Organometallics **1990**, *9*, 1135–1141 1135

Molecular Encapsulation of Transition-Metal Complexes in Cyclodextrins. 1. Synthesis and X-ray Crystal Structure of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]PF_6{\cdot}2\alpha\text{-CD}{\cdot}8H_2O$

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Received September 8, 1989

The mixed-sandwich complex $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]PF_6$ forms crystalline 2:1 host:guest inclusion compounds with α- and β-cyclodextrin (α-CD, β-CD) respectively. The compounds have been characterized by UV–vis, circular dichroism, and CP/MAS ^{13}C NMR spectroscopy. The crystal structure of the α-cyclodextrin adduct has been determined by single-crystal X-ray diffraction. $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]PF_6{\cdot}2\alpha\text{-CD}{\cdot}8H_2O$: triclinic, space group $P1$, a = 13.815 (1) Å, b = 13.929 (1) Å, c = 15.639 (2) Å, α = 94.23 (1)°, β = 87.15 (1)°, γ = 119.81 (1)°, V = 2603.9 Å^3, and D_{calcd} = 1.55 g cm^{-3} for Z = 1. The parameters could be refined by the full-matrix least-squares method to the final R value of 0.083 for 9965 reflections with $I > 2\sigma(I)$. In the crystal, two α-cyclodextrin molecules form a head-to-head dimer by means of intermolecular hydrogen bonding across the secondary hydroxyl faces of adjacent α-cyclodextrin monomers. The $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]^+$ cation is encapsulated within the cavity of the dimer and is tilted by an angle of 39° (C_5H_5)/40° (C_6H_6) against the mean planes of the α-CD molecules. The cyclopentadienyl and the benzene rings are parallel; Fe–centroid distances to the C_5H_5 and the C_6H_6 rings are 1.66 and 1.57 Å, respectively. The PF_6^- anion is located at the center of the primary hydroxyl side of the α-cyclodextrin molecule that includes the benzene ring. The dimers are stacked along the crystallographic c axis to form a channel-type structure. Eight water molecules of hydration per asymmetric unit fill the intermolecular space between the α-cyclodextrin dimers, forming a hydrogen-bond network within the crystal.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven, or eight (1→4)-linked α-D-glucopyranose residues (α-, β-, γ-CD, respectively). They are known to form inclusion compounds with a wide variety of guest molecules,[1] including transition-metal complexes.[2] As a consequence of the relatively nonpolar character of the CD cavity, transition-metal complexes of the right dimensions bearing hydrophobic ligands should be particularly suitable guests.

One of the most widely used hydrophobic ligands in transition-metal chemistry is the cyclopentadienyl ($\eta^5\text{-}C_5H_5$ = cp) ligand. The cyclopentadienyl ring can penetrate the α-CD cavity, as Harada et al.[3] have shown by the isolation of stable 2:1 α-CD inclusion complexes of ferrocene and some of its monosubstituted derivatives. In addition, second-sphere coordination by cyclodextrins of cyclopentadienyl transition-metal complexes other than ferrocenes has been reported for half-sandwich complexes of manganese,[4] iron,[5] and rhodium.[6]

A range of structurally related (η^6-arene)$Cr(CO)_3$ complexes have been shown to form crystalline 1:1 adducts with β- and γ-CD selectively.[4,7] α-CD did not form an adduct with any of the complexes tested, and it was assumed that this might be due to the inability of its smaller cavity to accommodate even a benzene ring, when inserted in a horizontal fashion.

However, no X-ray structural information on CD inclusion compounds of organometallic sandwich or half-sandwich complexes is available: the sole examples of crystallographically characterized adducts of transition-metal complexes with cyclodextrins reported to date are the 1:1 adducts formed with rhodium and platinum complexes in which a cyclobutane ring,[8] a trimethylphosphine,[9] and a cyclooctadiene ligand,[5] respectively penetrate the CD cavity.

In our laboratories a series of cyclopentadienyl(arene)-iron(II) complexes have been investigated recently.[10] Our interest in this class of compounds, which are currently used as photoinitiators for polymerization of epoxies,[10,11] has led us to investigate their potential as guest molecules for cyclodextrins. We report here the preparation and spectroscopic and structural characterization of CD inclusion compounds of $[cpFe(\eta^6\text{-}C_6H_6)]PF_6$. The crystalline hydrate of the α-CD adduct is the first example of a structurally characterized 2:1 adduct of cyclodextrins and a transition-metal complex.

Results and Discussion

1. Preparation and Properties of Inclusion Compounds. The sandwich complex $[cpFe(\eta^6\text{-}C_6H_6)]PF_6$ is almost insoluble in water at room temperature, but fairly soluble in hot water. It could, therefore, be cocrystallized with the cyclodextrins from hot aqueous solutions. The iron complex was dissolved at 80 °C in a minimum amount of water, and hot aqueous solutions of α- or β-CD were added in a 2-fold molar excess. After slow cooling to room temperature, orange–yellow crystals separated, which were

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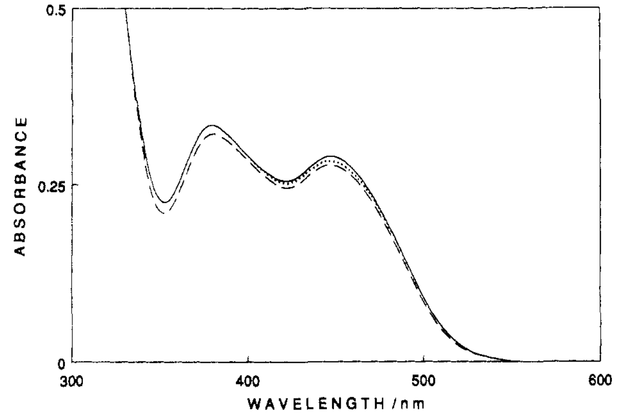

Figure 1. UV–vis absorption spectrum of [cpFe(η^6-C_6H_6)]PF_6 (—), in the presence of α-CD (···) and β-CD (- - -). Solvent: DMSO–water (1:1); 4.9 × 10^{-3} mM [cpFe(η^6-C_6H_6)]PF_6, 4.3 × 10^{-2}mM α-CD, 3.4 × 10^{-2}mM β-CD.

filtered off and washed with water to remove any remaining CD. Nonincluded iron complex was removed by washing with ethanol.

The stoichiometries of the inclusion compounds were determined by elemental analysis and ^{1}H NMR spectroscopy. The results show that stoichiometric 2:1 host:guest adducts were formed with both α- and β-CD, even when the CDs were reacted with the iron complex in a 1:1 molar ratio. This is in contrast to the structurally related but neutral ferrocene molecule, which forms a 2:1 adduct with α-CD but a 1:1 adduct with β-CD.[3] The fact that the benzene ligand of [cpFe(η^6-C_6H_6)]PF_6 penetrates the α-CD cavity is noteworthy, considering that (benzene)tricarbonylchromium and its substituted derivatives do not form inclusion compounds with α-CD at all.[4,7]

2. Spectroscopic Studies. (a) UV–Visible Absorption and Induced Circular Dichroism (ICD) Spectra. Figure 1 shows the UV–visible absorption spectrum of [cpFe(η^6-C_6H_6)]PF_6 in the absence and presence of α- and β-CD, respectively, in DMSO–water (1:1) solution. Both α- and β-CD caused a decrease of the absorption, indicating the inclusion of the iron complex in the CD cavities. Interestingly, β-CD led to a decreased absorption in the whole range from 330 to 550 nm, while α-CD decreased the absorption only in the visible part of the spectrum from about 400 to 550 nm.

The induced circular dichroism (ICD) spectra of [cpFe(η^6-C_6H_6)]BF_4 in the presence of α- and β-CD are shown in Figure 2. The tetrafluoroborate salt was used instead of the PF_6^- salt because of its higher solubility in water. An aqueous solution of the α-CD adduct [cpFe(η^6-C_6H_6)]BF_4·2α-CD·8H_2O did not show any ICD signal at all. In the presence of an excess of α-CD, however, a negative induced Cotton effect was observed at 450 nm, as was also observed by adding excess α-CD to solutions of the "free" guest complex. In contrast, β-CD-containing solutions of [cpFe(η^6-C_6H_6)]BF_4 showed a positive induced Cotton effect, indicating that the orientation of the iron complex in the β-CD cavity is different from that in the α-CD cavity.

According to the literature,[12] the observation of an ICD of cyclodextrin-chromophore inclusion complexes not only proves that complexation occurs but also that the sign of the ICD signal may provide information on the orientation of the guest molecule within the cavity. Thus, on the basis of the positive ICD signals and CPK molecular models, an axial inclusion geometry has been proposed, e.g., for the β-CD adducts of ferrocene[3] and the (benzene)chromium tricarbonyl complex.[4,7] The axial orientation suggested for the 2:1 adduct of ferrocene with α-CD[3] is, however, not in agreement with its negative ICD signal and those of a series of its derivatives in the presence of α-CD reported recently by Sokolov et al.[13]

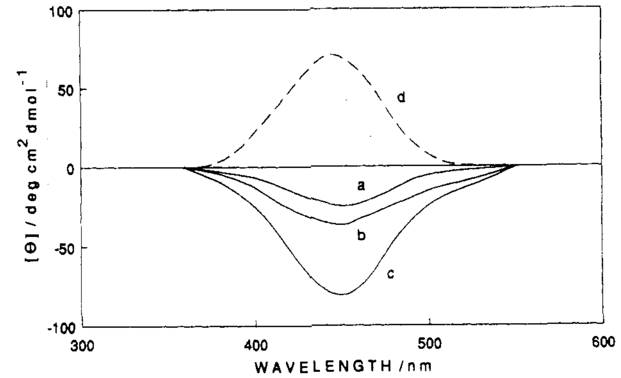

Figure 2. Induced circular dichroism spectra of aqueous solutions of (a) 24 mM [cpFe(η^6-C_6H_6)]BF_4 with a 3-fold molar excess of α-CD, of 5 mM adduct [cpFe(η^6-C_6H_6)]BF_4·2α-CD·8H_2O with (b) a 20-fold and (c) an approximately 60-fold (supersaturated solution) molar excess of α-CD, and of (d) 10 mM [cpFe(η^6-C_6H_6)]BF_4 with a 10-fold molar excess of β-CD.

Docking calculations of ferrocene complexation with cyclodextrins have revealed[14] that the ferrocene molecule tilts 40–45° at the upper rim of the α-CD torus within the 1:1 complex and that the tilt is maintained in the 2:1 complex. In the β-CD adduct, axial and equatorial orientation are of almost the same energy.

(b) Cross Polarization/Magic Angle Spinning (CP/MAS) ^{13}C NMR Spectra. According to the literature,[15] the ^{13}C NMR chemical shifts of α- and β-cyclodextrin in the solid state are solely determined by intramolecular, i.e., conformational, interactions. The chemical shifts of the signals for C-1 and C-4 carbons of the glucopyranose residues, respectively, reflect the ϕ and ψ dihedral angles around the glycosidic linkage.[16] A conformational change of the α-CD molecule induced by the inclusion of a guest molecule is reflected in the line shape and chemical shifts of C-1 and C-4 resonances.

The structure of the α-CD hydrate reveals that one of the α-(1→4) linkages adopts an unusual high-energy conformation, which results in a partially collapsed ring structure.[17] Within the range of chemical shifts assigned to the C-1 and C-4 carbons, respectively, one distinct resonance of each set of signals is significantly shifted to higher field relative to the other signals. These two resonances have tentatively been assigned to the C-1 and C-4 carbons involved in the "anomalous" linkage.[15] On formation of inclusion complexes, the α-CD is able to expand to a more symmetrical macrocyclic ring, thereby relieving the conformational strain imposed by the single high-energy linkage.[18]

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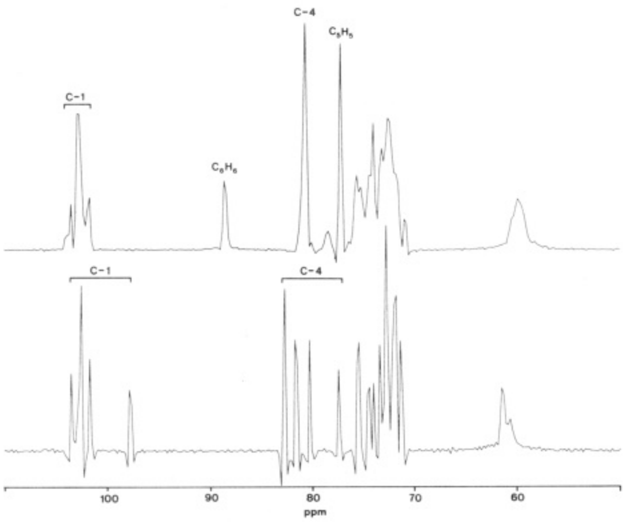

Figure 3. CP/MAS ^{13}C NMR spectra of [cpFe(η^6-C_6H_6)]PF_6·2α-CD·8H_2O (top) and α-cyclodextrin hydrate (bottom) (spinning rate, 4.5 kHz; contact time, 2 ms; repetition rate, 2 s).

The solid-state CP/MAS ^{13}C NMR spectra of α-CD and its 2:1 adduct with [cpFe(η^6-C_6H_6)]PF_6 are shown in Figure 3; resonances were assigned according to literature data.[15] Upon inclusion of the iron complex, there are significant changes observed in the C-1 as well as the C-4 resonances of α-CD. The resonances attributed to the C-1 carbons fall into a narrower chemical shift range compared to the corresponding resonances of α-CD, while the C-4 resonances collapse into one signal at 80.61 ppm. These results indicate similar dihedral angles for all glucopyranosyl residues and thus a more symmetrical conformation for the α-CD macrocycles as well as symmetry in the packing of the supramolecular entities. The C-2, C-3, and C-5 lines of the adduct overlap as in α-CD and are not readily assigned. The C-6 resonances are shifted slightly upfield and appear as an unresolved broad signal. The guest lines are rather sharp signals, and their chemical shifts (C_6H_6, 88.43 ppm; C_5H_5, 77.16 ppm) differ from those obtained from [cpFe(η^6-C_6H_6)]PF_6 in solution (C_6H_6, 88.53 ppm; C_5H_5, 76.81 ppm, in d_6-acetone) by less than 1 ppm.

In contrast to α-CD, the β-CD hydrate has an open circular conformation in the solid state[19] which does not change dramatically upon formation of inclusion complexes. In the spectrum of the 2:1 β-CD adduct of [cpFe(η^6-C_6H_6)]PF_6 all resonances of the cyclodextrin host appear as broad poorly resolved signals, while the guest resonances give sharp signals at 88.79 (C_6H_6) and 77.18 ppm (C_5H_5).

3. Crystal Structure of [cpFe(η^6-C_6H_6)]PF_6·2α-CD·8H_2O. (a) Outline of the Structure. The crystal structure consists of head-to-head arranged dimers of α-CD molecules linked together by hydrogen bonds between the 24 secondary hydroxy groups. The [cpFe(η^6-C_6H_6)]$^+$ cation is encapsulated within the cavity of the dimer, while the PF_6^- anion is located at the primary hydroxyl side of α-CD molecule B which encloses the benzene ring. Eight water molecules of hydration fill the intermolecular spaces between the dimers and form a hydrogen-bond network within the crystal (Figure 4).

A numbering scheme of the α-CD adduct is shown in Figure 5. The final atomic coordinates for the non-hydrogen atoms are given in Table I.

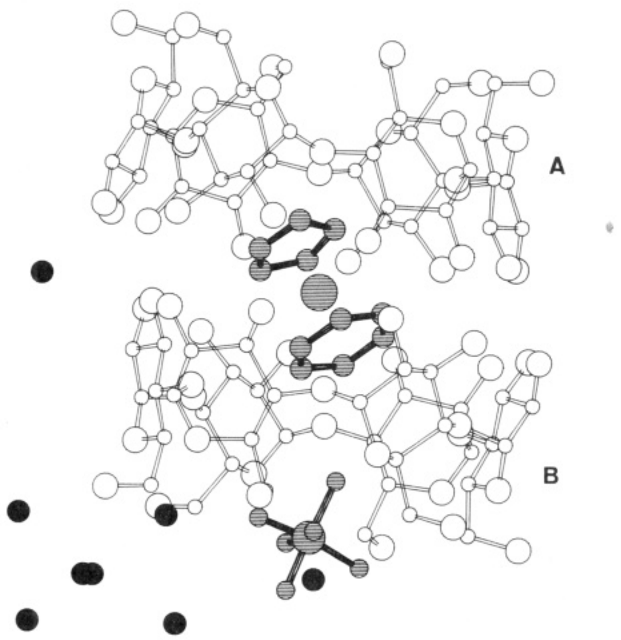

Figure 4. Side-on view of the head-to-head type molecular structure of [cpFe(η^6-C_6H_6)]PF_6·2α-CD·8H_2O. The guest molecules are shaded; water molecules are shown by black circles.

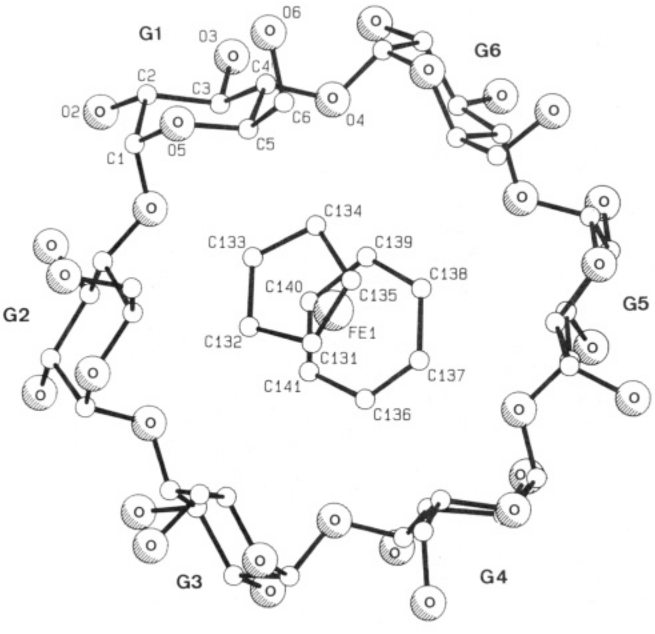

Figure 5. Numbering scheme of the guest cation and of cyclodextrin molecule A.

(b) Conformation of the α-CD Molecules. The α-cyclodextrin molecules are in the shape of a conical hexagon with local pseudo-6-fold symmetry as depicted in the space-filling representations. The six glucose units are in the C1 chair form, and the overall conformation of the macrocycle is "relaxed". The average bond distances and angles over the 12 glucose residues of a dimer are in good agreement with those of other α-cyclodextrin complexes. All primary hydroxy groups are in gauche, gauche orientation, that is, the C(6)–O(6) bonds point away from the center of the cavity (Figure 6). The geometrical data of the α-CD rings are given in Table II.

The 6 O(4) atoms and the 12 secondary hydroxy oxygen atoms are coplanar with a maximum deviation of 0.08 and 0.14 Å, respectively, from their least-squares planes. Considering the glycosidic oxygen atoms, both α-CD rings

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Table I. Fractional Atomic Coordinates[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Guest Molecules and Water Molecules									
Fe1	0.012	0.002	0.765	3.16 (4)	C137	−0.130 (1)	0.007 (1)	0.733 (1)	4.1 (4)
P1	0.0309 (6)	0.0280 (6)	0.3417 (6)	7.4 (2)	C138	−0.133 (2)	−0.094 (2)	0.695 (2)	5.3 (5)
F1	0.079 (3)	0.076 (3)	0.245 (3)	13 (2)	C139	−0.043 (2)	−0.090 (2)	0.641 (2)	7.0 (6)
F2	0.009 (3)	0.131 (3)	0.365 (3)	14 (2)	C140	0.050 (2)	0.022 (2)	0.634 (1)	4.4 (4)
F3	−0.080 (3)	−0.060 (4)	0.289 (3)	15 (2)	C141	0.052 (1)	0.120 (1)	0.669 (1)	4.0 (4)
F4	0.051 (3)	−0.071 (3)	0.289 (3)	9 (1)	OW1	0.5186 (8)	0.4903 (8)	0.2791 (8)	3.1 (2)
F5	0.156 (5)	0.086 (5)	0.376 (4)	13 (3)	OW2	0.5335 (8)	−0.0018 (8)	0.2696 (8)	3.1 (2)
F6	−0.030 (6)	−0.027 (6)	0.440 (5)	18 (4)	OW3	0.330 (1)	0.648 (1)	0.187 (1)	4.9 (3)
C131	0.048 (2)	0.054 (2)	0.893 (2)	5.2 (5)	OW4	0.350 (1)	0.683 (1)	0.365 (1)	4.8 (3)
C132	0.151 (1)	0.087 (1)	0.843 (1)	4.1 (4)	OW5	0.0121 (8)	0.4799 (8)	0.2803 (8)	3.3 (2)
C133	0.146 (1)	−0.011 (1)	0.804 (1)	4.1 (4)	OW6	0.682 (1)	0.355 (1)	0.369 (1)	5.7 (3)
C134	0.042 (2)	−0.110 (2)	0.822 (2)	5.9 (5)	OW7	0.665 (1)	0.322 (1)	0.187 (1)	6.2 (4)
C135	−0.017 (2)	−0.067 (2)	0.881 (2)	8.2 (8)	OW8	0.638 (2)	0.331 (2)	0.789 (2)	10.3 (7)
C136	−0.041 (2)	0.108 (1)	0.721 (1)	4.4 (4)					
CD: Molecule A[b]									
O12	0.3998 (9)	−0.1018 (9)	0.8815 (8)	3.4 (2)	C14	0.126 (1)	−0.289 (1)	0.9917 (9)	2.1 (2)
O13	0.1825 (9)	−0.2848 (9)	0.8407 (9)	3.9 (2)	C15	0.155 (1)	−0.218 (1)	1.0795 (9)	2.3 (2)
O14	0.0154 (7)	−0.3191 (7)	0.9704 (6)	2.0 (2)	C16	0.096 (1)	−0.294 (1)	1.155 (1)	2.7 (3)
O15	0.2723 (8)	−0.1693 (8)	1.0944 (7)	2.7 (2)	C21	0.423 (1)	0.317 (1)	1.052 (1)	2.5 (3)
O16	0.1221 (9)	−0.3802 (9)	1.1510 (8)	3.5 (2)	C22	0.481 (11)	0.283 (1)	0.981 (1)	2.7 (3)
O22	0.4995 (9)	0.3482 (9)	0.9095 (9)	4.0 (2)	C23	0.417 (1)	0.161 (1)	0.958 (1)	2.5 (3)
O23	0.4818 (9)	0.1304 (9)	0.8977 (8)	3.4 (2)	C24	0.396 (1)	0.095 (1)	1.0402 (9)	2.3 (2)
O24	0.3171 (7)	−0.0171 (7)	1.0168 (7)	2.5 (2)	C25	0.346 (1)	0.137 (1)	1.112 (1)	2.7 (3)
O25	0.4116 (8)	0.2557 (8)	1.1252 (7)	2.7 (2)	C26	0.348 (1)	0.094 (1)	1.199 (1)	3.6 (3)
O26	0.460 (1)	0.130 (1)	1.2217 (9)	4.5 (3)	C31	0.083 (1)	0.392 (1)	1.042 (1)	2.3 (2)
O32	0.1190 (9)	0.4437 (9)	0.8980 (8)	3.7 (2)	C32	0.175 (1)	0.444 (1)	0.971 (1)	2.5 (3)
O33	0.3338 (9)	0.4383 (9)	0.9016 (9)	4.0 (2)	C33	0.237 (1)	0.378 (1)	0.957 (1)	2.4 (2)
O34	0.3174 (8)	0.2903 (8)	1.0231 (7)	2.7 (2)	C34	0.282 (1)	0.367 (1)	1.0417 (9)	2.0 (2)
O35	0.1322 (7)	0.3862 (7)	1.1177 (7)	2.4 (2)	C35	0.188 (1)	0.324 (1)	1.1111 (9)	2.0 (2)
O36	0.3137 (9)	0.4449 (9)	1.2229 (8)	3.8 (2)	C36	0.232 (1)	0.333 (1)	1.201 (1)	2.8 (3)
O42	−0.3087 (8)	0.0747 (8)	0.8321 (7)	3.0 (2)	C41	−0.325 (1)	0.054 (1)	0.9828 (9)	1.9 (2)
O43	−0.0946 (8)	0.2811 (8)	0.8573 (8)	3.4 (2)	C42	−0.270 (1)	0.141 (1)	0.913 (1)	2.5 (2)
O44	0.0093 (7)	0.2788 (7)	1.0086 (6)	2.0 (2)	C43	−0.145 (1)	0.194 (1)	0.917 (1)	2.5 (3)
O45	−0.2865 (7)	0.1111 (7)	1.0640 (6)	2.2 (2)	C44	−0.105 (1)	0.247 (1)	1.0087 (9)	2.0 (2)
O46	−0.1466 (9)	0.3029 (9)	1.1794 (8)	3.6 (2)	C45	−0.167 (1)	0.156 (1)	1.074 (1)	2.4 (2)
O52	−0.4325 (7)	−0.3771 (7)	0.8106 (7)	2.6 (2)	C46	−0.138 (1)	0.206 (1)	1.167 (1)	2.9 (3)
O53	−0.4141 (9)	−0.1616 (9)	0.8168 (8)	3.4 (2)	C51	−0.412 (1)	−0.363 (1)	0.9641 (9)	1.9 (2)
O54	−0.2951 (7)	−0.0277 (7)	0.9665 (6)	2.0 (2)	C52	−0.445 (1)	−0.322 (1)	0.8867 (9)	2.1 (2)
O55	−0.4272 (7)	−0.3093 (7)	1.0407 (6)	2.1 (2)	C53	−0.373 (1)	−0.199 (1)	0.8843 (9)	2.0 (2)
O56	−0.4836 (8)	−0.1544 (8)	1.1382 (7)	3.0 (2)	C54	−0.379 (1)	−0.140 (1)	0.9704 (9)	1.9 (2)
O62	−0.0533 (8)	−0.4477 (8)	0.8220 (7)	3.0 (2)	C55	−0.355 (1)	−0.191 (1)	1.0451 (9)	2.0 (2)
O63	−0.2626 (9)	−0.4464 (9)	0.8102 (8)	3.4 (2)	C56	−0.378 (1)	−0.148 (1)	1.134 (1)	2.5 (3)
O64	−0.2974 (7)	−0.3310 (6)	0.9525 (6)	1.9 (2)	C61	−0.067 (1)	−0.432 (1)	0.977 (1)	2.4 (2)
O65	−0.1411 (7)	−0.4452 (7)	1.0459 (7)	2.4 (2)	C62	−0.133 (1)	−0.469 (1)	0.892 (1)	2.3 (2)
O66	−0.3486 (8)	−0.4997 (8)	1.1344 (7)	3.0 (2)	C63	−0.192 (1)	−0.405 (1)	0.8841 (9)	2.2 (2)
C11	0.344 (1)	−0.099 (1)	1.030 (1)	2.4 (2)	C64	−0.265 (1)	−0.408 (1)	0.9628 (9)	2.1 (2)
C12	0.323 (1)	−0.171 (1)	0.944 (1)	2.5 (3)	C65	−0.190 (1)	−0.375 (1)	1.0453 (9)	1.9 (2)
C13	0.202 (1)	−0.216 (1)	0.920 (1)	2.6 (3)	C66	−0.258 (1)	−0.390 (1)	1.128 (1)	2.9 (3)
CD: Molecule B[b]									
O12	−0.1482 (8)	0.3589 (8)	0.7224 (7)	2.9 (2)	O62	−0.4851 (8)	−0.0820 (8)	0.6520 (7)	2.8 (2)
O13	−0.3395 (8)	0.1474 (7)	0.6852 (7)	2.6 (2)	O63	−0.4606 (8)	−0.2805 (8)	0.6527 (7)	2.8 (2)
O14	−0.3045 (7)	0.0245 (7)	0.5427 (6)	2.0 (2)	O64	−0.3091 (7)	−0.2842 (7)	0.5290 (6)	2.1 (2)
O15	−0.1232 (7)	0.3132 (7)	0.4901 (6)	2.1 (2)	O65	−0.3973 (7)	−0.1078 (7)	0.4332 (6)	2.2 (2)
O16	−0.2946 (9)	0.1683 (9)	0.3663 (8)	3.5 (2)	O66	−0.4398 (9)	−0.2994 (9)	0.3289 (8)	3.7 (2)
O22	0.3509 (8)	0.4904 (8)	0.7340 (7)	3.0 (2)	C11	−0.081 (1)	0.362 (1)	0.5753 (9)	2.2 (2)
O23	0.1424 (8)	0.4969 (8)	0.7308 (8)	3.3 (2)	C12	−0.183 (1)	0.313 (1)	0.6367 (9)	2.1 (2)
O24	−0.0010 (7)	0.3346 (7)	0.5989 (6)	2.0 (2)	C13	−0.239 (1)	0.187 (1)	0.6336 (9)	2.0 (2)
O25	0.2844 (7)	0.4443 (7)	0.5071 (6)	2.2 (2)	C14	−0.272 (1)	0.1400 (9)	0.5411 (9)	1.8 (2)
O26	0.1430 (8)	0.4957 (8)	0.4131 (7)	3.1 (2)	C15	−0.166 (1)	0.196 (1)	0.4814 (9)	2.1 (2)
O32	0.4089 (9)	0.0980 (9)	0.7300 (8)	3.4 (2)	C16	−0.199 (1)	0.158 (1)	0.387 (1)	2.7 (3)
O33	0.3876 (9)	0.2947 (9)	0.7452 (8)	3.6 (2)	C21	0.337 (1)	0.441 (1)	0.5830 (9)	2.2 (2)
O34	0.3012 (7)	0.3293 (7)	0.6004 (6)	2.2 (2)	C22	0.302 (1)	0.496 (1)	0.656 (1)	2.3 (2)
O35	0.4264 (7)	0.1661 (7)	0.5053 (7)	2.3 (2)	C23	0.174 (1)	0.435 (1)	0.6700 (9)	2.2 (2)
O36	0.4924 (8)	0.3684 (8)	0.4227 (7)	3.0 (2)	C24	0.115 (1)	0.419 (1)	0.5844 (9)	1.9 (2)
O42	0.0778 (8)	−0.3653 (8)	0.6585 (7)	2.7 (2)	C25	0.164 (1)	0.375 (1)	0.5100 (9)	2.0 (2)
O43	0.2788 (9)	−0.1485 (9)	0.6928 (8)	3.8 (2)	C26	0.131 (1)	0.390 (1)	0.420 (1)	2.9 (3)
O44	0.2941 (7)	0.0121 (7)	0.5801 (6)	2.1 (2)	C31	0.410 (1)	0.100 (1)	0.577 (1)	2.4 (2)
O45	0.1558 (7)	−0.2494 (7)	0.4485 (6)	2.3 (2)	C32	0.433 (1)	0.170 (1)	0.660 (1)	2.7 (3)
O46	0.3710 (9)	−0.1083 (8)	0.3901 (8)	3.4 (2)	C33	0.360 (1)	0.223 (1)	0.669 (1)	2.3 (2)
O52	−0.3787 (8)	−0.4503 (8)	0.6434 (7)	2.7 (2)	C34	0.379 (1)	0.293 (1)	0.5900 (9)	2.1 (2)
O53	−0.1578 (8)	−0.4323 (8)	0.6526 (7)	2.7 (2)	C35	0.357 (1)	0.216 (1)	0.5090 (9)	1.9 (2)
O54	−0.0022 (7)	−0.2886 (7)	0.5341 (6)	2.0 (2)	C36	0.384 (1)	0.278 (1)	0.425 (1)	2.7 (3)
O55	−0.2680 (7)	−0.3882 (7)	0.4252 (7)	2.3 (2)	C41	0.081 (1)	−0.317 (1)	0.5138 (9)	2.0 (2)
O56	−0.131 (1)	−0.447 (1)	0.3285 (9)	4.4 (3)	C42	0.149 (1)	−0.294 (1)	0.5933 (9)	2.1 (2)

Table I (Continued)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
				CD: Molecule B^b					
C43	0.201 (1)	−0.172 (1)	0.6245 (9)	2.2 (2)	C55	−0.148 (1)	−0.323 (1)	0.4382 (9)	2.1 (2)
C44	0.2717 (9)	−0.0979 (9)	0.5526 (9)	1.7 (2)	C56	−0.097 (1)	−0.334 (1)	0.352 (1)	2.9 (3)
C45	0.204 (1)	−0.132 (1)	0.4666 (9)	2.0 (2)	C61	−0.412 (1)	−0.052 (1)	0.5090 (9)	2.2 (2)
C46	0.286 (1)	−0.081 (1)	0.391 (1)	2.4 (2)	C62	−0.471 (1)	−0.139 (1)	0.578 (1)	2.3 (2)
C51	−0.335 (1)	−0.393 (1)	0.4986 (9)	1.9 (2)	C63	−0.402 (1)	−0.1923 (9)	0.5930 (9)	1.8 (2)
C52	−0.311 (1)	−0.445 (1)	0.5699 (9)	2.2 (2)	C64	−0.382 (1)	−0.246 (1)	0.5117 (9)	2.0 (2)
C53	−0.185 (1)	−0.377 (1)	0.5911 (9)	1.9 (2)	C65	−0.332 (1)	−0.161 (1)	0.4406 (9)	2.0 (2)
C54	−0.1155 (9)	−0.3688 (9)	0.5104 (9)	1.8 (2)	C66	−0.330 (1)	−0.214 (1)	0.354 (1)	2.5 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] The first digit specifies the glucose residue, the second one the atom number in the glucose ring.

Table II. Geometrical Data for α-Cyclodextrin Molecules

	CD A	CD B
O(4)···O(4) Distances, Å		
O(4,G1)···O(4,G2)	4.24 (2)	4.34 (2)
O(4,G2)···O(4,G3)	4.27 (2)	4.21 (2)
O(4,G3)···O(4,G4)	4.20 (2)	4.36 (2)
O(4,G4)···O(4,G5)	4.28 (2)	4.20 (2)
O(4,G5)···O(4,G6)	4.20 (2)	4.28 (2)
O(4,G6)···O(4,G1)	4.26 (2)	4.26 (2)
O(4,G1)···O(4,G4)	8.35 (2)	8.41 (2)
O(4,G2)···O(4,G5)	8.46 (2)	8.66 (2)
O(4,G3)···O(4,G6)	8.64 (2)	8.56 (2)
Tilt Angles, deg		
G1	10.3 (6)	14.5 (6)
G2	12.7 (7)	20.0 (4)
G3	14.2 (5)	10.9 (4)
G4	9.4 (5)	14.0 (6)
G5	13.9 (4)	12.3 (9)
G6	12.0 (5)	14.7 (9)
Interglucose Hydrogen Bond Distances, Å		
O(2,G1)···O(3,G2)	2.84 (2)	3.49 (2)
O(2,G2)···O(3,G3)	3.12 (2)	3.03 (2)
O(2,G3)···O(3,G4)	2.75 (2)	3.01 (2)
O(2,G4)···O(3,G5)	2.86 (2)	2.91 (2)
O(2,G5)···O(3,G6)	2.95 (2)	3.08 (2)
O(2,G6)···O(3,G1)	2.91 (2)	2.83 (2)

are slightly elliptically distorted and elongated along the ligand planes of the guest molecule. The difference in the longest and shortest diagonal distances, which are measured between the glycosidic oxygen atoms, is 0.29 Å in cyclodextrin A and 0.25 Å in cyclodextrin B. Much larger values were found in, for example, the α-cyclodextrin–*m*-nitroaniline adduct (0.99 Å);[20] however, the geometry of the glycosidic oxygen atoms does not seem to be sensitive to a conformational change in the O(2)···O(3) region.

A more convenient measure to describe the orientation of each glucose residue relative to the macrocycle is the tilt angle, which is defined as the angle between the plane through the six glycosidic oxygen atoms and the plane through O(4)*, C(1), C(4), and O(4) atoms of each glucose residue. As all glucose units incline with their O(6) side turning to the inside of the macrocycle, larger tilt angles make the O(2)···O(3) side of the macrocyclic ring wider. In cyclodextrin A the tilt angles range from 9.4° to 14.2° with an average of 12.1°. In cyclodextrin B the values range from 10.9° to 20.0° with an average of 14.4°, showing the larger cavity of cyclodextrin B. This is reflected also in the interglucose hydrogen bonds formed between O(2) and O(3) atoms of adjacent glucose residues. The O(2)–O(3)* distances are in the range 2.75–3.12 Å (average 2.91) and 2.83–3.49 Å (average 3.06) for cyclodextrin A and B, respectively. The O(2,G1)···O(3,G2) distance of molecule B (3.49 Å) is only slightly less than the van der Waals O-H···O distance and may represent only weak hydrogen-bonding interaction.

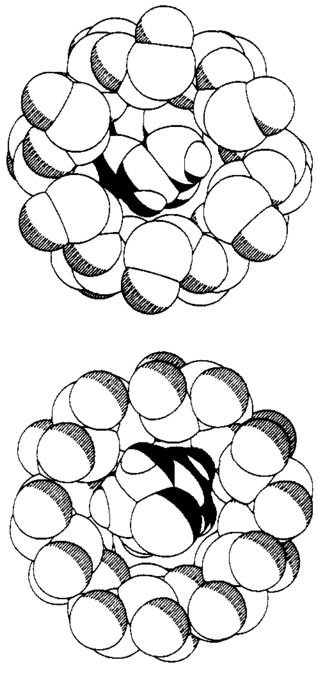

Figure 6. Plan view of the space-filling representation of [cpFe]$^+$·α-CD (molecule A) in the crystal of [cpFe(η^6-C_6H_6)]-PF_6·2α-CD·$8H_2O$ from the primary (top) and the secondary (bottom) hydroxyl side demonstrating the high symmetry of the α-CD and the penetration of the guest into the CD cavity. Oxygen atoms of the CD rings are shaded only.

(c) Guest Geometry and Host–Guest Interaction. The [cpFe(η^6-C_6H_6)]$^+$ cation is encapsulated within the cavity formed by the two α-CD moieties of a dimer as shown in Figure 4. The iron atom is located near the center of the cavity, and the complex axis [Cent(C_5H_5)–Fe–Cent(C_6H_6)] forms an angle of 33° with the crystallographic *c* axis. The cyclopentadienyl and the benzene rings are parallel and tilted by angles of 39° and 40°, respectively, against the mean planes of α-CD molecules A and B, defined by the oxygen atoms of the 12 secondary hydroxy groups. Two and three carbon atoms, respectively, of the cyclopentadienyl and the benzene ligand are located above (cyclopentadienyl) and below (benzene) these planes as shown in Table III. Fe–Centroid distances to the C_5H_5 and the C_6H_6 rings are 1.66 and 1.57 Å, respectively. These values are in good agreement with those found in the cations [cpFe(η^6-C_6Et_6)]$^+$ (1.68 and 1.55 Å)[21] and {[(η^5-C_5H_4)$(CH_2)_3$(η^6-C_6H_5)]Fe}$^+$ (1.62 and 1.59Å).[22] Bond

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Table III. Geometry of the Host–Guest Interactions

Distances,[a] Å			
CD A		CD B	
C131	−0.49 (2)	C136	0.35 (2)
C132	0.41 (2)	C137	0.72 (2)
C133	0.92 (2)	C138	0.26 (2)
C134	0.44 (3)	C139	−0.65 (3)
C135	−0.49 (4)	C140	−0.98 (2)
Fe1	1.39 (0)	C141	−0.54 (3)
		Fe1	1.12 (0)

Host–Guest Distances <3.5 Å	
C132–O(3,G3,CD B)	3.48 (3)
C133–O(2,G3,CD B)	3.35 (2)
C136–O(3,G4,CD A)	3.43 (3)
C137–O(2,G4,CD A)	3.34 (3)
C139–O(4,G5,CD B)	3.40 (4)
C140–O(4,G4,CD B)	3.50 (3)
C141–O(4,G3,CD B)	3.41 (3)

[a] Distances of the C_5H_5 and the C_6H_6 ring atoms from the mean planes of the 12 secondary hydroxy oxygen atoms of CD A and CD B, respectively.

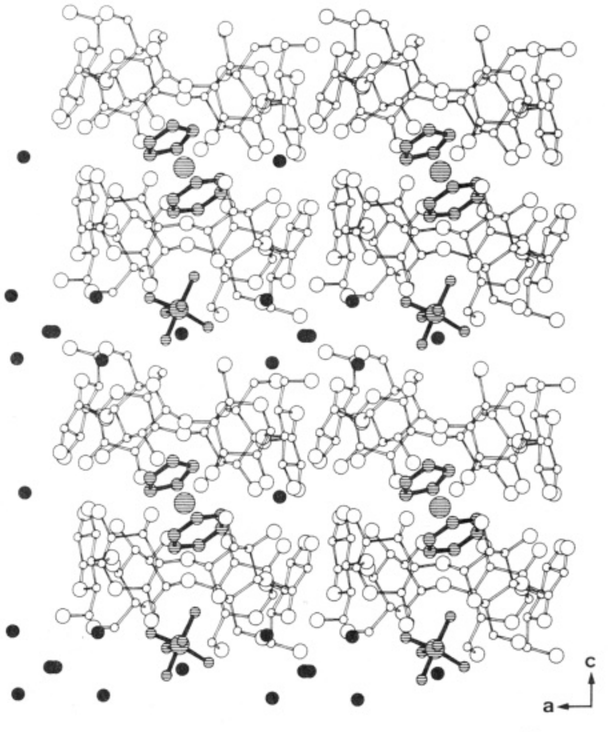

Figure 7. Channel-type molecular packing of [cpFe(η^6-C_6H_6)]-PF_6·2α-CD·8H_2O. The guest molecules are shaded; water molecules are shown by black circles.

distances of the guest molecule are within normal ranges with an average C–C length of 1.44 (3) Å. The shortest non-hydrogen intermolecular distance between the guest and the host molecules (Table III) is that of C137⋯O(2,G4) of cyclodextrin A of 3.34 Å. The distance of the hydrogen atom at C137 to O(2,G4) of cyclodextrin A is 2.46 Å, forming an angle C137–H⋯O(2,G4) of 153°. All these values suggest van der Waals contacts. The PF_6^- anion is located at the center of the primary hydroxyl side of cyclodextrin B, which includes the benzene ring.

(d) Molecular Packing and Hydrogen Bonding. The packing of α-cyclodextrin molecules in the crystal is shown in Figure 7. The head-to-head dimers are stacked along the crystallographic *c* axis forming parallel channels in which the guest cations and anions are lined up alternately (Figure 8). The α-CD molecules A and B are inclined by 8° and 3°, respectively, to the stack axis and are shifted laterally to each other by 1.2 Å.

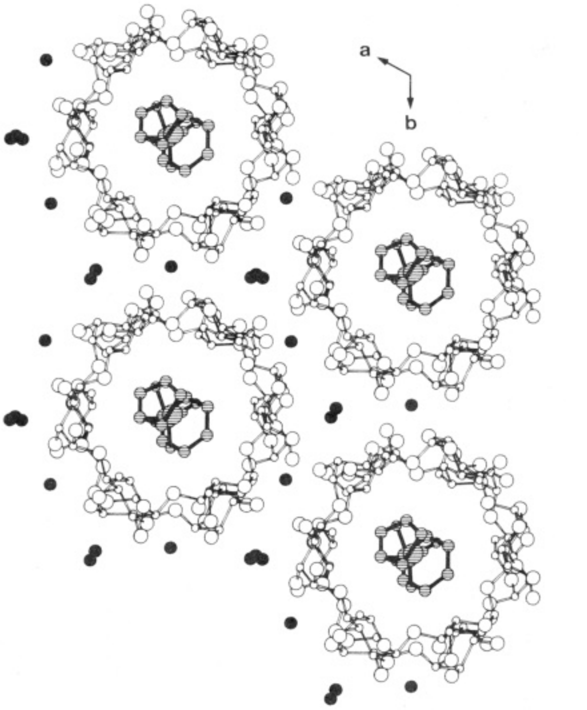

Figure 8. Crystal structure viewed down the *c* axis showing the hexagonal array of the CD channels. The guest molecules are shaded, water molecules are shown by black circles. Two α-CD molecules are drawn in each channel.

Eight water molecules of hydration per asymmetric unit fill the intermolecular spaces between the channels. All water molecules are involved in at least four, and all hydroxy groups in at least two, hydrogen bonds. A similar packing and hydrogen bonding scheme was found in the complex LiI_3·I_2·2α-CD·8H_2O,[23] in spite of the different guest molecules.

Conclusions

In this work we have shown that the mixed-sandwich complex [cpFe(η^6-C_6H_6)]PF_6 forms stable 2:1 host–guest inclusion compounds with both α- and β-cyclodextrin. The X-ray structural characterization of the α-CD adduct provides valuable insight into the inclusion geometry of a transition-metal sandwich complex in α-cyclodextrin. Further studies involving the structural features of supramolecular adducts formed between organometallic complexes and cyclodextrins as second-sphere ligands are in progress and will be reported in future publications.

Experimental Section

General Remarks. Cyclodextrins (α-CD, β-CD) were obtained from Fluka Chemie AG and used as received. The PF_6^- and BF_4^- salts of [cpFe(η^6-C_6H_6)]$^+$ were prepared by the method described by Nesmeyanov.[24] UV–vis spectra were recorded on a Shimadzu UV-240 spectrophotometer, CP/MAS ^{13}C NMR spectra on a Bruker AM 400 spectrometer, and circular dichroism spectra on a JASCO J-20 spectropolarimeter.

Preparation of Inclusion Compounds. [cpFe(η^6-C_6H_6)]PF_6 (172 mg, 0.5 mmol) was dissolved in 30 mL of water at 80 °C, and 10 mL of a hot aqueous solution of α-CD (973 mg, 1.0 mmol) was added. After stirring for 5 min at 80 °C, the hot mixture was filtered and allowed to cool slowly to room temperature overnight. The product that precipitated was filtered off and washed suc-

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Organometallics **1990**, *9*, 1141–1146 1141

Table IV. Crystal Data

formula	$[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]PF_6{\cdot}2\alpha\text{-CD}{\cdot}8H_2O$
cryst syst	triclinic
space group	$P1$
a, Å	13.815 (1)
b, Å	13.929 (1)
c, Å	15.639 (2)
α, deg	94.23 (1)
β, deg	87.15 (1)
γ, deg	119.81 (1)
V, Å^3	2604
Z	1
calc density, g/cm^3	1.552
no. of reflns	10226
no. of obs reflns	9965
no. of parameters	1432
final R factor	0.083

cesively with water and ethanol, giving 1.0 g (87%) of $[cpFe(\eta^6\text{-}C_6H_6)]PF_6{\cdot}2\alpha\text{-CD}{\cdot}8H_2O$ as orange–yellow crystals, mp 260 °C (dec). Anal. Calcd for $C_{83}H_{131}F_6FeO_{60}P{\cdot}8H_2O$: C, 40.96; H, 6.09; F, 4.68; Fe, 2.29; P, 1.27. Found: C, 41.23; H, 6.09; F, 4.70; Fe, 2.31; P, 1.24.

The α-CD adduct of the analogous BF_4^- salt was prepared and isolated in essentially the same manner in 26% yield. Anal. Calcd for $C_{83}H_{131}BF_4FeO_{60}{\cdot}8H_2O$: C, 41.96; H, 6.24; F, 3.20. Found: C, 41.80; H, 6.35; F, 3.21.

The β-CD adduct of the PF_6^- salt was prepared in a similar way, using hot saturated β-CD solutions, yield 44%. Anal. Calcd for $C_{95}H_{151}F_6FeO_{70}P{\cdot}7H_2O$: C, 41.64; H, 6.07; F, 4.16; Fe, 2.04; P, 1.13. Found: C, 41.38; H, 6.11; F, 4.25; Fe, 2.07; P, 1.16.

Crystal Structure Analysis. Crystals of $[cpFe(\eta^6\text{-}C_6H_6)]PF_6{\cdot}2\alpha\text{-CD}{\cdot}8H_2O$ were obtained as yellow, transparent prisms from aqueous solution. The sample crystal was sealed with epoxy to the end of a glass fiber. Crystal data are summarized in Table IV. A Nonius CAD4 automatic diffractometer was used for data collection with Cu Kα radiation and graphite monochromator. At room temperature the intensities of 10 226 independent reflections with $\theta < 70°$ were measured, of which 9965 were classified as observed with $I > 2\sigma(I)$. The crystal showed no significant intensity decay during data collection. The structure was solved with data from an isomorphous crystal of the complex $LiI_3{\cdot}I_2{\cdot}2\alpha\text{-CD}{\cdot}8H_2O$.[23] The coordinates of one cyclodextrin molecule were submitted to the program ORIENT of the DIRDIF program system.[25] In a subsequent electron density map 115 of the 132 atoms of the two cyclodextrin molecules could be localized. Successive full-matrix least-squares refinements and difference Fourier syntheses revealed the positions of all non-hydrogen atoms. Anisotropic temperature factors were introduced for all atoms. Due to the large number of parameters, further refinements were carried out in segments. The final R value was 0.083 for all 9965 data with $I > 2\sigma(I)$. Hydrogen atoms could not be localized. The positions of those of the guest molecule were calculated.

Acknowledgment. We thank Dr. P. Moser and K. Jäkel for the ICD measurements and Dr. H. Sauter for measurements of the solid-state NMR spectra. We are grateful to Dr. A. Alder for stimulating discussions of this work and to D. Konstanzer, T. Lochmann, and H. R. Walter for their skillful technical assistance.

Registry No. $[cpFe(\eta^6\text{-}C_6H_6)]PF_6{\cdot}2\alpha\text{-CD}{\cdot}8H_2O$, 125049-68-5; $[cpFe(\eta^6\text{-}C_6H_6)]BF_4{\cdot}2\alpha\text{-CD}{\cdot}8H_2O$, 125049-69-6; $[cpFe(\eta^6\text{-}C_6H_6)]PF_6{\cdot}2\beta\text{-CD}{\cdot}7H_2O$, 125049-70-9.

Supplementary Material Available: Listings of bond distances and angles, O···O distances suggesting hydrogen bonds, and anisotropic thermal parameters (9 pages); listings of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

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Reaction of $Cp_3U{=}CHPMeRPh$ with $CpCo(CO)_2$

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Received September 8, 1989

A terminal carbonyl of $CpCo(CO)_2$ inserts into the U=C bond of $Cp_3U{=}CHPMeRPh$ (R = Ph or Me) to produce $Cp(OC)CoC(OUCp_3){=}CHPMeRPh$. The structure of $Cp(OC)CoC(OUCp_3){=}CHPMe_2Ph$ has been confirmed by X-ray diffraction: space group $P2_12_12_1$; a = 15.645 (2) Å, b = 23.828 (3) Å, c = 15.140 (3) Å, $\alpha = \beta = \gamma = 90°$; final error indexes R = 0.0555, R_G = 0.0644 for 3433 unique data with $I > 3\sigma(I)$. Heating $Cp(OC)CoC(OUCp_3){=}CHPMeRPh$ leads to the formation of $Cp(OC)CoPMeRPh$.

We are interested in utilizing the oxygen affinity of actinides to activate small molecules.[1] In this regard we have determined that the α-carbon atom of $Cp_3U{=}CHPMeRPh$ ($Me = CH_3$, $Ph = C_6H_5$, $Cp = C_5H_5$) is a strong nucleophile[2] and that polar unsaturated molecules will insert into the uranium–carbon multiple bond[3–5] of $Cp_3U{=}CHPMeRPh$.[6–9] We are investigating the reactions of $Cp_3U{=}CHPMeRPh$ with a variety of metal carbonyls and have previously reported the reactions of $M(CO)_6$ (M = W, Mo, Cr),[10,11] $CpMn(CO)_3$,[12] and $[CpFe(CO)_2]_2$[13] with

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