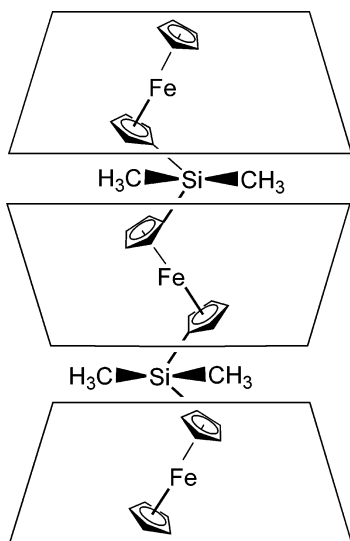


Figure 6.

host-guest inclusion complex was obtained in that case.<sup>47</sup> Oligo(ferrocenylsilane) trimer  $\text{FcSiMe}_2[(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2)]\text{Fc}$  also led to a 2:1 stoichiometry characterized by a tilted inclusion of the ferrocenyl subunits in the  $\beta$ -CD cavity ( $\varphi = 29^\circ$ ).<sup>48</sup> Concurrently, the inclusion of these trimeric species in  $\gamma$ -CD has been reported.<sup>49</sup> Of particular interest is the fact that  $\text{FcSiMe}_2[(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)]\text{Fc}$  formed a 3:1 complex with channel-type packing in the solid state. The obtained hybrid organic-organometallic pseudo-(poly)rotaxane structures appear to be good models for the corresponding higher oligo(ferrocenylsilanes) and even poly(ferrocenylsilanes) (Figure 6).

Solid state  $^2\text{H}$  NMR spectroscopy experiments<sup>50</sup> and reports on the inclusion compound formed between Fc and  $\beta$ -CD<sup>51-53</sup> indicated that inclusion into the cavity altered the dynamics in the solid state of the guest molecule compared to that observed for pure compound. In particular, spin lattice relaxation time measurements, rotating frames, and second moment analysis have been used to investigate molecular motions in  $\beta$ -CD and its solid inclusion complexes with Fc, [3]-ferrocenophane-1,3-dione, and ruthenocene.<sup>54</sup> In all complexes, up to six different molecular motions were observed, including reorientational jumps of  $\text{H}_2\text{O}$  molecules included within the CD framework, rotation of the  $\text{CH}_2\text{OH}$  group around the C-C bond, reorientation of  $\text{H}_2\text{O}$  molecules located within the  $\beta$ -CD host lattice, and proton transfer along the H-bond. The interactions between  $\alpha$ -CD and Fc have also been studied in the solid state. The exact crystal structure of the  $\alpha$ -CD-Fc inclusion compound has been fully determined by a X-ray analysis, which shows that the Fc molecule is encapsulated by the dimer of the  $\alpha$ -CD in a tail-to-tail orientation and inclined by  $42^\circ$  relative to the 6-fold axes of the  $\alpha$ -CD of the dimer.<sup>55</sup> Mössbauer spectroscopy revealed a reorientation of Fc and some of its ring-substituted derivatives with  $\alpha$ -CD.<sup>56</sup> In that case, activation energies for the reorientation increase with an increase in size of the

substituents on the cyclopentadienyl rings of the guests molecules. Recently, the single crystal of a  $\beta$ -CD-Fc (4:5 stoichiometry) inclusion complex was prepared by hydrothermal treatment, showing that four of the five Fc's were included in the cavities of four  $\beta$ -CDs along the axial orientation of the tetramer, while another was coincided between two  $\beta$ -CDs from the equatorial orientation.<sup>57</sup>

The  $\text{Fc}^+$  oxidized form of Fc and its interactions with CDs have also been the subject of numerous investigations. For example, a  $^1\text{H}$  NMR study revealed that  $\beta$ -CD stabilizes Fc with respect to the  $\text{Fc}^+$  ions about 2-4 times more effectively than does  $\alpha$ -CD and 2-6 times more effectively than does  $\gamma$ -CD.<sup>58</sup>  $^1\text{H}$  NMR line broadening measurements also showed that the electron self-exchange rate for ((trimethylamino)-methyl) $\text{Fc}^+/\text{Fc}$  in  $\text{D}_2\text{O}$  as solvent is decreased by ca. 20-50-fold in the presence of excess  $\beta$ -CD.<sup>59</sup> The selective hydrophobic encapsulation of Fc leads to a coupling of electron transfer to host (CD) transfer which decreases the self-exchange rate by increasing the thermal activation barrier. A redox asymmetry effect upon the isolated electron transfer event is believed to be responsible for the increase in the activation barrier. The same observations have been made for Fc-monocarboxylate anion and bisferrocenyl cationic complexes whose rate constants for the oxidations substantially decrease upon inclusion in native  $\beta$ -CD or modified CDs.<sup>60-62</sup> The decreased reactivities of the inclusion complexes are attributed to decreased thermodynamic driving forces and steric hindrance to the approach of the oxidant. A systematic electrochemical study of Fc,  $\text{Fc}^+$ , and other mono- and disubstituted Fc derivatives with different  $\beta$ -CDs (heptakis(2,6-di-*O*-methyl)- $\beta$ -CD; heptakis(2,3,6-tri-*O*-methyl)- $\beta$ -CD (= permethylated- $\beta$ -CD); 2-hydroxypropyl- $\beta$ -CD; sulfated- $\beta$ -CD) in mixed organic-aqueous media clearly demonstrated that the formation constants ( $K_f$ ) of the supramolecular complexes greatly depend on the organic cosolvent, the difference of substituents on Fc, and the type of CDs.<sup>63</sup> Increasing the steric bulk and the rigidity of Fc substituents generally leads to a decrease in the  $K_f$  values, consistent with an axial inclusion of Fc into the CD cavity and the substituent protruding out. NMR and conductometry responses of  $\text{Fc}^+$  solution in the presence of CD confirm that  $\text{Fc}^+$  is not significantly included in the  $\beta$ -CD cavity. Nevertheless, the binding interaction between  $\text{Fc}^+$  and the sulfated CD is higher than that with neutral Fc, probably due to the presence of  $-\text{SO}_3^-$  functionalities. Similarly, the interplay between the sidearm anion of the mono[6-deoxy-6-(2-butenedinitrile-2,3-dimercapto sodium salt)]- $\beta$ -CD and a ferrocenium drug revealed a charge transfer between the cyclodextrin and the guest.<sup>64</sup>

**2.1.1.1.2. Applications of Cyclodextrin-Ferrocene Complexes.** Interaction between Fc and CD has been used to elaborate mediators and molecular sensors<sup>65,66</sup> or to assist organic reactions such as asymmetric inductions<sup>67,68</sup> or condensation reactions.<sup>69</sup> In particular, the influence of complexation between Fc derivatives and  $\beta$ -CD has been investigated in the electrocatalytic oxidation of NADH.<sup>70</sup> As shown by a cyclic voltammetric study on a microdisk electrode, the presence of  $\beta$ -CD blocks the electrocatalytic reaction, probably because of a rapid complexation of acetylferrocenium with  $\beta$ -CD. As another example, a voltammetric study of the effect of the  $\alpha$ - and  $\beta$ -CDs on the mediator abilities of water-soluble ferrocenes  $\text{FcCOOH}$  and  $\text{FcCH}_2\text{NH}^+\text{Me}_2$  has been performed for the glucose oxidase-catalyzed oxidation of D-glucose. The complexation of these

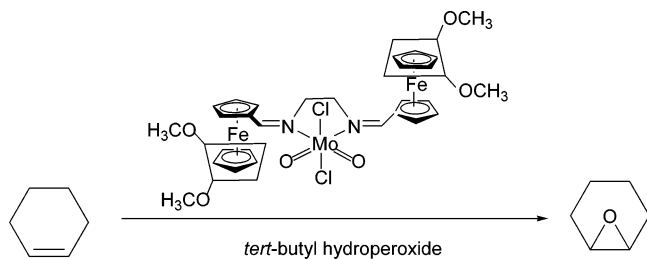


Figure 7.

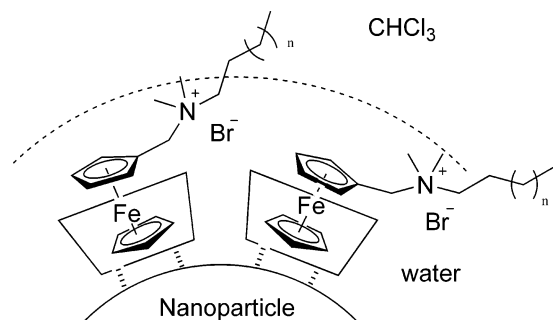


Figure 8.

organometallic mediators with the host molecules strongly affects the electrochemical response, whose significant amplification suggests the creation of simple biosensors for cyclodextrins.<sup>71</sup>

Interestingly, the ability of Fc to bind strongly to  $\beta$ -CD has also been exploited to investigate the suitability of  $\beta$ -CD as a model in the field of enzyme mimetic chemistry. Impressive rate accelerations were observed in the presence of  $\beta$ -CD during the hydrolysis of some ferrocenylacrylate esters.<sup>72–75</sup> For instance, the hydrolysis of *p*-nitrophenyl ester was found to be  $\sim 10^7$ -fold higher than that of the ethyl ester when complexed with  $\beta$ -CD.<sup>75</sup> Computational studies have shown that the huge difference in rates cannot be attributed to structural or steric differences but is directly connected with the formation of a highly strained acyl CD that adversely affects the partitioning of the tetrahedral intermediate toward products unless the substrate has a particularly good leaving group.<sup>76,77</sup>

Recently, catalytically active second-sphere coordination adducts have been prepared in dichloromethane by Gonçalves et al. Thus, a dioxomolybdenum(VI) complex bearing the diimine ligand *N,N'*-bis(ferrocenylmethylene)ethylenediamine encapsulated within the cavity of permethylated  $\beta$ -CD catalyzed with high selectivity the liquid-phase epoxidation of cyclooctene using *tert*-butyl hydroperoxide as the oxidant (Figure 7).<sup>78</sup> The same authors also reported that the methyltrioxorhenium(VII) complexed by a 4-ferrocenylpyridine- $\beta$ -CD adduct was not effective as a catalyst for the epoxidation of cyclooctene by hydrogen peroxide due to its poor solubility in the reaction medium.<sup>79</sup>

The strong affinity of Fc derivatives for the  $\beta$ -CD was also used to modify the surface of CD capped nanoparticles.<sup>80,81</sup> Thus, Kaifer et al. showed that hydrophilic  $\beta$ -CD capped nanoparticles can be solubilized in chloroform by adding cationic Fc's that have long aliphatic chains, as schematically represented in Figure 8.<sup>82</sup> Through a series of solubility experiments, it has been proved that the presence of a water thin layer surrounding the surface particles was required to stabilize the CD-Fc inclusion complexes. Flocculation of gold nanoparticles has also been achieved by the same author using a dimeric Fc guest (Figure 9).<sup>83</sup>

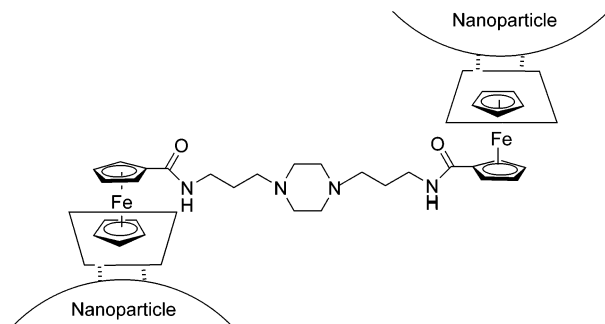


Figure 9.

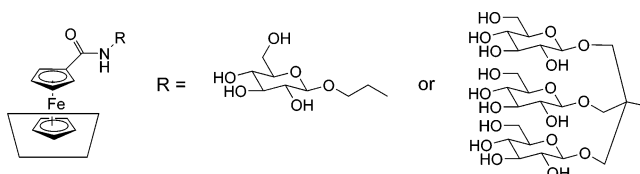


Figure 10.

Flocculation properties in this system were controlled through host-guest interactions. For instance, competitive binding of a monomeric Fc guest resulted in partial redissolution of the precipitated aggregates.

Dendrimers with 4, 8, and 16 Fc peripheral residues and their interactions with  $\beta$ -CD have been investigated as well.<sup>84</sup> Compounds with 16 Fc peripheral residues showed the lowest solubility in  $\beta$ -CD containing aqueous solution, suggesting that steric hindrance due to the increased proximity of Fc subunits prevents full complexation by the 16  $\beta$ -CD hosts. Unsymmetric dendrimers containing only one Fc unit have been synthesized to investigate the effect of dendrimer growth and shape on the  $\beta$ -CD complexation.<sup>85</sup> Results showed that increasing dendrimer growth inhibits binding of  $\beta$ -CD to the ferrocenyl dendrimer. Similar results were reported with ferrocenyl glycodendrimer, whose carbohydrate branches shielded the Fc core from solvent interaction and consequently greatly affect the electrochemical properties of Fc (Figure 10).<sup>86</sup> The system can be compared to proteins containing a redox active unit in their polypeptidic framework.

Interestingly, Fc derivatives interact with highly ordered monolayers of  $\beta$ -CD modified with seven thioether moieties.<sup>87</sup> Measurements of the thermodynamics of the complexation of ferrocenemethanol in such monolayers yielded a complexation constant of  $9.9 \times 10^3 \text{ M}^{-1}$  and a  $\Delta G^\circ$  of  $-5.4 \text{ kcal/mol}$ . A monolayer composed of cationic Fc was found to bind with  $\beta$ - and  $\gamma$ -CD.<sup>88</sup> The CD hosts are believed to interact with the monolayer assembly in two ways: by inclusion of the Fc moiety within the CD cavity and, surprisingly, by interactions between the counterions and hydrophilic CD. The host-guest equilibrium involving the redox guest 11-(ferrocenylcarbonyloxy)undecanethiol (FcSH) in a self-assembled monolayer (SAM) on gold electrode surfaces and a  $\beta$ -CD host in solution has been investigated by cyclic voltammetry.<sup>89</sup> Stability constants for the inclusion complexes of  $\beta$ -CD and the ferrocenyl or ferricenium forms of the FcSH-SAMs have been evaluated as  $3.6 \times 10^4$  and  $3.2 \times 10^4 \text{ M}^{-1}$ , respectively.

Host films of condensation polymers of  $\beta$ -CD and of carboxymethylated  $\beta$ -CD have been used to evaluate the molecular inclusion equilibria accompanying Fc and ferrocenecarboxylic acid electrode charge transfer.<sup>90</sup> Depending on the pH, the oxidation product of the ferrocenecar-

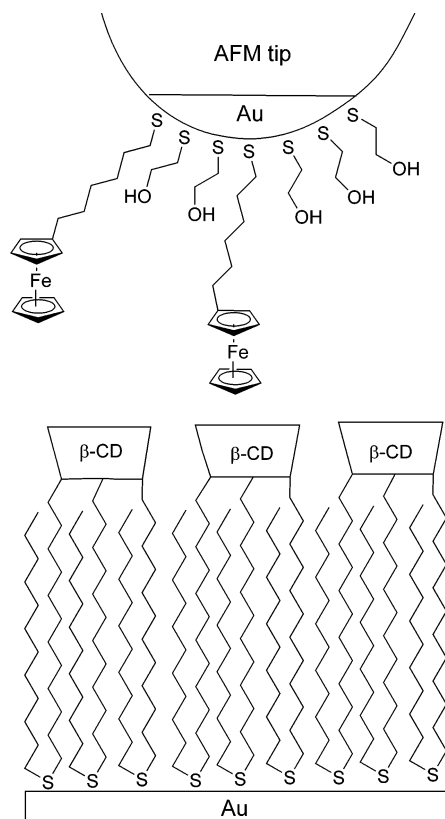


Figure 11.

boxylic acid is partially released from the  $\beta$ -CD polymer film or precipitates inside the film. The interaction between Fc moieties immobilized in mixed SAMs (2-hydroxyethanethiol and 6-ferrocenylhexanethiol (1–2%)) on AFM tips and SAMs of  $\beta$ -CD heptasulfide receptor adsorbed on Au(111) can be resolved by dynamic single molecule force spectroscopy (Figure 11).<sup>91,92</sup> The analysis showed that AFM measurements can be used to obtain characteristic rupture forces for host–guest complexes, even under conditions where the kinetics of binding is rapid on the AFM time scale.

A recent study has shown that carboxymethyl  $\beta$ -cyclodextrin can be efficiently intercalated into Mg–Al double hydroxide layers by ion exchange of the interlayer nitrate anions.<sup>93</sup> Neutral Fc molecules can then be included within CD cavities. These organometallic–organic–inorganic nano-hybrid materials are able to separate hydrophobic and hydrophilic derivatives of Fc by preferential partitioning of the latter.

**2.1.1.2. Other Derivatives.** As observed with Fc, the complex  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)_2]\text{PF}_6$ <sup>94</sup> forms 2:1 inclusion complexes with the  $\alpha$ -CD. The  $\alpha$ -CD molecules are arranged head-to-head to form a dimer. The cation is encapsulated within the cavity of the dimer, while the  $\text{PF}_6^-$  anion is located outside the cavities. The complex cation is tilted against the mean planes of the oxygen atoms of the 12 secondary hydroxyl groups of the  $\alpha$ -CD molecules by angles of 42/43°. The thermodynamics parameters for association of Fc, ruthenocene, and osmocene in ethylene glycol in the range 25–90 °C were determined by Sokolov et al. using circular dichroism. The association constants were found to be 510, 660, and 790  $\text{M}^{-1}$  for Fc, ruthenium, and osmium compounds, respectively.<sup>95,96</sup> The same author reported that  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2]$  has high mobility within the  $\beta$ -CD cavity, undergoing rapid isotropic rotation ( $E_a = 43.2 \text{ kJ}\cdot\text{mol}^{-1}$ ). At low temperatures, reorientation of the cyclopentadienyl

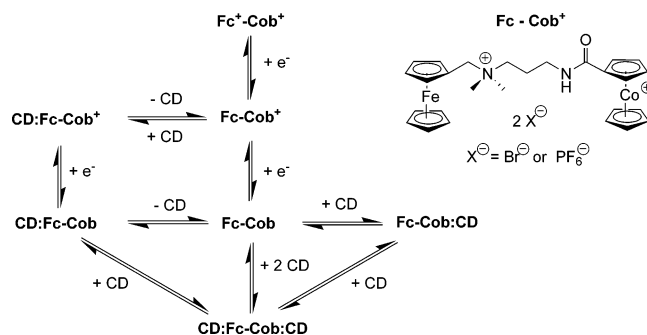


Figure 12.

rings was also observed.<sup>54</sup> It was found that inclusion of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2]$  in  $\beta$ -CD cavity slowed the oxidation of ruthenocene by iodine.<sup>97</sup> Nevertheless, the <sup>13</sup>C NMR MAS spectrum revealed that longer exposure to iodine vapor induces the formation of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ . Matsue et al. reported that the retention of radionuclides formed by irradiation of  $\beta$ -CD–metallocenes inclusion compounds decreases in the order Fe > Ru > Os. After the reaction, the metals are found as metallocenes.<sup>98–100</sup> Metallocenes are considered as rocket materials,  $\beta$ -CD as a canon, and nuclear recoil induced by nuclear reaction as an energy source (rocket fuel).

The separation of racemates of planar–chiral cyclopentadienyl rhodium complexes into enantiomers can be achieved by liquid chromatography using aqueous  $\beta$ -CD as a mobile phase.<sup>101</sup> The origin of this separation was attributed to the formation of an inclusion compound between the CD and the rhodium complex.

The utilization of electrochemical (redox) conversions to modulate the strength of host–guest interactions has been widely described.<sup>11</sup> As an example, though the positively charged cobaltocenium  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$  does not interact appreciably with the  $\beta$ -CD, it has been found that its reduced form, i.e., the cobaltocene, forms a stable 1:1 inclusion complex with the  $\beta$ -CD.<sup>102</sup> This “electrochemical activation” has been used by Kaifer et al. to bind  $\beta$ -CD to a series of poly(propyleneimine) dendrimers containing 4, 8, and 16 cobaltocenium units.<sup>103</sup> The same author has also shown that a 1:1 inclusion complex between cobaltocene and  $\beta$ -CD can be obtained when the reduction of a strong 1:2 complex between cobaltocenium and the octaanionic form of calix-[6]arene hexasulfonate is performed in the presence of  $\beta$ -CD.<sup>104</sup>

Mixed cobaltocenium–Fc heterobimetallic complexes and  $\beta$ -CD were investigated by electrochemistry.<sup>105</sup> The two metallocene subunits were connected either by a cationic ammonium group or by uncharged amide functions (Figure 12). Cyclic voltammetric experiments revealed that the inclusion process depended on the oxidation states of the Fc and cobaltocene subunits. The oxidized forms were not bound whereas the reduced ones form stable inclusion complexes. This supramolecular interaction constitutes an example of a three-state, host–guest system under redox control.

Recently, Turel et al. have reported that titanocene dihalides of formula  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiX}_2]$  (X = F, Cl) can form second-sphere coordination adducts with the  $\beta$ -CD and  $\gamma$ -CD. Changes in the NMR spectra suggested a shallow penetration of the titanocene into the  $\beta$ -CD cavity and a deeper penetration in the case of the  $\gamma$ -CD.<sup>106</sup> From the NMR data, the authors assume that  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{H}_2\text{O})(\text{Cl})]^+$  and  $[(\eta^5\text{-$



$C_5H_5)_2Ti(H_2O)_2]^{2+}$  are the species incorporated in the CD cavity when the starting material is  $[(\eta^5-C_5H_5)_2TiCl_2]$  and that cleavage of the cyclopentadienyl–titane bond occurs partially in the case of  $[(\eta^5-C_5H_5)_2TiF_2]$ . Contrary to the case of  $[(\eta^5-C_5H_5)_2TiCl_2]$ , Gonçalves et al. have reported that the analogous molybdenum complex  $[(\eta^5-C_5H_5)_2MoCl_2]$  is the species incorporated in the  $\beta$ -CD cavity rather than the hydrolysis products  $[(\eta^5-C_5H_5)_2Mo(H_2O)(Cl)]^+$  and  $[(\eta^5-C_5H_5)_2Mo(H_2O)_2]^{2+}$ .<sup>107</sup> The existence of a true 1:1 inclusion complex was proved by using a combination of solid-state physical methods and ab initio calculations. The potential antiproliferative and cytotoxic activities of inclusion complexes between  $[(\eta^5-C_5H_5)_2MoCl_2]$  and the permethylated  $\beta$ -CD or the 2-hydroxypropyl- $\beta$ -CD were also evaluated.<sup>108</sup> The inclusion complex with the permethylated  $\beta$ -CD was the most effective antiproliferative and cytotoxic agent, exhibiting a 60%, hardly reversible, viability decrease in adenocarcinoma and low toxicity toward healthy cells.

### 2.1.2. Adducts with Mixed Sandwich Complexes

Contrary to the cases of the sandwich complexes, the formation of second-sphere coordination adducts between CD and mixed sandwich complexes has been scarcely studied. The first example of a structurally characterized adduct of CD and such complexes was reported by Klingert and Rihs in 1990.<sup>109</sup> As shown by elemental analysis and  $^1H$  NMR spectroscopy, the mixed sandwich complex  $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_6)]PF_6$  formed crystalline 2:1 (host–guest) inclusion complexes with the  $\alpha$ -CD and the  $\beta$ -CD. It should be noticed that this stoichiometry is in contrast to that of the structurally related neutral Fc molecule, which forms a 2:1 adduct with  $\alpha$ -CD but a 1:1 adduct with the  $\beta$ -CD. The crystal structure of the  $\alpha$ -CD adduct has been determined by single-crystal X-ray diffraction. In the crystal, two  $\alpha$ -CDs form a head-to-head dimer by means of intermolecular hydrogen bonding across the secondary hydroxyl faces of adjacent  $\alpha$ -CD monomers. The  $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_6)]^+$  cation is encapsulated within the cavity and is tilted by an angle of  $39^\circ$  ( $C_5H_5$ )/ $40^\circ$  ( $C_6H_6$ ) against the mean planes of the  $\alpha$ -CD molecules. The complex  $[Ru(\eta^5-C_5H_5)(\eta^6-C_6H_6)]PF_6$  formed a 2:1 inclusion complex with  $\alpha$ -CD, as observed with the complex  $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_6)]PF_6$ .<sup>110</sup> The  $\alpha$ -CD molecules are arranged head-to-head to form a dimer. The cation is encapsulated within the cavity of the dimer and tilted against the mean planes of the oxygen atoms of the 12 secondary hydroxyl groups of the  $\alpha$ -CD molecules by angles of  $36^\circ$ . Finally, the formation of inclusion complexes between CDs and a range of cyclopentadienyl(arene)iron(II) sandwich and (tetramethylcyclobutadiene)cobalt complexes has also been reported by Klingert and Rihs.<sup>111</sup>

### 2.1.3. Adducts with Half-Sandwich Complexes

The first example of half-sandwich complexes interacting with CD was reported by Harada in 1985.<sup>112,113</sup> A range of ( $\eta^6$ -arene) chromium tricarbonyl complexes has been shown to form crystalline adducts with the  $\beta$ -CD and  $\gamma$ -CD, with the aromatic ring of the complex being bound within the cavity of the CD (Figure 13). The formation of the inclusion compounds was selective.  $\beta$ -CD formed 1:1 inclusion compounds with benzene, toluene, and *o*-xylene chromium tricarbonyl complexes, and not with *m*-xylene, *p*-xylene, guaiacol, methyl anthranilate mesitylene, or hexamethylbenzene chromium tricarbonyl complexes.<sup>113,114</sup> Whereas  $\alpha$ -CD did not form inclusion complexes with any arene chromium

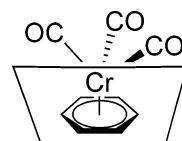


Figure 13.

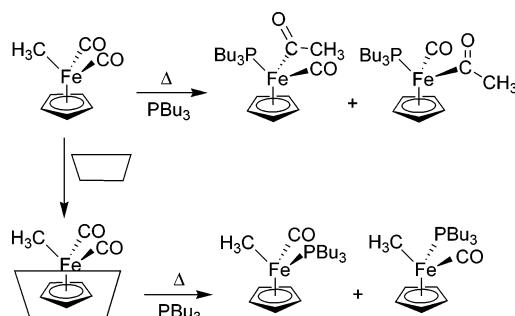


Figure 14.

complexes,  $\gamma$ -CD formed 1:1 inclusion complexes with all arene chromium complexes tested. Interestingly, the  $^{13}C$  CP/MAS NMR spectrum of a crystalline sample of the  $[(\eta^6-C_6H_6)_2Cr(CO)_3]/\beta$ -CD inclusion compound is strictly analogous to the spectrum obtained in solution, indicating that the carbonyl moiety rotates freely along its principal coordination axis.<sup>115</sup>

In 1991, Harada et al. also reported the first example of half-sandwich iron complexes encapsulated by CD.<sup>116</sup> The authors communicated the preparation of inclusion compounds between native CDs and the  $[(\eta^5-C_5H_5)Fe(CO)_2(CH_3)]$  complex and reported that the included complexes insert carbon monoxide and sulfur dioxide into the Fe–R bond in the solid state. The trend observed for insertion activity was  $\gamma$ -CD >  $\beta$ -CD  $\gg$   $\alpha$ -CD, showing that CD is capable of controlling the activity of the alkyl iron complex. The reactivity of the included iron complex was also observed by Welker et al.<sup>117</sup> Whereas the complexes  $[(\eta^5-C_5H_5)Fe(CO)_2(CH_3)]$  and  $[(\eta^5-(CH_3)C_5H_4)Fe(CO)_2(CH_3)]$  normally participate in CO insertion/alkyl migration reactions when they are heated in the presence of phosphines, the inclusion compounds of these complexes participated in ligand substitution reactions with no CO insertion/alkyl migration products when heated with phosphines, as shown in Figure 14. This result was attributed to a slowing down of the alkyl migration rate due to ligand–cyclodextrin steric interactions. Unfortunately, it was found that this ligand substitution reaction was not enantioselective. Under electrochemical conditions, the reactivity of the  $[(\eta^5-C_5H_5)Fe(CO)_2(CH_3)]$ - $\beta$ -CD inclusion complex was different. Thus, Pospisil et al. have reported that the  $[(\eta^5-C_5H_5)Fe(CO)_2(CH_3)]$ - $\beta$ -CD inclusion complex undergoes a CO insertion into the methyl–metal bond.<sup>118</sup> In the presence of free CO, an enhanced rate of acyl migration from the metal center to the cyclopentadienyl ligand was even observed. Qualitative  $^1H$  NMR experiments have revealed that  $[(\eta^5-C_5H_5)Fe(CO)_2NH_3]PF_6$  formed adducts with  $\alpha$ -CD and  $\beta$ -CD.<sup>8,119</sup> The formation of inclusion compounds between CD and various mononuclear half-sandwich complexes of iron, i.e.,  $[(\eta^5-C_5H_5)Fe(L)_2X]$  ( $X = Cl, I; L = CO, dppe$ ) and  $[(\eta^5-C_5H_5)Fe(L)_2L']PF_6$  ( $L' =$  neutral donor ligand), and one binuclear complex,  $[(\eta^5-C_5H_5)(dppe)Fe]_2-\mu-CN]PF_6$ , was investigated by Diaz et al.<sup>120,121</sup> A 1:1 stoichiometry for the inclusion compounds containing mononuclear organometallic complexes and a 2:1 stoichiometry for the inclusion compound

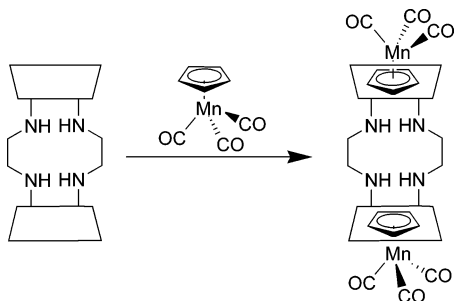


Figure 15.

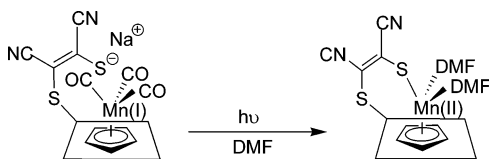


Figure 16.

containing the binuclear organometallic complex have been found. Interestingly, the inclusion compounds  $[(\eta^5\text{-C}_5\text{H}_5)\text{-}(\text{dppf})\text{Fe-NCCCH}_3]\text{PF}_6\text{-}\gamma\text{-CD}$  and  $[(\eta^5\text{-C}_5\text{H}_5)(\text{dppm})\text{Fe-NCCCH}_3]\text{PF}_6\text{-}\gamma\text{-CD}$  exhibited an unusual laminar structure. The synthesis of a 1:1 adduct between the  $\beta\text{-CD}$  and various cationic iron complexes of formula  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{L}]\text{BF}_4$  ( $\text{L}$  = aromatic nitriles, triphenylphosphine, triphenyl phosphite) has been achieved by Sokolov et al. to obtain potential nonlinear optics materials.<sup>122</sup> The formation of inclusion complexes was strongly hindered by the presence of the bulky aromatic nitrile or phosphines. Finally, characterization in the solid state by several methods has revealed that  $\beta\text{-cyclodextrin}$  forms stable 1:1 crystalline inclusion complexes with  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CN}]$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CN})_2]\text{K}$ , but not with the bis(diphenylphosphine)ethane complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{dppf})\text{CN}]$ .<sup>123</sup> Consequently, it has been concluded that cyclopentadienyl complexes form stable inclusion complexes with  $\beta\text{-CD}$  if the cyclopentadienyl ligand can penetrate deeply into the CD cavity.

The formation of adducts between CD and  $\eta^5\text{-pyrrolyl}$ <sup>124</sup> or cyclopentadienyl<sup>125</sup> manganese tricarbonyl complexes has been investigated using various techniques. As in the case of ( $\eta^6\text{-arene}$ ) chromium tricarbonyl complexes, these manganese complexes formed 1:1 inclusion complexes with the organic ligand included within the cavity. In 1995, the inclusion compound of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3]$  with a  $\beta\text{-CD}$  dimer bridged with two 1,2-diaminoethanes was prepared as the first example of CD dimer inclusion compounds with organotransition metal complexes (Figure 15).<sup>126</sup> The spectroscopic studies and elemental analysis revealed that the stoichiometry of the inclusion compound in water is identical to its stoichiometry in the solid state. The mono[6-deoxy-6-(2-butenedinitrile-2,3-dimercapto sodium salt)]- $\beta\text{-CD}$  can also encapsulate  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3]$ .<sup>127</sup> Upon irradiation of the inclusion compound in DMF solution, an interesting intramolecular photosubstitution resulting in the formation of a very stable self-included compound was observed (Figure 16). A similar phenomenon has been reported by the same authors when the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3]$  is included in the host cavity of the mono[6-deoxy-6-(2-aminoethylthio-1,2-dicyano ethylenylthio)]- $\beta\text{-CD}$  and irradiated in DMF solution at 20 °C.<sup>128</sup>

The inclusion compounds formed between  $\beta\text{-CD}$  and the dicarbonyl molybdenum complexes  $[(\text{L})\text{Mo}(\eta^4\text{-C}_6\text{H}_8)(\text{CO})_2]\text{-}$

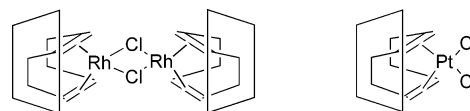


Figure 17.

$\text{BF}_4$  and the neutral derivatives  $[(\text{L})\text{Mo}(\eta^3\text{-C}_6\text{H}_7)(\text{CO})_2]$  ( $\text{L}$  = ( $\eta^5\text{-C}_5\text{H}_5$ ) or ( $\eta^5\text{-C}_9\text{H}_7$ )) were investigated by Gonçalves et al.<sup>129</sup> The cationic and neutral cyclopentadienyl analogues formed stable 2:1 (host-guest) channel-type inclusion compounds in a crystalline state. By contrast, the  $\eta^5\text{-indenyl}$  analogues formed only weak complexes with the  $\beta\text{-CD}$ . The ab initio calculations revealed that the steric hindrance arising from the presence of the indenyl ligand is a possible explanation for the experimentally observed lower stability of these compounds. Half-sandwich complexes of molybdenum of the type  $[(\text{L})\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2]$  ( $\text{L}$  = ( $\eta^5\text{-C}_5\text{H}_5$ ),  $\text{C}_5\text{H}_4\text{SiMe}_3$ ,  $\text{C}_9\text{H}_7$ ) formed stable, crystalline 1:1 inclusion complexes with the  $\beta\text{-CD}$ .<sup>130</sup> Channel-type structures were observed with the ligands ( $\eta^5\text{-C}_5\text{H}_5$ ) and  $\text{C}_9\text{H}_7$ , suggesting that the organometallic complexes are fully enclosed within the CD cavity. A completely different result was obtained with the ligand  $\text{C}_5\text{H}_4\text{SiMe}_3$ , as the arrangement of the CD molecules was more similar to that of the free  $\beta\text{-CD}$  hydrate.

## 2.2. Organometallic Complexes Bearing Alkyl, Diene, $\pi$ -Allyl, or Carbonyl Ligands

Contrary to the cases of organometallic complexes bearing cyclopentadienyl and arene ligands, there are few reports concerning this class of second-sphere coordination adducts. In 1986, Harada and Takahashi reported that  $\beta\text{-CD}$  and  $\gamma\text{-CD}$  can form adducts with metal complexes bearing COD or NBD ligands.<sup>131–133</sup> 1:1 and 2:1 inclusion complexes were obtained in high yields by the treatment of  $\beta\text{-CD}$  with monomeric complexes  $[\text{PtX}_2(\text{COD})]$  ( $\text{X}$  = Cl, Br, and I) and with dimeric complexes  $[\text{Rh}(\mu\text{-Cl})\text{L}]_2$  ( $\text{L}$  = COD, NBD), respectively. On the basis of spectroscopic and analytical measurements, it was proposed that the COD or NBD ligand was included within the cavity as schematically shown in Figure 17. The thermal stability of the organometallic compounds was found to be increased when they are included in the cavity. For instance, the decomposition temperatures of the complex  $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$  and the  $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2\text{-}\beta\text{-CD}$  adduct were ca. 200 °C and 275 °C, respectively.<sup>131</sup> Interestingly, the  $[\text{PdCl}_2(\text{COD})]\text{-}\beta\text{-CD}$  or  $[\text{PtCl}_2(\text{COD})]\text{-}\beta\text{-CD}$  inclusion complexes were evaluated as command-cure catalysts in the hydrosilylation reactions.<sup>134–136</sup> The  $[\text{PdCl}_2(\text{COD})]\text{-}\beta\text{-CD}$  adduct was a good catalyst whereas the complex  $[\text{PdCl}_2(\text{COD})]$  was not active. The  $[\text{PtCl}_2(\text{COD})]\text{-}\beta\text{-CD}$  adduct was also an effective catalyst, contrary to the complex  $[\text{PtCl}_2(\text{COD})]$ , which was too active at low temperature for the hydrosilylation reaction. Inclusion complexes of methylated  $\beta\text{-CD}$  with  $[\text{PdCl}_2(\text{COD})]$  or  $[\text{PtCl}_2(\text{COD})]$  have been used to produce porous metal-silica hybrid materials.<sup>137</sup> The CDs are templates for the structure of the silica and lead to a uniform “worm-type” pore system. After the templating step, the organometallic compounds can be employed as in situ precursors for the preparation of metal nanoparticles within the pore system, thus leading to a one-step synthesis of silica-supported metal catalysts.

Although Harada has reported that  $\alpha\text{-CD}$  cannot bind to transition metal complexes containing a COD ligand, a 1:1 adduct between the  $\alpha\text{-CD}$  and the complex  $[\text{Rh}(\text{COD})(\text{NH}_3)_2]\text{-PF}_6$  has been isolated by Stoddart et al.<sup>138,139</sup> The X-ray



structure of the 1:1 adduct revealed that the cyclooctadiene ligand adopts a boat conformation with one of the two  $-\text{CH}_2-\text{CH}_2-$  units in the CD cavity. Intramolecular hydrogen bonds between the  $\text{NH}_3$  ligand and the hydroxyl group of the CD could be the driving force for the formation of the 1:1 adduct. The analogous complex  $[\text{Rh}(\text{COD})(\text{H}_2\text{N}-\text{NH}_2)]\text{PF}_6$  was found to be more stable than  $[\text{Rh}(\text{COD})-(\text{NH}_3)_2]\text{PF}_6$ . The association constant for the  $[\text{Rh}(\text{COD})-(\text{H}_2\text{N}-\text{NH}_2)]\text{PF}_6-\alpha\text{-CD}$  inclusion complex was determined by  $^1\text{H}$  NMR spectroscopy and was equal to  $520\text{ mol}^{-1}\cdot\text{kg}^{138}$ . The  $\beta\text{-CD}$  was also able to encapsulate the complex  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{NBD}')]$  ( $\text{NBD}' = 2\text{-formylnorbornadiene}$ ) in its cavity.<sup>140</sup>

The formation of adducts between CD and various  $\pi$ -allylpalladium complexes was investigated by Harada et al. in 1985.<sup>141,142</sup> The dimeric complexes  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-X})_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and the analogous crotyl and 2-methylallyl complexes ( $\text{X} = \text{Cl}$ ) do not interact with the  $\alpha\text{-CD}$  but form 1:1 inclusion compounds with  $\beta\text{-CD}$  and/or  $\gamma\text{-CD}$ . From the examination of CPK models, it was concluded that the  $\pi$ -allylpalladium complexes are too large to fit in the  $\alpha\text{-CD}$  cavity.

Although tricarbonyl( $\eta^4$ -1,3-diene)iron complexes are useful transition metal  $\pi$ -complexes for organic synthesis, the formation of adducts between these compounds and CD derivatives has not been reported. However, it was found that a broad range of racemic planar chiral tricarbonyl( $\eta^4$ -diene)iron complexes can be separated into their enantiomers by chiral HPLC on commercial  $\beta\text{-CD}$  columns, showing that these compounds can interact with  $\beta\text{-CD}$ .<sup>143</sup>

A 1:1 inclusion complex between allyl-di-*n*-butyltin chloride and  $\beta\text{-CD}$  was prepared by Marton et al. in good yield by a coprecipitation method.<sup>144</sup> A Mössbauer spectroscopy study indicates that the metal center displays a pentacoordination, probably due to Sn–O long-range contacts with the hydroxyl groups of the secondary face of the  $\beta\text{-CD}$ . Although no definitive evidence has been obtained, the authors suggest that inclusion occurred via one of the butyl groups.

CDs form inclusion compounds with some mononuclear and binuclear metal carbonyl complexes. While  $\text{Fe}(\text{CO})_5$  and  $\text{Co}(\text{NO})(\text{CO})_3$  form 1:1 inclusion complexes with the  $\beta\text{-CD}$  and the  $\gamma\text{-CD}$ , these metal carbonyl complexes form 2:1 inclusion complexes with the  $\alpha\text{-CD}$ .<sup>6,145</sup> Aime et al. have studied by  $^{13}\text{C}$  CP/MAS NMR spectroscopy the  $\text{Fe}(\text{CO})_5-\beta\text{-CD}$  inclusion compound.<sup>146</sup> It was found that the metal carbonyl complex  $\text{Fe}(\text{CO})_5$  reorients isotropically within the  $\beta\text{-CD}$  cavity and shows rapid axial–equatorial exchange. The formation of a 1:1 inclusion complex between  $\text{Cr}(\text{CO})_6$  and  $\gamma\text{-CD}$  was proved by the same authors.<sup>146</sup> As in the case of the  $\text{Fe}(\text{CO})_5-\beta\text{-CD}$  inclusion compound, a rapid and isotropic reorientation of  $\text{Cr}(\text{CO})_6$  within the  $\gamma\text{-CD}$  cavity was observed. Note that a different behavior was observed with the  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3-\beta\text{-CD}$  inclusion complex. Indeed,  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  reorients only about its principal axis in the  $\beta\text{-CD}$  cavity.<sup>115</sup> CD can also bind to dinuclear metal complexes such as  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Co}_2(\text{CO})_8$ , and  $\text{Co}_2(\text{CO})_6\text{L}_2$  ( $\text{L} = \text{PMe}_3, \text{PEt}_3, \text{P}(\text{OMe})_3$ ).<sup>6,146</sup> While  $\text{Co}_2(\text{CO})_8$  forms an inclusion complex with the  $\beta\text{-CD}$  and  $\gamma\text{-CD}$ , the other binuclear metal carbonyl complexes form only inclusion complexes with the  $\gamma\text{-CD}$ . Note that the tributylphosphine derivative of the cobalt carbonyl complex did not form inclusion complexes with the CDs. A series of 1:1 inclusion complexes between cobalt cluster complexes and  $\gamma\text{-CD}$  was

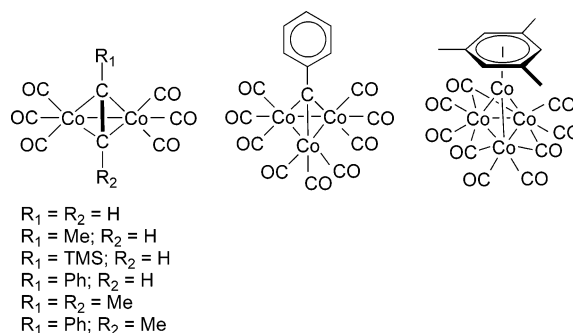


Figure 18.

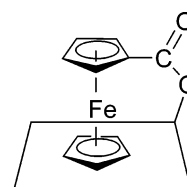


Figure 19.

prepared by Shimada et al. by adding the cobalt cluster to a 2-fold molar excess of saturated aqueous  $\gamma\text{-CD}$  solution at  $40\text{ }^\circ\text{C}$ .<sup>147</sup> The structures of cobalt clusters interacting with the  $\gamma\text{-CD}$  are displayed in Figure 18. The metal cluster complexes included in the  $\gamma\text{-CD}$  were found to be thermally more stable than the free complexes.

### 3. Cyclodextrins Acting Simultaneously as First- and Second-Sphere Ligands

The formation of adducts between CDs and organometallic complexes exhibiting simultaneous first- and second-sphere coordination was reported for the first time by T. Osa in 1985.<sup>148–151</sup> Data obtained from induced circular dichroism studies on CDs bearing a Fc derivative suggest that one of the cyclopentadienyl rings of Fc is included within the CD cavity as shown in Figure 19. In this complex, the first-sphere cyclodextrinylcyclopentadiene carboxylate ligand is acting as a second-sphere ligand for the unsubstituted first-sphere cyclopentadienyl ligand. The lability of the  $\text{NH}_3$  ligands of  $[\text{Rh}(\text{COD})(\text{NH}_3)_2]\text{PF}_6$  in the presence of  $\alpha\text{-CD}$  or methylated  $\alpha\text{-CD}$  has been attributed to a displacement of the  $\text{NH}_3$  ligands by the hydroxyl groups of the CD.<sup>138,139</sup> If this suggestion is true and the COD ligand of the complex still enters into the cavity, the resulting adduct is another example of simultaneous first- and second-sphere coordination. The reaction products obtained after irradiation of inclusion complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3-\text{mono}[6\text{-deoxy-6-(2-butenedinitrile-2,3-dimercapto sodium salt)]-\beta\text{-CD}$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3-\text{mono}[6\text{-deoxy-6-(2-aminoethyl thio-1,2-dicyanethylenylthio)]-\beta\text{-CD}$ ] also belong undoubtedly to this type of adduct (see Figure 16, for example).<sup>127,128</sup> Surprisingly, the formation of an adduct exhibiting simultaneous first- and second-sphere coordination was not observed with the titanocene  $\text{di}[\text{mono}[6\text{-deoxy-6-(2-butenedinitrile-2,3-dimercapto)]-\beta\text{-CD}]$ .<sup>152</sup> The lack of interaction between the cyclopentadienyl ligands and the  $\beta\text{-CD}$  cavity was attributed to the inability of the CD to complex a cyclopentadienyl ring of the titanocene due to structural hindrance.

The possibility to obtain first- and second-sphere coordination adducts with  $\alpha\text{-CD}$ s containing phosphine or phosphite units has been extensively investigated by Matt et al.<sup>153–157</sup> Both modified  $\alpha\text{-CD}$ s readily formed transition

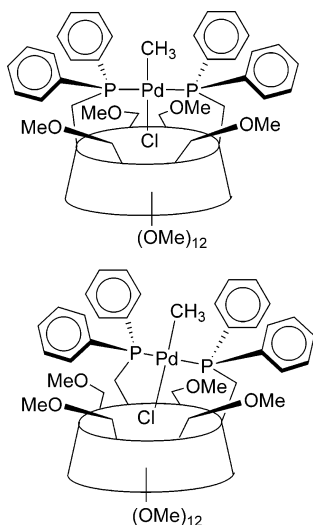


Figure 20.

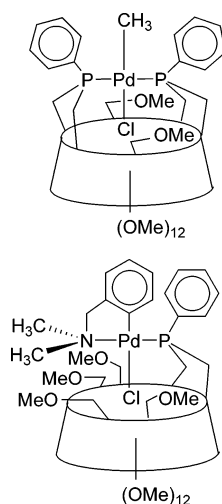


Figure 21.

metal–chelate complexes in which the metal centers were immobilized at the entrance or outside the cavity. The structures of these adducts will not be discussed intensively here, as most of them do not possess a metal–carbon bond. Surprisingly, Matt et al. have reported that the reaction of  $[\text{PdClMe}(\text{COD})]$  with  $\alpha$ -CDs containing two C(5)-linked  $\text{CH}_2\text{PPh}_2$  units afforded organometallic complexes with the Pd–methyl moiety outside the cavity and the Pd–chloride moiety inside the cavity, as schematically represented in Figure 20.<sup>158,159</sup> The preference of the cavity for the polarized Pd–Cl moiety rather than for the less-polar Pd–organic fragments was also observed with other modified  $\alpha$ -CDs. Indeed, reaction of  $[\text{PdClMe}(\text{COD})]$  with phosphinidene-capped  $\alpha$ -CDs gave rise to organometallic complexes where the metal–chloride bond points toward the center of the cavity as shown in Figure 21.<sup>160</sup> The ability of the  $\alpha$ -CD cavity to recognize a metal–chloride bond rather than organic groups in nonaqueous media is likely a consequence of the absence of stronger competing supramolecular forces such as the hydrophobic effect which usually plays a prevailing role in the formation of CD inclusion complexes.

Note that the reaction product between  $\beta$ -CD and the (1,1'-ferrocenediyl)dimethylsilane can be considered as a first- and second-sphere coordination adduct (Figure 5).<sup>46</sup> Indeed, the  $\beta$ -CD bound to the cyclopentadienyl ring partially includes a ferrocenyl moiety.

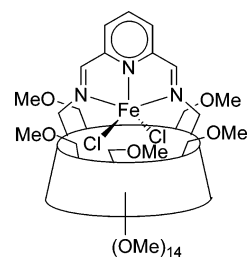


Figure 22.

#### 4. Cyclodextrin Acting Simultaneously as First- and Transient Second-Sphere Ligands

When a CD covalently connected to a ligand of the organometallic complex includes temporarily in its cavity a substrate that reacts with the organometallic complex, the CD can be considered as a first- and transient second-sphere ligand. This phenomenon is observed when the organometallic complex is involved in catalytic processes. Such a type of coordination likely occurs during the ethylene polymerization catalyzed by an iron complex containing tridentate nitrogen ligands based on 2,6-bis(imino)pyridine-capped  $\beta$ -CD.<sup>161</sup> As shown in Figure 22, the *endo*-oriented 1,3-diiminopyridine– $\text{FeCl}_2$  unit bridges the entrance of the  $\beta$ -CD derivative and compels the substrate to enter into the cavity by the secondary face to interact with the catalytic site. After activation with a large excess of methylaluminoxane ( $\text{Al/Fe} > 2000$  equiv), the iron complex depicted in Figure 22 polymerized ethylene in toluene with a maximum turnover frequency of  $125 \text{ h}^{-1}$ . This catalytic activity remains 1000 times lower than that of conventional Brookhart/Gibson iron catalysts, possibly because the catalytic center was surrounded by five coordinating methoxy groups. Note that the iron complex based on the  $\alpha$ -CD was not active at all in ethylene polymerization, suggesting that the cavity of the  $\alpha$ -CD was not sufficiently large to allow the chain growing process.

Water-soluble palladium complexes based on  $\beta$ -CD modified by nitrile groups displayed high catalytic activity and selectivity in two-phase Wacker oxidation of 1-octene. The high catalytic activities of these catalysts based on modified  $\beta$ -CDs were explained by the coordination of the double bond of the included substrate with the palladium ion attached to the CD.<sup>162</sup>

The substrate selectivity observed during the hydrogenation of a 1:1 mixture of olefins and the increase in the linear to branched aldehyde ratio during the hydroformylation of 1-octene were attributed to the formation of transient adducts between the substrate and water-soluble rhodium complexes bearing  $\beta$ -CD-modified diphosphines (Figure 23).<sup>163–166</sup> Indeed, no substrate selectivity or increase in aldehydes ratio was observed when the reactions were conducted in the presence of a free  $\beta$ -CD analogous catalyst,  $[\text{PhN}(\text{CH}_2\text{PPh}_2)_2\text{-Rh}(\text{COD})]\text{BF}_4$ . It must be pointed out that the reactions were performed in an aqueous–organic two-phase system with an aqueous phase containing 30% DMF. The presence of an aqueous phase is supposed to force inclusion of the substrate in the cavity during the catalysis. In a one-phase medium composed of DMF, the formation of transient adducts between substrate and a rhodium complex modified by a phosphinite  $\beta$ -CD ligand seems also possible (Figure 24).<sup>167</sup> Indeed, Ichikawa et al. have explained the reactivity difference between 1-decene and 4-phenyl-1-butene in the hydroformylation reaction by assuming that the 4-phenyl-

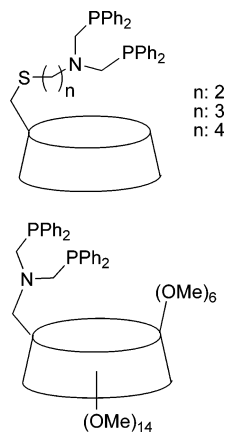


Figure 23.

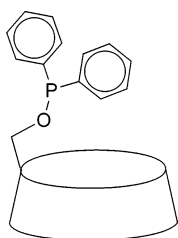


Figure 24.

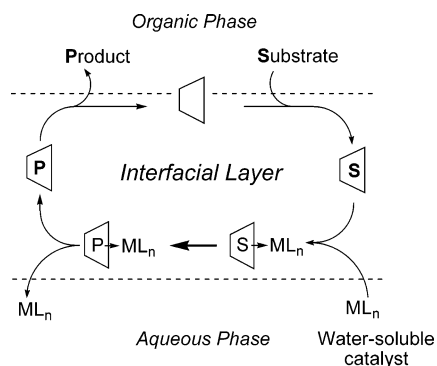
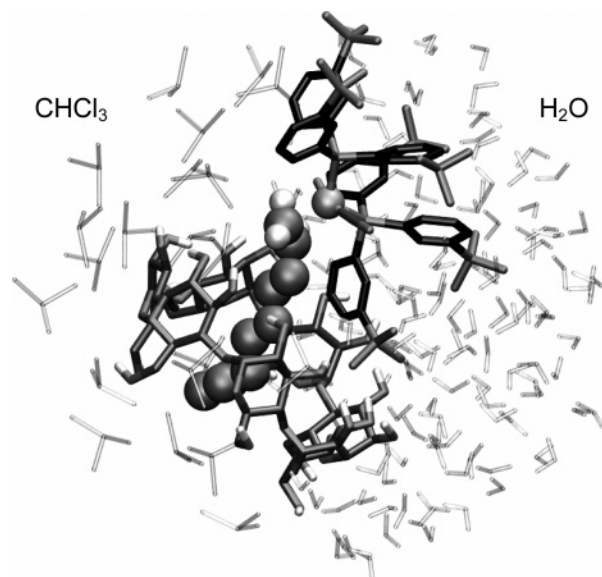


Figure 25. Principle of the aqueous organometallic catalysis mediated by CD.

1-butene fits better into the cavity of the  $\beta$ -CD–Rh complex than the 1-decene.

### 5. Cyclodextrins as Transient Second-Sphere Ligands

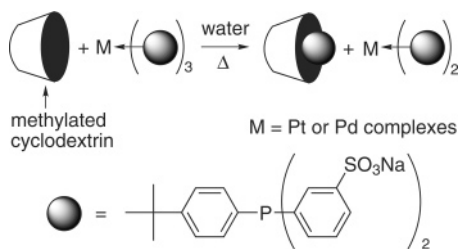
The CD can be considered as a transient second-sphere ligand when the CD is used as mass transfer promoter in aqueous organometallic catalysis. In fact, it is postulated that the substrate included in the CD cavity binds to the water-soluble organometallic catalyst to form transient second-sphere coordination adducts at the organic–aqueous interface or in the bulk aqueous phase (Figure 25). Although the formation of such transient species has never been spectroscopically observed, their existence at the organic–aqueous interface has recently been suggested by molecular dynamic studies. For instance, in the hydroformylation reaction of 1-decene using  $[\text{RhH}(\text{CO})(\text{TPPTS})_2]$  as an active species, the 1-decene has been shown to be both coordinated to the rhodium and included in the native  $\beta$ -CD cavity at a chloroform–water interface (Figure 26).<sup>168</sup> Furthermore, one sulfonate was found to be hydrogen bonded to the OH's of the CD, strengthening the attractions between the rhodium complex and its host.

Figure 26.  $[\text{RhH}(\text{CO})(\text{TPPTS})_2(1\text{-decene})]^{6-}$  complexed with native  $\beta$ -CD with selected solvent molecules at the chloroform–water interface.

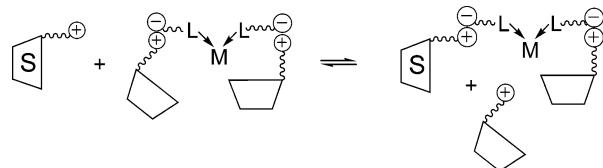
Native CDs are effective mass transfer promoters for the deoxygenation of allylic alcohols,<sup>169</sup> oxidation of olefins,<sup>170–172</sup> and reduction of  $\alpha,\beta$ -unsaturated acids,<sup>173</sup>  $\alpha$ -keto esters,<sup>174</sup> or conjugated dienes.<sup>175</sup> In the case of the deoxygenation of allylic alcohols into alkenes, the proposed mechanism includes the formation of a cobalt complex coordinated by the oxygen atoms of the hydroxyl groups on the  $\beta$ -CD.<sup>169</sup> Another example of the CD-promoted reactions is the reduction of aryl alkyl ketones and aromatic aldehydes into hydrocarbons catalyzed by a dimer of chloro(1,5-hexadiene)-rhodium(I).<sup>176</sup> However, note that only the  $\beta$ -CD promoted the reaction. Indeed, the yields in the presence of  $\alpha$ -CD were lower than those observed without CD. Adverse effects of native CDs on transition metal catalyzed reactions have also reported in two other reactions. The reduction of aldehydes using the ruthenium complex  $[\text{RuCl}_2(\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\text{SO}_3\text{Na}))_2]^{177}$  and the hydroformylation of 1-hexene using the rhodium catalyst  $[\text{HRh}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_6\text{H}_4\text{SO}_3\text{Na}))_3]^{178}$  were inhibited by addition of  $\beta$ -CD and  $\alpha$ -CD to the reaction medium, respectively. Although no spectroscopic evidence has been obtained, the detrimental effect of the CD was attributed to interactions between the CD and the catalyst.

Interestingly, chemically modified CDs such as the partially *O*-methylated CDs show a better catalytic activity than native CDs in numerous reactions such as the Wacker oxidation,<sup>179,180</sup> hydrogenation of aldehydes,<sup>181,182</sup> Suzuki cross-coupling reaction,<sup>183</sup> and hydroformylation<sup>184–188</sup> or hydrocarboxylation<sup>189,190</sup> of olefins. Methylated  $\beta$ -CDs were also used successfully to perform substrate-selective reactions in a two-phase system.<sup>191–195</sup> This outstanding effect of methylated  $\beta$ -CD on reaction rate was attributed to its slight surface activity and to the presence of a deep hydrophobic host cavity that properly accommodates the substrate. Concurrently to the complexation of the substrate, it was also found that the CDs can form inclusion complexes with the hydrosoluble phosphine used to dissolve the organometallic catalyst in the aqueous phase.<sup>196–200</sup> This interaction has rather negative effects on the reaction selectivity. In fact, by trapping the phosphine ligand, the CD induces a displacement of the equilibria between the different organometallic species toward phosphine low coordinated species.<sup>201,202</sup>





**Figure 27.** Formation of low-coordinated complexes by means of methylated cyclodextrin.



**Figure 28.** Principle of supramolecular catalysis with a CD noncovalently bound to the catalyst.

Interestingly, the above CD–phosphine interaction was found to be very efficient to generate low-coordinated organometallic species by addition of native  $\beta$ -cyclodextrin or randomly methylated  $\beta$ -cyclodextrin to an aqueous solution of hydrosoluble platinum or palladium complexes bearing appropriate phosphines (Figure 27).<sup>201,203</sup> The existence of second-sphere coordination adducts in which the local bulkiness around the metallic center was high appeared to be an essential intermediate step in the formation of phosphine coordinatively unsaturated complexes.

To overcome the negative effect of the CD–phosphine interaction, the use of strong chelating bidentate phosphines such as sulfoxantphos<sup>204</sup> or phosphines such as bis(3-sulfonatophenyl)-(4-(4-*tert*-butylphenyl)phenyl)phosphine where the group recognized by the CD is far away from the phosphorus atom<sup>205</sup> has been proposed. Interestingly, in the case of the sulfoxantphos ligand, the catalytic results showed that, concurrently to the constraint generated by the bulky sulfonated xantphos ligand, the additional steric stress of the cyclodextrin cavity on the substrate compelled the latter to react preferentially by its terminal carbon, leading to very high regioselectivity toward linear aldehyde.

Another strategy to avoid interaction between the CD and the phosphine consisted in using  $\alpha$ -CDs instead of  $\beta$ -CDs. Indeed, these  $\alpha$ -CDs have smaller cavities, prohibiting inclusion processes of the phosphine aromatic cycles inside the CD cavity.<sup>206,207</sup> Moreover, grafting an alkylammonium chain on a  $\alpha$ -CD resulted in new catalytic supramolecular species where the cyclodextrin behaved both as a transient first- and second-sphere ligand simultaneously and as a supramolecular shuttle able to carry the substrate to a hydrosoluble organometallic catalyst (Figure 28).<sup>208</sup> To our knowledge, this constitutes the first example of a CD-based system where the CD acts as a coexisting transient first- and second-sphere ligand.

## 6. Conclusion

Organometallic inclusion complexes now form a viable and challenging interdisciplinary topic which offers much scope for the design of new supramolecular entities and new uses for these advanced materials. Our aim in this review was to convince chemists that CDs constitute a very useful tool for that purpose. Indeed, above and beyond the chemistry of covalent bonds, most of the studies that have been carried

out to date in that field have been directed at defining the potential of CDs as second-sphere ligands for altering the behavior of the organometallic guest when included in the CD cavity. This ability depends on the structure of the host in close relation to that of the guest. The knowledge is now at hand to design supramolecular edifices offering electrochemical, sensor, mediator, or catalytic properties. It is hoped that this review has clearly pointed out the very substantial progress that has already been made in the field of organometallic inclusion and that the advances made so far will stimulate chemists to explore new supramolecular materials and new applications.

## 7. Abbreviations

CD	cyclodextrin
COD	cycloocta-1,5-diene
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Fc	ferrocene
Fc <sup>+</sup>	ferrocenium
K <sub>f</sub>	formation constant
NBD	norbornadiene
NBD'	2-formylnorbornadiene

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