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Encapsulation of Cyano(cyclopentadienyl) Complexes of Iron with β-cyclodextrin

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Inclusion compounds have been prepared comprising β-cyclodextrin (CD) molecules as the host and half-sandwich cyano complexes of iron as the guests. High yields of crystalline one-to-one adducts were obtained by treatment of $CpFe(CO)_2CN$ and $K[CpFe(CO)(CN)_2]$ with β-CD. In the case of CpFe(dppe)CN [dppe = bis(diphenylphosphine)ethane], a non-stoichiometric product is obtained and it is evident that the organometallic guests are easily liberated from the host cavities. The products were characterized in the solid-state by elemental analysis, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), FTIR and CP MAS NMR (^{13}C, ^{31}P) spectroscopy. Additional information concerning the possible structure of the inclusion compounds was obtained from *ab initio* calculations using a two-layer approximation. The best organometallic-β-CD interaction is obtained with deep inclusion of the cyclopentadienyl ring, a geometry that is not possible in the case of the CpFe(dppe)CN system due to the size and orientation of the dppe ligand.

Keywords: Cyclodextrins; Iron; Cyano complexes; Inclusion complexation; *Ab initio* calculations

INTRODUCTION

It is well known that the coordinating influence of many transition metal complexes extends beyond their covalently-bonded first-sphere ligands to non-covalently bound chemical species in the so-called second-sphere [1]. Considerable insight into the nature of this important phenomenon has been gained by studying the interaction of molecular receptors with transition metal complexes [1]. Initial success was achieved using crown ethers as hosts for neutral and cationic complexes carrying protic ligands (NH_3, H_2O, CH_3CN, etc.) in their first coordination spheres. In these cases, hydrogen bonds and electrostatic interactions provide the dominant sources of supramolecular stabilization.

Cyclodextrins have also been exploited as second-sphere ligands [2]. These are cyclic oligosaccharides consisting of six, seven or eight (1 → 4)-linked α-D-glucopyranose units (α-, β- and γ-CD, respectively). They form inclusion complexes with smaller molecules which fit into their 5–8 Å cavity [3,4]. Particularly suitable guests are those bearing hydrophobic ligands, such as cyclopentadienyl ($Cp = \eta^5{-}C_5H_5$) and η^6-arene groups. With these ligands, the weaker categories of non-covalent bonding, e.g. van der Waals and charge transfer interactions, assume considerable importance. Second-sphere coordination adducts have been reported with ferrocene and its derivatives [5–14], titanocene and molybdenocene dihalides [15,16], aromatic ruthenium complexes [17], mixed sandwich complexes such as $[(\eta^5{-}C_5H_5)Fe(\eta^6{-}C_6H_6)](PF_6)$ [18–20], and half-sandwich complexes such as $CpFe(CO)_2X$ (X = Cl, Me) [21–23], $[CpFe(CO)_2NH_3][PF_6]$ [24], $CpMn(CO)_3$ [25], $(\eta^6{-}C_6H_6)Cr(CO)_3$ [26], $Cp'Mo(\eta^3{-}C_3H_5)(CO)_2$ [27], $Cp'Mo(\eta^3{-}C_6H_7)(CO)_2$ and $[Cp'Mo(\eta^4{-}C_6H_8)(CO)_2](BF_4)$ (Cp′ = Cp, Ind) [28].

In the present work, we focus on the interaction of β-cyclodextrin with the half-sandwich cyano

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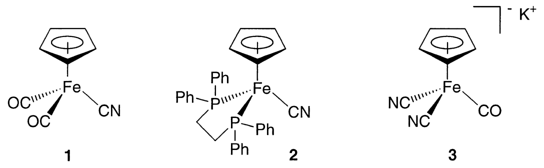
complexes CpFe(CO)$_2$CN, CpFe(dppe)CN and K[CpFe(CO)(CN)$_2$]. The formed adducts have been characterized in the solid-state by a range of techniques and *ab initio* calculations have been used to generate likely inclusion geometries. Where possible, the results obtained for CpFe(CO)$_2$CN and CpFe(dppe)CN are compared with results in the literature for CpFe(CO)$_2$X and CpFe(dppe)X (X = Cl, I, Me). The formation of an inclusion compound between β-CD and K[CpFe(CO)(CN)$_2$] is particularly interesting as, to the best of our knowledge, this is the first example of the encapsulation of an anionic cyclopentadienyl-carbon monoxide metal compound.

RESULTS AND DISCUSSION

Synthesis and Characterization of Inclusion Compounds

The three iron complexes CpFe(CO)$_2$CN (**1**), CpFe(dppe)CN (**2**) and K[CpFe(CO)(CN)$_2$] (**3**) have different solubilities, which means that more than one method is required to prepare inclusion compounds with β-CD. Thus, the potassium salt **3** is soluble in water and the familiar co-crystallization method from aqueous solution was used to prepare the corresponding adduct K[CpFe(CO)(CN)$_2$]·β-CD (**3a**). Elemental analysis indicated that the host-to-guest ratio in **3a** was 1:1. The yield was almost quantitative on the basis of a 1:1 stoichiometric inclusion compound. Complexes CpFe(CO)$_2$CN (**1**) and CpFe(dppe)CN (**2**), on the other hand, are insoluble in water but soluble in organic solvents (Scheme 1). A method was used therefore that combines a saturated aqueous solution of β-CD with a solution of the organometallic in dichloromethane. The products **1a** and **2a**, designated as CpFe(CO)$_2$CN·β-CD (**1a**) and CpFe(dppe)CN·β-CD (**2a**), were isolated by filtration and rinsed first with dichloromethane to remove unchanged iron complexes, and then with water to remove any remaining free cyclodextrin hydrate. As for **3a**, **1a** was obtained as a 1:1 inclusion compound in good yield. These results are comparable with those reported in the literature for other cyclopentadienyl-carbon monoxide iron complexes. Thus, the compounds CpFe(CO)$_2$Me [21,22], CpFe(CO)$_2$X (X = Cl, I) [23] and [CpFe(CO)$_2$NH$_3$][PF$_6$] [24] also form 1:1 adducts with β-CD. Unlike **1a** and **3a**, Compound **2a** could not be obtained in an analytically pure form. This was an initial indication that the interaction between the cyano complex **2** and β-CD is weak. Results reported for CpFe(dppe)I seem to support this conclusion. Thus, Díaz and Arancibia studied the interaction of β-CD with CpFe(dppe)I in DMSO solution by UV–Vis absorption spectroscopy [23]. A 1:1 complex was formed but with a very low association constant of $K = 4.8 \times 10^{-4}\,\mathrm{M}^{-1}$. In contrast to our results, however, these authors were able to isolate a 1:1 solid inclusion compound.



SCHEME 1

Compounds **1a**–**3a** were obtained as microcrystalline powders and examined by powder XRD (Fig. 1). The first conclusion is that the adducts do not contain measurable amounts of phases corresponding to non-included organometallic components **1**–**3**. The patterns for **1a** and **3a** are quite different from that of β-CD hydrate, suggesting that true inclusion complexes exist in the solid state [4]. Compound **2a**, on the other hand, exhibits a pattern very similar to that of the host structure. This indicates that the major phase in **2a** comprises β-CD molecules arranged in a herringbone-type pattern, as found in either pristine β-CD hydrate or β-CD inclusion compounds with small alcohols [29].

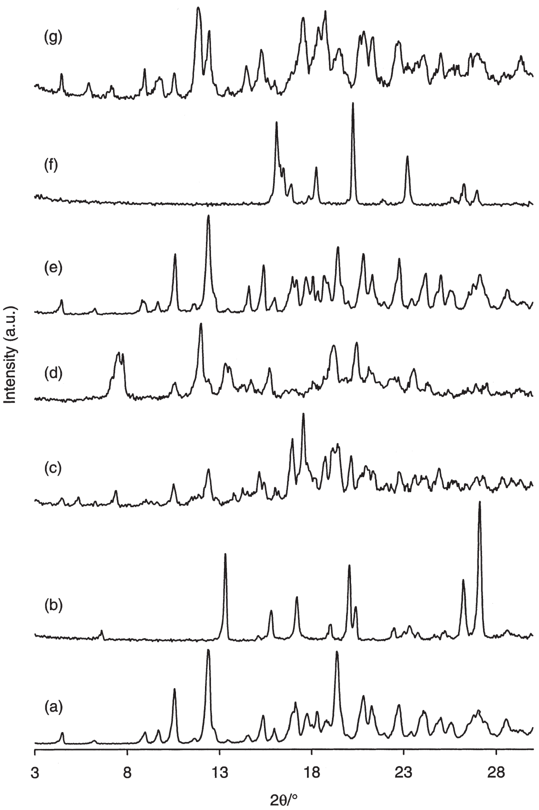


FIGURE 1 Powder XRD patterns of (a) β-CD hydrate, (b) CpFe(CO)$_2$CN (**1**), (c) CpFe(CO)$_2$CN·β-CD (**1a**), (d) CpFe(dppe)CN (**2**), (e) CpFe(dppe)CN·β-CD (**2a**), (f) K[CpFe(CO)(CN)$_2$] (**3**), and (g) K[CpFe(CO)(CN)$_2$]·β-CD (**3a**).

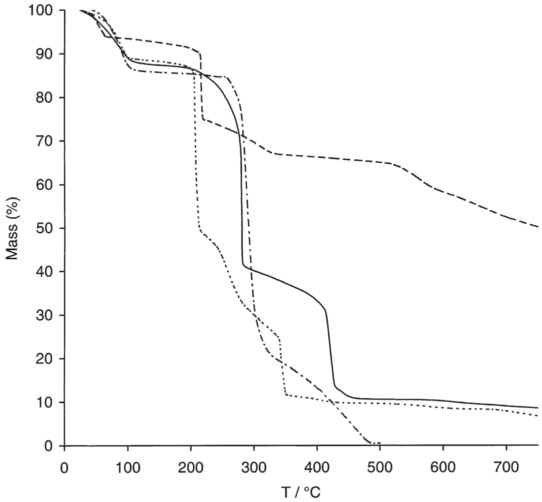


FIGURE 2 TGA of CpFe(CO)$_2$CN·β-CD (**1a**) (—), CpFe(CO)$_2$CN (**1**) (– – –), pristine β-CD hydrate (–·–·-), and a physical mixture of β-CD and **1** in a 1:1 molar ratio (···).

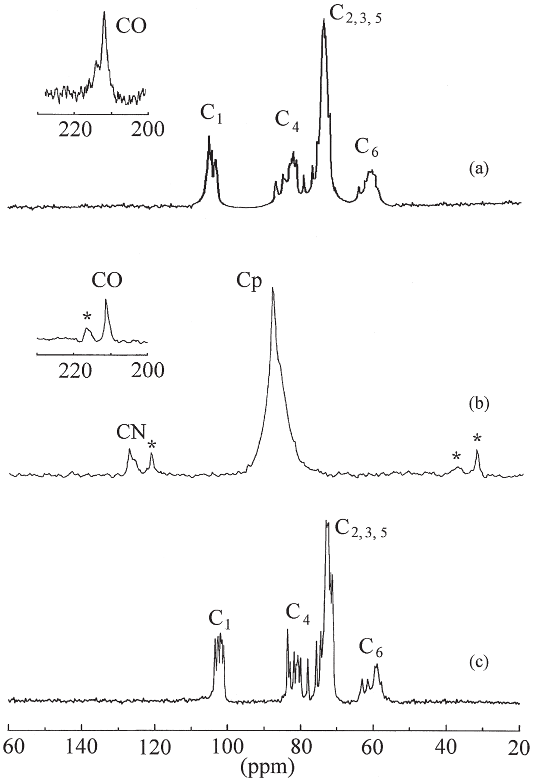


FIGURE 3 Solid state ^{13}C CP MAS NMR spectra of (a) CpFe(CO)$_2$CN·β-CD (**1a**), (b) CpFe(CO)$_2$CN (**1**) and (c) free β-CD hydrate. (*denotes spinning side bands.)

Thermogravimetric analysis (TGA) of β-CD shows loss of hydrated water up to 130°C (14.4%, 10–11 water molecules per β-CD molecule, Fig. 2). There is no further change until 260°C when the compound starts to melt and decompose, characterized by an intense, sharp peak in the differential thermogravimetric (DTG) profile at 287°C. At 500°C, 100% mass loss is complete. The thermogravimetric behavior of CpFe(CO)$_2$CN·β-CD (**1a**) up to 300°C is quite similar to that of β-CD in that there is an initial mass loss of 12.5% up to 130°C, attributed to loss of hydrated water, followed by an abrupt mass loss of 46% between 200 and 290°C (DTG maximum at 279°C). At higher temperatures, the TG profiles of **1a** and pure β-CD are quite different. Compound **1a** undergoes a second abrupt mass loss of 18.4% between 410 and 430°C, and at 500°C the total mass loss is 89.4%.

TGA studies were also performed for the pure organometallic **1** and a physical mixture of **1** and β-CD in a 1:1 molar ratio (Fig. 2). The physical mixture exhibits a very different TG profile from that of **1a** in the temperature range 190–500°C. Most notably, decomposition occurs at a lower temperature as revealed by a sharp step in the TG curve with a DTG maximum at 205°C. A similar step is observed for the free organometallic **1** (216°C), which implies that decomposition of the organometallic component in the mixture promotes decomposition of β-CD at a lower temperature than that observed for pure β-CD. The absence of any step at around 210°C in the TG curve of **1a** suggests that the compound does not contain any free non-included organometallic component.

The β-CD adducts CpFe(dppe)CN·β-CD (**2a**) and K[CpFe(CO)(CN)$_2$]·β-CD (**3a**) were also examined by TGA (not shown). Compound **2a** exhibited very similar thermal behavior to that of pure β-CD except that decomposition took place at a lower temperature (DTG maximum at 258°C). At 500°C, the total mass loss was 98.8%. In the case of Compound **3a**, there was an initial mass loss of 12.7% up to 100°C, followed by a gradual mass loss of 77% between 200 and 400°C. At 500°C, the total mass loss was 93.6%.

The KBr IR spectra of compounds **1a–3a** show the typical bands previously reported for bulk KBr spectra of β-CD, indicating no chemical modification of the cyclodextrin host [30]. In addition, sharp carbonyl and/or cyanide stretching absorptions of the guest molecules are observed (Table I). The equivalent bands for the non-included complexes **1–3** are generally broader, probably due to intermolecular interactions (CH···O and CH···π contacts, which are known to be present in carbonyl/Cp-containing organometallics [31]). Inclusion of CpFe(CO)$_2$CN (**1**) in β-CD results in a shift of the ν(CO) bands to lower wavenumbers (Table I). By contrast, the ν(C ≡ N) stretching vibrations occur at higher wavenumbers relative to **1**. These observations can be explained by the presence of well-localized hydrogen bonding between the carbonyl and the OH groups of the β-CD, leaving the CN mainly undisturbed. Two ν(C ≡ N) stretching vibrations were observed for **2a** while only one is observed for the free complex **2**. This may be explained by a mixture of products in **2a**, e.g. 1:1 and 2:1 host-to-guest complexes (see below). The

TABLE I Selected IR data for included and non-included cyano complexes

Compound	ν(C ≡ O) [cm^{-1}]*	ν(C ≡ N) [cm^{-1}]*
CpFe(CO)$_2$CN (**1**)	2056, 2006	2118
CpFe(CO)$_2$CN·β-CD (**1a**)	2045, 2003	2124
CpFe(dppe)CN (**2**)	–	2062
CpFe(dppe)CN·β-CD (**2a**)	–	2056, 2069
K[CpFe(CO)(CN)$_2$]† (**3**)	1952, 1972	2084, 2096
K[CpFe(CO)(CN)$_2$]·β-CD (**3a**)	1970	2050, 2092

*Solid-state KBr IR spectra (ν_{sym}, ν_{asym}). †Solid-state KBr IR spectrum [44,45]: ν(C ≡ O) = 1950, 1970 cm^{-1}; ν(C ≡ N) = 2080 cm^{-1}.

splitting of the carbonyl band in complex **3** must arise from crystal effects and/or Fermi resonance.

The ^{13}C CP MAS NMR spectra of CpFe(CO)$_2$CN·β-CD (**1a**) and K[CpFe(CO)(CN)$_2$]·β-CD (**3a**) are shown in Figs. 3 and 4, respectively, and for comparison the spectra of pristine β-CD hydrate and the complexes **1** and **3** are also given. The spectrum of β-CD hydrate is similar to that reported previously and exhibits multiple resonances for each type of carbon atom [32–34]. This has been mainly correlated with different torsion angles about the (1 → 4) linkages for C-1 and C-4 [32,33], and with torsion angles describing the orientation of the hydroxyl groups [34]. The different carbon resonances are assigned to C-1 (101–104 ppm), C-4 (78–84 ppm), C-2,3,5 (71–76 ppm) and C-6 (57–65 ppm). The spectrum of **1a** differs from that of pristine β-CD hydrate in that the resonances for **1a** are considerably broader (Fig. 3). In the case of **3a**, this effect is much more pronounced to the extent that the β-CD carbons C-1, C-2,3,5 and C-6 are observed as single broad peaks (Fig. 4). This is common for cyclodextrin inclusion compounds and indicates that β-CD adopts a symmetrical conformation in the complex, with each glucose unit in a similar environment [27,28,35].

The ^{13}C CP MAS NMR spectra of **1a**–**3a** each contain resonances for the carbon atoms of the guest molecules, in particular those assigned to the Cp, CN, CO and dppe groups (Table II). The singlets for the Cp carbons of **1a** and **3a** appear at $\delta = 85.8$ and 82.5 ppm, respectively, both shifted slightly to higher field compared to the values for the free complexes **1** and **3** ($\delta = 87$ and 83.6 ppm, respectively). The ^{31}P CP MAS NMR spectrum of **2a** exhibits a singlet for coordinated dppe ligand at δ 103.0, equal to that of the free complex CpFe(dppe)CN (**2**) (103.2 ppm). This value is comparable to those observed for the inclusion compounds CpFe(dppe)I·β-CD (112.6) and [Cp(dppe)Fe-(μ-CN)-Fe(dppe)Cp](PF$_6$) (δ 104.7, 101.0) [23], and also the cyano complex Cp(dppe)Fe-CN-Re(CH$_3$)O$_3$ (δ 102, CH$_3$CN) [36].

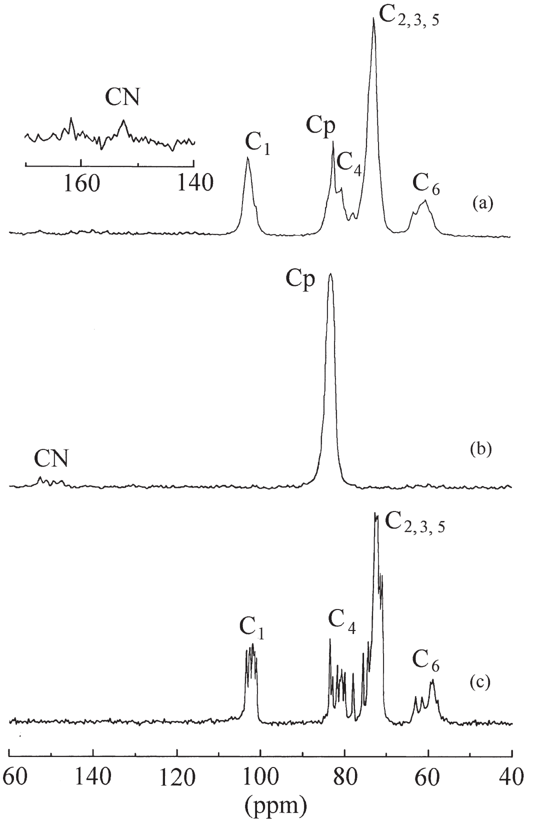


FIGURE 4 Solid state ^{13}C CP MAS NMR spectra of (a) [CpFe(CO)(CN)$_2$]K·β-CD (**3a**), (b) [CpFe(CO)(CN)$_2$]K (**3**) and (c) free β-CD hydrate.

Ab Initio Calculations

The molecular structures of the free organometallics **1**–**3** have been determined at the B3LYP/LANL2DZ level. To the best of our knowledge, there are no experimental data for these systems. However, the calculated structural parameters are in good agreement with available theoretical and experimental

TABLE II Selected ^{31}P and ^{13}C MAS NMR data for included and non-included cyano complexes

Compound	δ(^{31}P)	δ(^{13}C) C ≡ O	δ(^{13}C) C ≡ N
CpFe(CO)$_2$CN* (**1**)	–	211.3	127.6
CpFe(CO)$_2$CN·β-CD (**1a**)	–	211.0	126.0
CpFe(dppe)CN (**2**)	103.2 (68)†	–	145.4
CpFe(dppe)CN·β-CD (**2a**)	103.0 (121)	–	152
K[CpFe(CO)(CN)$_2$]‡ (**3**)	–	219.6, 218.2	152.4, 151.0, 149.2, 147.3
K[CpFe(CO)(CN)$_2$]·β-CD (**3a**)	–	n/o¶	153

* ^{13}C NMR (CDCl$_3$): $\delta = 210.5$ (C ≡ O) and 126.2 (C ≡ N). † Full width at half maximum (FWHM, Hz) given in parenthesis. ‡ ^{13}C NMR (CDCl$_3$): $\delta = 218.0$ (C ≡ O) and 160.3 (C ≡ N). ¶ Not observed.

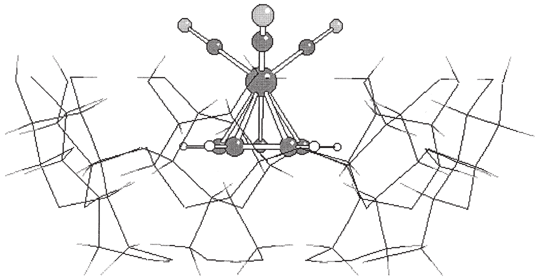


FIGURE 5 Schematic representation of the lowest energy structure for the inclusion compound **1a**. It also represents the best inclusion geometry for **3a**, as the structural changes are indistinguishable at this schematic level.

data for similar systems [16,28,37–43], considering that calculated r_e values are generally longer than the experimental r_0 counterparts. For instance, the calculated structure of **1** can be compared with the X-ray structure of CpFe(CO)$_2$Cl [40]: average Fe–Cp distance (calculated: 219 pm; experimental: 208 pm), Fe–CO distance (178 pm; 177 pm), C–O bond length (117 pm; 112.5 pm), (CO)–Fe–(CO) bond angle (96°; 94°). Average *ab initio* values for Fe–CN and C–N bond lengths are 190 and 119 pm, respectively. Relative to the structure of **1**, the negative charge of the anion in **3** leads to an increase in the Fe–Cp distance and to a decrease in the Fe–CO and C–O distances. The calculated structure of **2** presents the general features observed for several Fe–dppe complexes [41–43], such as the relative orientation of the phenyl groups and the envelope conformation of the C–P–Fe–P–C chelate. Typical Fe–dppe parameters are the Fe–P bond length (calculated: 229 pm; experimental: 222 pm), P–C bond length (189 pm; 184 pm) and P–Fe–P bond angle (87°; 87°).

Concerning the inclusion compounds, the best organometallic-β-CD interaction geometry for **1** and **3** was found to be the one with the Cp ligand inside the cavity (Fig. 5). This preference follows that previously found for other Cp-organometallics and β-CD, using the same theoretical approach, and has also been proposed for several ferrocene derivatives [38,39]. However, this structure corresponds to a minimum in shallow potential surface, and a tilt angle as high as 15° (as defined in Fig. 6) raises the energy less than 1 kJ mol^{-1}. Since RT $\approx$ 2.3 kJ mol^{-1} at room temperature, the orientation of the organometallic in the crystal will be easily allowed to vary in order to adjust the interactions of the CN and CO ligands with the neighboring CDs. The observed shifts of the carbonyl and cyano stretching frequencies, reported above (Table I), suggest that at least in **1a** the CO groups are engaged in hydrogen bonding with the next CD while CN groups are not. A tilt motion can achieve the required orientation of the CO and CN ligands.

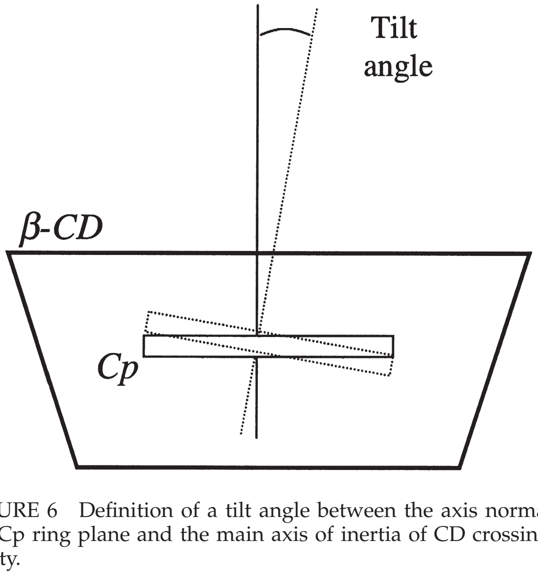


FIGURE 6 Definition of a tilt angle between the axis normal to the Cp ring plane and the main axis of inertia of CD crossing its cavity.

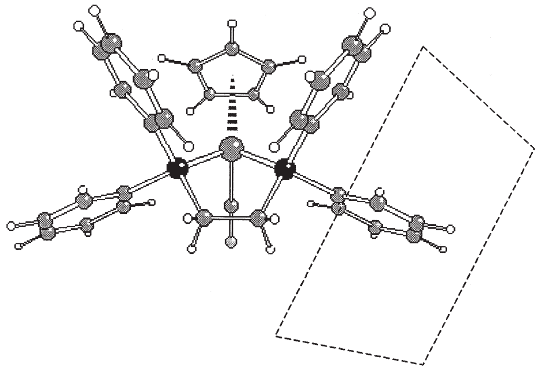


FIGURE 7 *Ab initio* structure of **2**, showing the CD position for the inclusion of a phenyl group. Inclusion of the Cp ring is prevented by steric factors.

A quite different situation arises in the case of the inclusion compound **2a**. The presence of the bulky dppe substituents prevents an effective inclusion of the Cp moiety due to the steric repulsion with the CD rim (Fig. 7). Due to the particular structure of the dppe ligand, only two of the phenyl groups are accessible to moderate inclusion in the CD cavity, as depicted in Fig. 7. This would lead to a possible 2:1 CD/organometallic inclusion ratio. However, the computed interaction energy for the inclusion process is fairly small and results repulsive when the BSSE correction is included. This result is in agreement with the lack of stability experimentally observed for **2a**.

CONCLUDING REMARKS

Characterization in the solid-state by several methods has revealed that β-cyclodextrin forms stable 1:1 crystalline inclusion compounds with the cyano complexes CpFe(CO)$_2$CN and K[CpFe(CO)(CN)$_2$], but not with the bis(diphenylphosphine)ethane complex CpFe(dppe)CN. *Ab initio* calculations help to rationalize the successful formation or otherwise of a stable inclusion compound, by generating possible inclusion geometries. Analysis of these different configurations also sheds light on the likely nature of host-guest interactions. This information can be compared with experimental observations, e.g. FTIR evidence of the interaction of the first-sphere ligand CO with β-CD. This combined experimental and theoretical approach has been used by us with a similar degree of success for other related β-CD-guest systems, namely with the molybdenum complexes $Cp'Mo(\eta^3-C_6H_7)(CO)_2$, $[Cp'Mo(\eta^4-C_6H_8)(CO)_2](BF_4)$ ($Cp' = Cp$, indenyl) [28], and Cp_2MoCl_2 [16]. A general conclusion from these studies is that cyclopentadienyl complexes are likely to form stable inclusion compounds with β-CD if the Cp ligand can penetrate deeply into the CD cavity. Concerning mononuclear cyclopentadienyl-carbon monoxide iron compounds, it is evident that both neutral and ionic complexes can be encapsulated within the cavity of β-CD to give 1:1 adducts, such as the cation in $[CpFe(CO)_2NH_3][PF_6]$ and the anion in $K[CpFe(CO)(CN)_2]$. Less stable interaction geometries result with the introduction of bulky first-sphere ligands (dppe), or replacement of Cp by indenyl.

EXPERIMENTAL SECTION

General Remarks

Solvents were dried by standard procedures (THF and Et_2O over Na/benzophenone ketyl; CH_2Cl_2 and CH_3CN over CaH_2), distilled under argon and kept over 4 Å molecular sieves (3 Å for CH_3CN). Microanalyses were performed at the ITQB. Infrared spectra were recorded on a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets. TGA studies were performed using a Mettler TA3000 system at a heating rate of $5\,K\,min^{-1}$ under a static atmosphere of air. Powder X-ray diffraction (XRD) data were collected on a Philips X'pert diffractometer using Cu Kα radiation filtered by Ni ($\lambda = 1.5418$ Å). Solid-state NMR spectra were recorded at room temperature on a (9.4 T) Bruker MSL 400P spectrometer (operating at 100.62 MHz for ^{13}C and 162 MHz for ^{31}P). ^{13}C CP MAS NMR spectra were recorded with a 4.5 μs ^{1}H 90° pulse, 2 ms contact time, a spinning rate of 9 kHz and 12 s recycle delays. Chemical shifts are quoted in parts per million from TMS. ^{31}P $\{^{1}H\}$ MAS NMR spectra were recorded using 45° pulses with interpulse delays of 60 s and a spinning rate of 14 kHz. Chemical shifts are quoted in parts per million from H_3PO_4 (85%).

Starting Materials

β-CD was obtained from Wacker Chemie (München) and recrystallized before use. The following compounds were prepared as described in the literature: $CpFe(CO)_2CN$ (**1**) [44,45], CpFe(dppe)CN (**2**) [46], and $K[CpFe(CO)(CN)_2]$ (**3**) [47]. ^{13}C CP MAS NMR of **1**: $\delta = 211.3$ (CO), 127.6 (CN), 87.0 (Cp). ^{13}C CP MAS NMR of **2**: $\delta = 145.4$ (CN), 138.8, 136.9, 132.9, 128.3 (Ph), 79.3 (Cp), 27.9 (CH_2). ^{31}P MAS NMR of **2**: $\delta = 103.2$. ^{13}C CP MAS NMR of **3**: $\delta = 219.6$, 218.2 (CO), 152.4, 151.0, 149.2, 147.3 (CN), 83.6 (Cp).

Preparation of $CpFe(CO)_2CN{\cdot}\beta$-CD (1a)

A solution of β-CD (0.35 g, 0.31 mmol) in water (10 ml) was treated with a solution of $CpFe(CO)_2CN$ (**1**) (0.062 g, 0.31 mmol) in dichloromethane (7 ml) and the mixture kept at 40°C for 5 h. The suspension was filtered and the pale brown powder washed several times with water, dichloromethane, and vacuum dried. Yield: 0.38 g (80%). $(C_8H_5O_2NFe){\cdot}(C_{42}H_{70}O_{35}){\cdot}12H_2O$ (1553.46): calcd C 38.64, H 6.42, N 0.90, Fe 3.59; found C 38.31, H 6.11, N 0.78, Fe 3.33. IR (KBr): $\nu = 3386$ (vs), 2925 (s), 2124 (m), 2045 (s), 2003 (s), 1429 (s), 1385 (sh), 1383 (m), 1374 (m), 1334 (m), 1303 (m), 1201 (m), 1157 (vs), 1100 (s), 1080 (vs), 1053 (s), 1029 (vs), 1003 (m), 945 (m), 937 (m), 861 (m), 755 (m), 702 (s), 607 (m), 575 (s), 530 (s) cm^{-1}. ^{13}C CP MAS NMR: $\delta = 211.0$ (s, CO), 126.0 (br, CN), 103.8, 103.2, 102.9, 102.2, 101.4 (β-CD, C-1), 85.8 (s, Cp), 83.9, 82.1, 81.1, 80.3, 78.3 (β-CD, C-4), 76.0, 74.8, 73.4, 73.0, 72.6, 71.6 (β-CD, C-2,3,5), 63.5, 60.8, 60.0, 59.5 (β-CD, C-6).

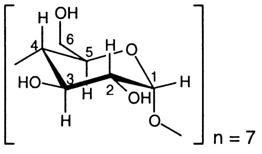


DIAGRAM 1

Reaction of β-CD With CpFe(dppe)CN (2a)

A solution of β-CD (0.35 g, 0.31 mmol) in water (10 ml) was treated with a solution of CpFe(dppe)CN (**2**) (0.17 g, 0.31 mmol) in dichloromethane (6 ml) and the mixture kept at 50°C for 24 h. The mixture was centrifuged and the supernatant decanted. The brown powder was washed several times with water, dichloromethane, and vacuum dried (0.26 g). $(C_{32}H_{29}NP_2Fe){\cdot}(C_{42}H_{70}O_{35}){\cdot}12H_2O$ (1895.61): calcd C 46.85, H 6.54, N 0.74, Fe 2.95; found C 39.17, H 6.67, N 0.24, Fe 0.84. IR (KBr): $\nu = 3386$ (vs), 3059 (m), 2926 (s), 2069(s), 2056 (s), 1481 (m), 1457 (m), 1432 (s), 1418 (m), 1384 (m), 1334 (m), 1307 (m), 1245 (m), 1157 (vs), 1121 (m), 1097 (s), 1080 (vs), 1056 (s), 1029 (vs), 1004 (m), 946 (m), 938 (m), 864 (m), 817 (m), 795 (m), 756 (m), 745 (m), 705 (s), 696 (vs), 673 (m), 578 (m), 533 (vs), 525 (s), 510 (m) cm^{-1}. ^{13}C CP MAS NMR: $\delta = 152.0$ (br, CN), 128.3 (br, Ph), 103.6, 102.9, 102.0, 101.4 (β-CD, C-1), 83.9, 83.0, 81.1, 80.5 (β-CD, C-4), 78.1 (C-4 and Cp), 75.9, 73.4, 71.5 (β-CD, C-2,3,5), 63.5, 59.5 (β-CD, C-6), 28.0 (br, CH_2). ^{31}P MAS NMR: $\delta = 103.0$.

Preparation of $K[CpFe(CO)(CN)_2]\cdot\beta$-CD (3a)

Method a: A solution of β-CD (0.35 g, 0.31 mmol) and $K[CpFe(CO)(CN)_2]$ (**3**) (0.074 g, 0.31 mmol) in water (10 ml) was kept at 40°C for 2 h. A yellow microcrystalline powder gradually precipitated from the solution after evaporation at 30°C for 3 weeks. The solid was collected by filtration, washed with cold water and dried *in vacuo* at room temperature. Yield: 0.38 g (78%). Crystals were obtained by diffusion of 1,4-dioxane to a saturated solution of **3a** in water for four weeks. *Method b*: A solution of β-CD (0.35 g, 0.31 mmol) and $K[CpFe(CO)(CN)_2]$ (**3**) (0.07 g, 0.31 mmol) in water (10 ml) was left in an ultra-sound bath for 2 h. The yellow solution was then frozen with liquid nitrogen and left in a liophilizer to obtain a voluminous solid product. Yield: 0.45 g (94%). $(C_8H_5N_2OKFe)\cdot(C_{42}H_{70}O_{35})\cdot10H_2O$: calcd C 38.61, H 6.16, N 1.80, Fe 3.59; found C 38.48, H 6.03, N 1.67, Fe 3.39. IR (KBr): $\nu = 3390$ (vs), 2929 (s), 2092 (s), 2050 (m), 1970 (s), 1481 (m), 1457 (m), 1432 (s), 1418 (m), 1384 (m), 1334 (m), 1307 (m), 1245 (m), 1157 (vs), 1121 (m), 1097 (s), 1080 (vs), 1056 (s), 1029 (vs), 1004 (m), 946 (m), 938 (m), 864 (m), 817 (m), 795 (m), 756 (m), 745 (m), 705 (s), 696 (vs), 673 (m), 578 (m), 533 (vs), 525 (s), 510 (m) cm^{-1}. ^{13}C CP MAS NMR: $\delta = 153.0$ (br, CN), 103.1 (br, β-CD, C-1), 82.5 (Cp), 80.5, 77.7 (β-CD, C-4), 73.1 (br, β-CD, C-2,3,5), 63.2, 60.3 (β-CD, C-6).

Ab Initio Calculations

Ab initio calculations were carried out using the GAUSSIAN 98w program package [48] running on a personal computer (Pentium 830 MHz, 320 MB RAM). For the free organometallic, the geometry was fully optimized at the B3LYP level using the Dunning/Huzinaga valence double-zeta basis set for the first period elements [49], and the Los Alamos Effective Core Potentials plus double-zeta [50] for the Mo atom (LanL2DZ option of GAUSSIAN 98). Harmonic vibrational frequencies were calculated at the same level, using analytic second derivatives. The basis set superposition error (BSSE) correction for the inclusion energies has been estimated by counterpoise calculations, using the MASSAGE option of GAUSSIAN 98.

Concerning the inclusion compounds, several possible inclusion geometries were tested by single point calculations using the two layer approximation of Morokuma *et al.* (ONIOM keyword of GAUSSIAN 98) [51–53]. The organometallic was treated at high layer, using the effective core potentials described above (B3LYP/LanL2DZ) while the β-CD was set as low layer, and optimized at the HF level with the Stevens/Basch/Krauss Effective Core Potential minimal basis [54,55].

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References

[1] Colquhoun, H.M., Stoddart, J.F. and Williams, D.J. (1986), *Angew. Chem. Int. Ed. Engl.* **25**, 487–582.

[2] Fenyvesi, E., Szente, L., Russel, N.R. and McNamara, M. (1996) In: Szejtli, J. and Osa, T., eds, Comprehensive Supramolecular Chemistry (Pergamon Press, Oxford) **Vol. 3**, pp 305–366.

[3] Szejtli, J. (1998), *Chem. Rev.* **98**, 1743.

[4] Saenger, W. (1980), *Angew. Chem. Int. Ed. Engl.* **19**, 344–362.

[5] Breslow, R., Trainor, G. and Ueno, A. (1983), *J. Am. Chem. Soc.* **105**, 2739–2744.

[6] Harada, A. and Takahashi, S. (1984), *J. Chem. Soc., Chem. Commun.*, 645.

[7] Harada, A., Hu, Y., Yamamoto, S. and Takahashi, S. (1988), *J. Chem. Soc., Dalton Trans.*, 729.

[8] Odagaki, Y., Hirotsu, K., Higuchi, T., Harada, A. and Takahashi, S. (1990), *J. Chem. Soc., Perkin Trans.* **1**, 1230–1231.

[9] Imashiro, F., Kuwahara, D., Kitazaki, N. and Terao, T. (1992), *Mag. Res. Chem.* **30**, 796.

[10] Kuwahara, D., Imashiro, F. and Terao, T. (1993), *Chem. Phys. Lett.* **204**, 533.

[11] Bakhtiar, R. and Kaifer, A.E. (1998), *Rapid Commun. Mass Spectrom.* **12**, 111–114.

[12] Kaifer, A.E. (1999), *Acc. Chem. Res.* **32**, 62–71.

[13] Osella, D., Carretta, A., Nervi, C., Ravera, M. and Gobetto, R. (2000), *Organometallics* **19**, 2791–2797.

[14] Ferreira, P., Gonçalves, I.S., Pillinger, M., Rocha, J., Santos, P. and Teixeira-Dias, J.J.C. (2000), *Organometallics* **19**, 1455–1457.

[15] Turel, I., Demsar, A. and Kosmrlj, J. (1999), *J. Mol. Recogn. Macro. Chem.* **35**, 595–604.

[16] Braga, S.S., Gonçalves, I.S., Pillinger, M., Ribeiro-Claro, P. and Teixeira-Dias, J.J.C. (2001), *J. Organomet. Chem.* **632**, 11–16.

[17] Meister, G., Stoeckli-Evans, H. and Süss-Fink, G. (1993), *J. Organomet. Chem.* **453**, 249–253.

[18] Klingert, B. and Rihs, G. (1990), *Organometallics* **9**, 1135–1141.

[19] Klingert, B. and Rihs, G. (1991), *J. Inclusion Phenom.* **10**, 255–265.

[20] Klingert, B. and Rihs, G. (1991), *J. Chem. Soc., Dalton Trans.*, 2749–2760.

[21] Shimada, M., Harada, A. and Takahashi, S. (1991), *J. Chem. Soc., Chem. Commun.*, 263.

[22] Patel, P.P. and Welker, M.E. (1997), *J. Organomet. Chem.* **547**, 103–112.

[23] Díaz, C. and Arancibia, A. (1998), *J. Incl. Phenom. Mol. Recogn.* **30**, 127–141.

[24] Alston, D.R., Slawin, M.Z., Stoddart, J.F. and Williams, D.J. (1985), *Angew. Chem. Int. Ed. Engl.* **24**, 786–787.

[25] Song, L., Meng, Q. and You, X. (1995), *J. Organomet. Chem.* **498**, C1–C5.

[26] Harada, A., Saeki, K. and Takahashi, S. (1989), *Organometallics* **8**, 730–733.

[27] Braga, S.S., Gonçalves, I.S., Lopes, A.D., Pillinger, M., Rocha, J., Romão, C.C. and Teixeira-Dias, J.J.C. (2000), *J. Chem. Soc., Dalton Trans.*, 2964–2968.

[28] Lima, S., Gonçalves, I.S., Ribeiro-Claro, P., Pillinger, M., Lopes, A.D., Ferreira, P., Teixeira-Dias, J.J.C., Rocha, J. and Romão, C.C. (2001), *Organometallics* **20**, 2191–2197.

[29] Saenger, W. and Steiner, T. (1998), *Acta Cryst.* **A54**, 798–805.

[30] Sabapathy, R.C., Bhattacharyya, S., Cleland, W.E. and Hussey, C.L. (1998), *Langmuir* **14**, 3797–3807.

[31] Calhorda, M.J. (2000), *Chem. Commun.*, 801–810.

[32] Gidley, M.J. and Bociek, S.M. (1988), *J. Am. Chem. Soc.* **110**, 3820–3829.

[33] Heyes, S.J., Clayden, N.J. and Dobson, C.M. (1992), *Carbohydr. Res.* **233**, 1–14.

[34] Veregin, R.P., Fyfe, C.A., Marcessault, R.H. and Tayler, M.G. (1987), *Carbohydr. Res.* **160**, 41.

[35] Li, J., Harada, A. and Kamachi, M. (1994), *Bull. Chem. Soc. Jpn* **67**, 2808–2818.

[36] Gonçalves, I.S., Kühn, F.E., Lopes, A.D., Parola, A.J., Pina, F., Sotomayor, J. and Romão, C.C. (1998), *J. Organomet. Chem.* **560**, 117–124.

[37] de Azevedo, C.G., Calhorda, M.J., Carrondo, M.A.A.F.d.C.T., Dias, A.R., Duarte, M.T., Galvao, A.M., Gamelas, C.A., Gonçalves, I.S., da Piedade, F.M. and Romao, C.C. (1997), *J. Organomet. Chem.* **544**, 257–276.

[38] Godinez, L.A., Patel, S., Criss, C.M. and Kaifer, A.E. (1995), *J. Phys. Chem.* **99**, 17449.

[39] Isnin, R., Salam, C. and Kaifer, A.E. (1991), *J. Org. Chem.* **56**, 35.

[40] Jens, V.K.J. and Weiss, E. (1979), *Acta Crystallogr.* **C41**, 895.

[41] Ruiz, J., González, M.A., Román, E. and Garland, M.T. (1990), *J. Chem. Soc., Dalton Trans.*, 21.

[42] Riley, P.E. and Davis, R.E. (1983), *Organometallics* **2**, 286.

[43] Riley, P.E., Capshew, C.E., Pettit, R. and Davis, R.E. (1978), *Inorg. Chem.* **17**, 408–414.

[44] Piper, T.S., Cotton, F.A. and Wilkinson, G. (1955), *J. Inorg. Nucl. Chem.* **1**, 165–174.

[45] Reger, D.L. (1975), *Inorg. Chem.* **14**, 660–662.

[46] Treichel, P.M. and Molzahn, D.C. (1979), *Synth. React. Inorg. Met.-Org. Chem.* **9**, 21–29.

[47] Coffey, C.E. (1963), *J. Inorg. Nucl. Chem.* **25**, 179–185.

[48] Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P. M.W., Johnson, B.G., Chen, W., Wong, M.W., Andres, J.L., Head-Gordon, M., Replogle, E.S. and Pople, J.A.(1998) GAUSSIAN 98 (Revision A.1), Gaussian, Inc., Pittsburgh PA.

[49] Dunning, Jr., T.H. and Hay, P.J. (1976) In: Schaefer, H.F., ed, Modern Theoretical Chemistry (Plenum Press, New York) **Vol. 3**, p 1.

[50] Wadt, W.R. and Hay, P.J. (1985), *J. Chem. Phys.* **82**, 284.

[51] Humbel, S., Sieber, S. and Morokuma, K. (1996), *J. Chem. Phys.* **105**, 1959.

[52] Matsubara, T., Sieber, S. and Morokuma, K. (1996), *J. Quantum Chem.* **60**, 1101.

[53] Svensson, M., Humbel, S., Froese, R.D.J., Matsubara, T., Sieber, S. and Morokuma, K. (1996), *J. Phys. Chem.* **100**, 19357.

[54] Stevens, W., Basch, H. and Krauss, J. (1984), *J. Chem. Phys.* **81**, 6026.

[55] Stevens, W.J., Krauss, M., Basch, H. and Jasien, P.G. (1992), *Can. J. Chem.* **70**, 612.