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Encapsulation of half-sandwich complexes of molybdenum with β-cyclodextrin

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Received 11th May 2000, Accepted 11th July 2000
Published on the Web 9th August 2000

β-Cyclodextrin formed stable, crystalline 1 : 1 host : guest inclusion compounds, in high yields, with half-sandwich complexes of molybdenum of the type $MoCp'(\eta^3\text{-}C_3H_5)(CO)_2$ ($Cp' = Cp$, $C_5H_4SiMe_3$ or C_9H_7). The products have been characterised in the solid state by elemental analysis, FTIR spectroscopy, TGA, powder X-ray diffraction and ^{13}C MAS NMR spectroscopy. Channel-type structures were formed with $Cp' = Cp$ and C_9H_7, while with $Cp' = C_5H_4SiMe_3$ the arrangement of the cyclodextrin molecules was more similar to that of pristine β-cyclodextrin hydrate.

Introduction

Cyclodextrins form inclusion compounds with a wide variety of molecules including transition metal complexes and organometallic compounds. Particularly suitable guests are those bearing hydrophobic ligands such as cyclopentadienyl ($Cp = \eta^5\text{-}C_5H_5$) and η^6-arene groups. β-Cyclodextrin (β-CD) consists of seven α(1→4)-linked glucopyranose units which define a slightly V-shaped toroidal cavity. The cavity diameter is in the range 6.0–6.5 Å, the height of the torus is 7.9 Å, and the cavity volume is approximately 262 Å^3.[1,2] Secondary hydroxyl groups at the 2 and 3 positions are located on the wider opening and primary hydroxyl groups at the 6 position on the other. The outer rims of the torus are therefore hydrophilic, while the cavity is rendered hydrophobic because of the presence of glycosidic oxygens and C–H units. The primary hydroxyl groups may freely rotate about the C-5–C-6 bond so as to minimise interaction energy, thereby reducing the effective diameter of the cavity.

Cyclodextrins are known to form complexes with ferrocene and its derivatives,[3] titanocene dihalides,[4] aromatic ruthenium complexes,[5] mixed sandwich complexes such as $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]PF_6$,[6] and half-sandwich complexes such as $FeCp(CO)_2Me$,[7] $MnCp(CO)_3$,[8] and $Cr(\eta^6\text{-}C_6H_6)(CO)_3$.[9] Metallocene dihalides are potent organometallic antitumor agents and cyclodextrin inclusion compounds are interesting for pharmaceutical use.[4] Encapsulated half-sandwich complexes have been shown to exhibit markedly different physical and chemical properties compared to those of the bulk material, for example in their non-linear optical properties[10] and ligand substitution/insertion reactions.[7] To the best of our knowledge, inclusion compounds between cyclodextrins and half-sandwich complexes of molybdenum have not been reported. This paper describes a structural study in the solid state for the compounds formed between β-cyclodextrin and the complexes $MoCp'(\eta^3\text{-}C_3H_5)(CO)_2$ ($Cp' = Cp$, $C_5H_4SiMe_3$ or indenyl).

Experimental

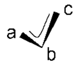
General methods

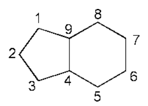
All air-sensitive reactions and manipulations were performed using standard Schlenk techniques under an oxygen-free and water-free nitrogen atmosphere. Solvents were dried by standard procedures (hexane and Et_2O over sodium–benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and kept over 4 Å molecular sieves.

Infrared spectra were recorded on a Unican Mattson Model 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 XRD data were collected on a Philips X'pert diffractometer using Cu-Kα radiation filtered by Ni ($\lambda = 1.5418$ Å). Microanalyses were performed at the Technical University of Munich. ^1H NMR spectra were measured in solution using a Bruker CXP 300 spectrometer. Solid-state ^{29}Si and ^{13}C NMR spectra were recorded at 79.49 and 100.62 MHz respectively, on a (9.4 T) Bruker MSL 400P spectrometer, ^{29}Si MAS NMR spectra with 40° pulses, spinning rates 5.0–5.5 kHz and 60 s recycle delays and ^{29}Si CP MAS NMR spectra at 25 °C with 5.5 μs ^1H 90° pulses, 8 ms contact time, a spinning rate of 5.0 kHz and 60 s recycle delays. Chemical shifts are quoted in parts per million from TMS. ^{13}C CP MAS NMR spectra were recorded 25 °C with a 4.5 μs ^1H 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.

Starting materials

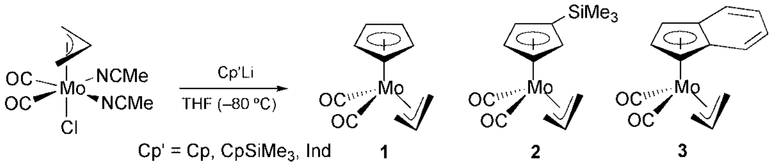
β-CD was obtained from Wacker Chemie (München) and recrystallised before use. The following compounds were prepared as described in the literature: $C_5H_4SiMe_3Li$,[11] $MoCp(\eta^3\text{-}C_3H_5)(CO)_2$ **1**,[12a] and $Mo(C_9H_7)(\eta^3\text{-}C_3H_5)(CO)_2$ **3**.[12a] ^{13}C CP MAS NMR: **1**, δ 238.94 (CO), 92.5 (Cp), 68.44 (br, C_b, see below for allyl group labelling scheme) and 42.52 (br, $C_{a/c}$); **3**, δ 240.08 (CO), 126.67 ($C^{5/8}$, see below for indenyl group labelling scheme), 123.95 ($C^{6/7}$), 112.62 ($C^{4/9}$), 87.88 (C^2), 80.17 ($C^{1/3}$) and 51.6 (br, $C_{a/b/c}$).





$Mo(C_5H_4SiMe_3)(\eta^3\text{-}C_3H_5)(CO)_2$ 2. Cold (−80 °C) THF (30 mL) was slowly transferred *via* a stainless steel needle to a

DOI: 10.1039/b003763j



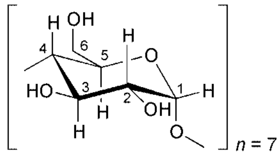
Scheme 1

Schlenk tube which contained a mixture of $Mo(\eta^3\text{-}C_3H_5)Cl(NCMe)_2(CO)_2$ [12a] (2.00 g, 6.44 mmol) and $C_5H_4SiMe_3Li$ (0.93 g, 6.44 mmol) at −80 °C. After slow warming to room temperature with stirring the reaction mixture was left for 18 h. The orange-brown solution was evaporated to dryness and the residue extracted with hexane at 40 °C for some hours. Upon filtration and concentration of the resulting yellow solution the compound precipitated as a yellow powder. Recrystallisation from hexane–diethyl ether (−30 °C) gave yellow crystals of $Mo(C_5H_4SiMe_3)(\eta^3\text{-}C_3H_5)(CO)_2$ **2** (2.04 g, 96%). Found: C, 47.17; H, 5.46. $C_{13}H_{18}MoO_2Si$ requires C, 47.27; H, 5.49%. Selected $\tilde{\nu}_{max}/cm^{-1}$ 2955m, 2896m, (CO) 1914vs, (CO) 1851vs, 1392m, 1251s, 1162m, 1045m, 837s, 755s (KBr). δ_H ($CDCl_3$, 300 MHz, 25 °C) 5.23 (s, 2 H, $C_5\mathit{H}_4SiMe_3$), 5.17 (s, 2 H, $C_5\mathit{H}_4SiMe_3$), 3.99 (m, 1 H, *meso* of C_3H_5), 2.73 (d, 2 H, *syn* of C_3H_5), 0.82 (d, 2 H, *anti* of C_3H_5) and 0.19 (s, 9 H, $C_5H_4Si\mathit{Me}_3$). ^{13}C CP MAS NMR (25 °C): δ 236.0 (s, CO), 92.3 (s, $\mathit{C}_5H_4SiMe_3$), 88.24 (s, $\mathit{C}_5H_4SiMe_3$), 69.0 (s, C_b), 40.97 (br, $C_{a/c}$) and 0.66 (s, $C_5H_4Si\mathit{Me}_3$). ^{29}Si CP MAS NMR (25 °C): δ 0.59.

Synthesis of inclusion compounds

General. A saturated aqueous solution of β-CD (0.50 g, 0.44 mmol) at 40 °C was treated with a solution of $MoCp'(\eta^3\text{-}C_3H_5)(CO)_2$ (0.44 mmol) in CH_2Cl_2. After reaction at room temperature for 1 h the suspension was filtered and the pale yellow powder washed several times with CH_2Cl_2, water and vacuum dried.

β-CD/MoCp(η^3-C_3H_5)(CO)$_2$ 1a. Yield: 0.58 g, 83%. Found: C, 38.30; H, 6.40; Mo, 5.74. $C_{10}H_{10}MoO_2\cdot C_{42}H_{70}O_{35}\cdot 13H_2O$ requires C, 38.38; H, 6.56; Mo, 5.89%. IR: $\tilde{\nu}_{max}/cm^{-1}$ 3378vs, 2925s, 2899 (sh), 1945vs, 1869vs, 1427m, 1416 (sh), 1385 (sh), 1370m, 1334m, 1303m, 1157vs, 1080vs, 1029vs, 947m, 939m, 705s, 578s and 531s (KBr). ^{13}C CP MAS NMR (25 °C): δ 236.0 (s, CO), 104.0 (β-CD, C-1), 92.3 (s, Cp), 90.4 (s, Cp), 81.7 (β-CD, C-4), 80.8 (β-CD, C-4), 73.0 (β-CD, C-2,3,5), 68.0 (s, C_2), 60.6 (β-CD, C-6), 39.3 (br, $C_{1/3}$) and 35.8 (sh).



β-CD/Mo($C_5H_4SiMe_3$)(η^3-C_3H_5)(CO)$_2$ 2a. Yield: 0.55 g, 74%. Found: C, 38.20; H, 6.70; Mo, 5.48. $C_{13}H_{18}MoO_2Si\cdot C_{42}H_{70}O_{35}\cdot 13H_2O$ requires C, 38.46; H, 6.81; Mo, 5.59%. IR: $\tilde{\nu}_{max}/cm^{-1}$ 3387vs, 2926s, 1943s, 1864s, 1639m, 1460 (sh), 1415m, 1369m, 1157s, 1079s, 1028vs, 948m, 939 (sh), 757m, 708m, 610m, 580m and 533m (KBr). ^{13}C CP MAS NMR (25 °C): δ 103.8, 103.2, 102.6, 101.5 (β-CD, C-1), 83.9, 82.1, 81.2, 78.3 (β-CD, C-4), 76.3, 72.9 (β-CD, C-2,3,5), 63.7, 61.9, 60.8 and 60.1 (β-CD, C-6).

β-CD/Mo(C_9H_7)(η^3-C_3H_5)(CO)$_2$ 3a. Yield: 0.64 g, 88%. Found: C, 40.36; H, 6.23; Mo, 6.02. $C_{14}H_{12}MoO_2\cdot C_{42}H_{70}O_{35}\cdot 12H_2O$ requires C, 40.53; H, 6.44; Mo, 5.78%. IR: $\tilde{\nu}_{max}/cm^{-1}$ 3370vs, 2929s, 1949s, 1870s, 1636m, 1457 (sh), 1412m, 1369m, 1337m, 1302m, 1156s, 1086s, 1053s, 1028vs and 947m (KBr). ^{13}C CP MAS NMR (25 °C): δ 236.79 (CO), 124.16 ($C^{5/8}$, $C^{6/7}$), 112.22 ($C^{4/9}$), 103.74 (β-CD, C-1), 89.00 (C^2), 82.5 (sh), 81.55, 80.20 (β-CD, C-4; $C^{1/3}$), 72.77 (β-CD, C-2,3,5), 60.90 (β-CD, C-6), 54.3 (C_b) and 48.10 (br, $C_{a/c}$).

Results and discussion

Preparation of inclusion compounds

The replacement of the cyclopentadienyl (Cp = η^5-C_5H_5) ligand by other *pentahapto* cyclic analogues (Cp′) has been a successful means of controlling the stability, reactivity and several other physico-chemical properties of many organometallic complexes. Indenyl (η^5-C_9H_7) complexes have long been known to display increased reactivity when compared to their Cp analogues.[12,13] Recently, some of us found a procedure to prepare complexes of general formula $M(\eta^5\text{-}Cp')(\eta^3\text{-}C_3H_5)(CO)_2$ (M = Mo or W; Cp′ = Cp, C_5H_4Me, Cp*, Ind, *etc.*) in very good isolated yields.[12] This consists of the treatment of $Mo(\eta^3\text{-}C_3H_5)Cl(NMe)_2(CO)_2$ with LiCp′ in THF at −80 °C (Scheme 1). After slow warming to room temperature the product is taken to dryness and extracted with hexane, giving $MoCp'(\eta^3\text{-}C_3H_5)(CO)_2$ in good yields. By following this method and treating $LiC_5H_4SiMe_3$ with $Mo(\eta^3\text{-}C_3H_5)Cl(NCMe)_2(CO)_2$, the novel allyl complex $Mo(C_5H_4SiMe_3)(\eta^3\text{-}C_3H_5)(CO)_2$ **2** was obtained. The IR spectrum shows the two expected CO stretching vibrations and at room temperature the solution ^1H NMR reveals only one set of signals for the allyl ligand, presumably due to very rapid fluxional averaging of the allylic protons. The complexes $MoCp'(\eta^3\text{-}C_3H_5)(CO)_2$ (Cp′ = Cp or C_5H_4Me) exhibit similar temperature-dependent dynamic behaviour in solution.[12,13]

Since $MoCp'(\eta^3\text{-}C_3H_5)(CO)_2$ complexes are insoluble in water and, moreover, are air sensitive, the co-crystallisation method from aqueous solutions, which is usually employed with water-soluble compounds to obtain inclusion complexes with cyclodextrins, cannot be used in this case. We found that the following method was the best.[14] A saturated aqueous solution of β-CD at 40 °C was treated with a solution of the organometallic compound $MoCp'(\eta^3\text{-}C_3H_5)(CO)_2$ [Cp′ = Cp (**1**), $C_5H_4SiMe_3$ (**2**) or C_9H_7 (**3**)] in CH_2Cl_2. Pale yellow precipitates formed at the interface between the two solvents during reaction at room temperature. After 1 hour the products were isolated and washed several times with dichloromethane to remove the unchanged molybdenum complexes. This process did not liberate the included guests from the cyclodextrin cavities. Finally, the products were washed with water to remove any remaining free cyclodextrin and vacuum dried. Microcrystalline powders were obtained in good yield, designated as β-CD/$MoCp'(\eta^3\text{-}C_3H_5)(CO)_2$ [Cp′ = Cp (**1a**), $C_5H_4SiMe_3$ (**2a**) or C_9H_7 (**3a**)]. Compounds **1a**–**3a** were stable for long periods if stored under an inert atmosphere. Exposure to air resulted in a colour change to green within one week.

Properties of inclusion compounds

Elemental analysis showed that the β-CD : Mo ratios in the adducts β-CD/$MoCp(\eta^3\text{-}C_3H_5)(CO)_2$ **1a**, β-CD/$Mo(C_5H_4\text{-}CpSiMe_3)(\eta^3\text{-}C_3H_5)(CO)_2$ **2a** and β-CD/$Mo(C_9H_7)(\eta^3\text{-}C_3H_5)(CO)_2$ **3a** were approximately 1 : 1. The products were further characterised in the solid state by powder X-ray diffraction (XRD), MAS NMR (^{13}C, ^{29}Si), TGA and FTIR spectroscopy.

Table 1 IR data for dicarbonyl(η^3-allyl) complexes and the inclusion compounds

Complex	$\tilde{\nu}$(CO)^a/cm^{-1}	$\Delta\tilde{\nu}$(CO)/cm^{-1}
1 MoCp(η^3-C_3H_5)$(CO)_2$^{b}	1924, 1849	—
1a β-CD/MoCp(η^3-C_3H_5)$(CO)_2$	1945, 1869	21, 20
2 Mo($C_5H_4SiMe_3$)(η^3-C_3H_5)$(CO)_2$	1914, 1851	—
2a β-CD/Mo($C_5H_4SiMe_3$)(η^3-C_3H_5)$(CO)_2$	1943, 1864	29, 13
3 Mo(C_9H_7)(η^3-C_3H_5)$(CO)_2$^{c}	1923, 1849	—
3a β-CD/Mo(C_9H_7)(η^3-C_3H_5)$(CO)_2$	1949, 1870	26, 21

^{a} Solid-state IR spectra (KBr). ^{b} Solution IR (CH_2Cl_2, cm^{-1}): 1946, 1859. ^{c} Solution IR (CH_2Cl_2, cm^{-1}): 1946, 1861.

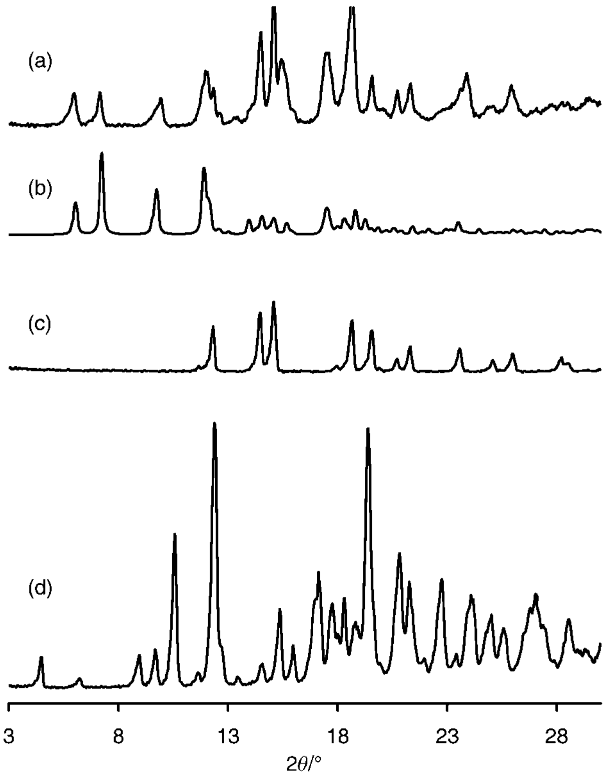


Fig. 1 Powder XRD of (a) β-CD/Mo(C_9H_7)(η^3-C_3H_5)$(CO)_2$ **3a**, (b) β-CD/[FeCp(η^6-C_6H_5R)]PF_6 (R = mesityl), (c) free Mo(C_9H_7)(η^3-C_3H_5)$(CO)_2$ **3**, and (d) free β-CD hydrate. The program PowderCell[16] was used to produce the simulated pattern (b) from the crystal structure data for the 2 : 1 inclusion compound formed between β-CD and [FeCp(η^6-C_6H_5R)]PF_6.[6c]

The KBr IR spectra of compounds **1a**, **2a** and **3a** showed the typical bands previously reported for bulk KBr spectra of β-CD,[15] indicating no chemical modification of the cyclodextrin host. In addition, some characteristic absorption bands of the guest were observed. The two ν(CO) stretching vibrations of the guest molecules appeared as sharp bands in the range 1980–1830 cm^{-1} (Table 1). These spectra were different from those of the complexes in the solid, which show broad bands probably due to intermolecular interactions, and were similar to those of the complexes in solution. This similarity was also clearly evident in the positions of the bands (Table 1). Thus, the ν(CO) stretching vibrations of the inclusion compounds were shifted by 13–30 cm^{-1} to higher frequency compared to those of the complexes in the solid, but appeared at almost the same frequencies compared to those of the complexes in CH_2Cl_2 solution. These results suggest that the guest complexes are isolated from each other in the cyclodextrin cavities as in solution.

Powder XRD and TGA provided further evidence for the encapsulation of the organometallic guests with β-CD in the solid state. Compounds **1a** and **3a** gave similar powder XRD patterns characterised by low angle peaks at about 15.0, 12.3, 9.0, 7.4, 6.1, 5.8, 5.0 and 4.8 Å (Fig. 1). These patterns do not match with those of the free components (pristine β-CD hydrate or the organometallic guest). This is an initial indication for the formation of true inclusion complexes.[2] It is known that cyclodextrin inclusion compounds usually crystallise from water to give "channel" or "cage" structures in which the cyclodextrin molecules are stacked like coins in a roll or arranged in a herringbone pattern.[2] Crystal structure determinations for two β-CD inclusion compounds of the sandwich complexes [FeCp(η^6-C_6H_5R)]PF_6 (R = mesityl or biphenyl) revealed a channel-type structure consisting of head-to-head dimers of β-CD molecules stacked along the crystallographic *c* axis.[6c] The exact orientation of the guest molecules could not be determined due to disorder. Fig. 1 shows a simulated powder diffraction pattern calculated from the crystal structure data of Klingert and Rihs for the β-CD inclusion compound of the ferrocene derivative with R = mesityl. There is a good match between this pattern and that of compound β-CD/Mo(C_9H_7)(η^3-C_3H_5)$(CO)_2$ **3a**, especially at low angles (2θ 3–20°). These results strongly suggest that the β-CD adducts **1a** and **3a** are channel-type inclusion compounds similar to those reported by Klingert and Rihs (Fig. 2). It is interesting that a β-CD inclusion compound of the [1]ferrocenophane [Fe{(η^5-C_5H_4)$_2$-$SiMe_2$}] also gave a very similar powder diffraction pattern.[17] A different result was obtained in the case of compound **2a** (Fig. 3). The powder XRD of **2a** reveals similar peaks to those of the host structure but shifted to higher 2θ, with some significant modifications of the intensity of some peaks. There is no indication for the presence of free organometallic **2**. A similar result was obtained by Díaz and Arancibia for the encapsulation of the half-sandwich complex FeCpCl$(CO)_2$ with β-CD.[14]

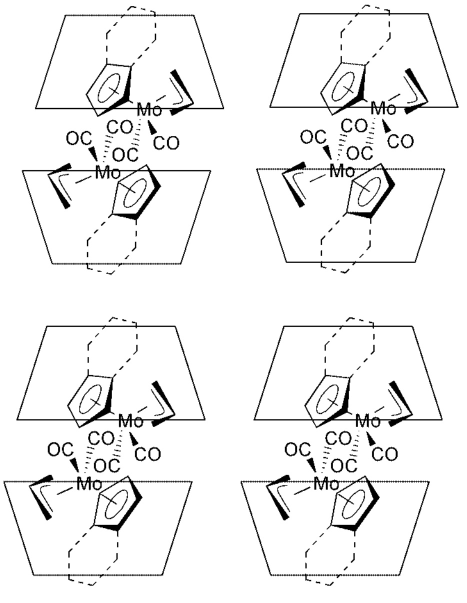


Fig. 2 Representation of proposed channel-type structure for the inclusion compounds β-CD/MoCp(η^3-C_3H_5)$(CO)_2$ **1a** and β-CD/Mo(C_9H_7)(η^3-C_3H_5)$(CO)_2$ **3a**.

Fig. 4 shows the results of thermogravimetric analysis of β-CD/MoCp(η^3-C_3H_5)$(CO)_2$ **1a**, the organometallic MoCp(η^3-C_3H_5)$(CO)_2$ **1**, pristine β-CD hydrate and a physical mixture of β-CD and **1** in a 1 : 1 molar ratio. TGA of β-CD showed loss of hydrated water up to 130 °C (14.4%, 10–11 water molecules per β-CD molecule), the maximum rate of mass loss occurring at 90 °C. There was no further change until 260 °C when the compound starts to melt and decompose, characterised by a strong, sharp peak in the differential thermogravimetric (DTG) profile at 287 °C. At 500 °C, mass loss was complete. The organometallic **1** did not undergo any change until 70 °C, at which point it starts to sublime. Mass loss was 47% in the temperature range 70–160 °C, the maximum rate of loss occurring at 149 °C. In the case of the mixture each component behaved

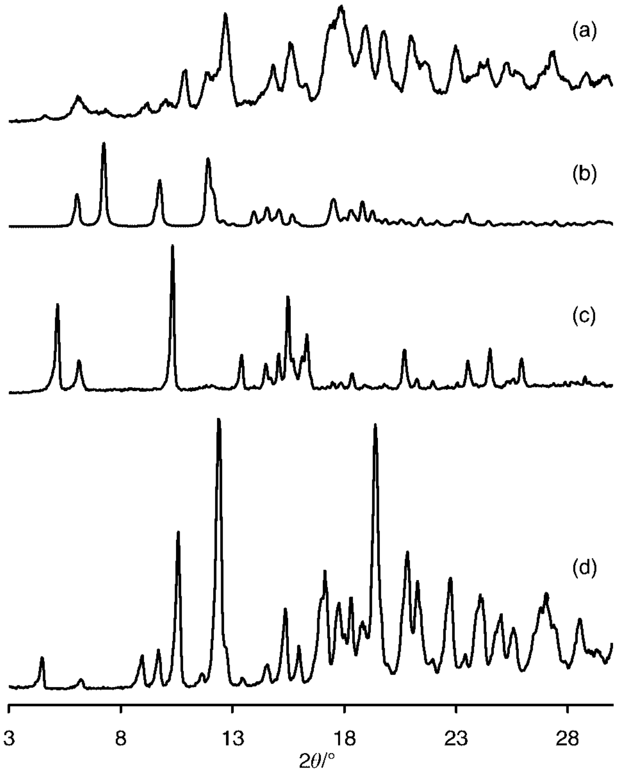


Fig. 3 Powder XRD of (a) β-CD/Mo($C_5H_4SiMe_3$)(η^3-C_3H_5)$(CO)_2$ **2a**, (b) β-CD/[Fe(Cp)(η^6-C_6H_5R)]PF_6 (R = mesityl), (c) free Mo(C_5H_4-$SiMe_3$)(η^3-C_3H_5)$(CO)_2$ **2**, and (d) free β-CD hydrate. Details as in Fig. 1.

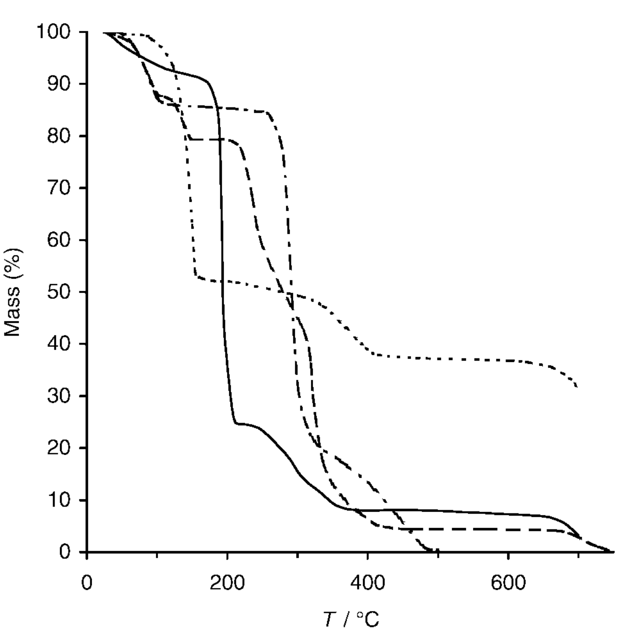


Fig. 4 TGA of β-CD/MoCp(η^3-C_3H_5)$(CO)_2$ **1a** (——), free MoCp-(η^3-C_3H_5)$(CO)_2$ **1** (-----), free β-CD hydrate (—-—-), and a physical mixture of β-CD and **1** in a 1 : 1 molar ratio (–––).

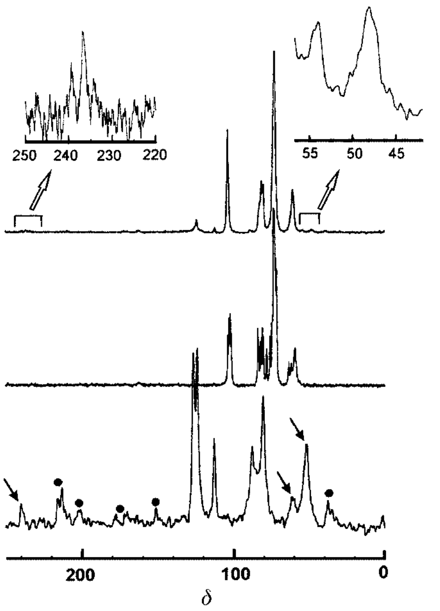


Fig. 5 Solid state ^{13}C CP MAS NMR spectra of Mo(C_9H_7)(η^3-C_3H_5)-$(CO)_2$ **3** (bottom), free β-CD hydrate (middle) and β-CD/Mo(C_9H_7)-(η^3-C_3H_5)$(CO)_2$ **3a** (top). ● denotes spinning side band.

basically independently. Well defined steps are visible in the TG profile corresponding to the points where the bulk organometallic sublimes (around 141 °C), and β-CD melts and decomposes (two resolved steps around 236 and 321 °C). In the case of the inclusion compound **1a** there was no change up to 170 °C except for gradual loss of hydrated water (10%, 9–10 water molecules per β-CD). Decomposition occurred above this temperature, characterised by a strong, sharp peak in the DTG profile at 193 °C. A total mass loss of 65% was recorded between 170 and 210 °C. A further mass loss of 15% occurred between 210 and 360 °C. Very similar TG profiles were obtained for compounds **1a**, **2a** and **3a**. The decomposing points for **2a** and **3a** were at 217 and 215 °C respectively. These results suggest that the molybdenum complexes are isolated from each other by encapsulation in the β-CD cavities. The lower decomposing points of the inclusion compounds compared to that of free β-CD may be due to the promoting effects of molybdenum on the decomposition of cyclodextrin. Similar results were obtained for the inclusion compound of cyclodextrin with (benzene)tricarbonylchromium complex.[9]

The solid-state ^{13}C CP MAS NMR spectrum of β-CD/Mo(C_9H_7)(η^3-C_3H_5)$(CO)_2$ **3a** is shown in Fig. 5. Also shown for comparison are the spectra of pristine β-CD hydrate and free Mo(C_9H_7)(η^3-C_3H_5)$(CO)_2$ **3**. The spectrum of free β-CD hydrate is similar to that previously reported and exhibits multiple resonances for each type of carbon atom.[18] This has been mainly correlated with different torsion angles about the (1→4) linkages for C-1 and C-4, and with torsion angles describing the orientation of the hydroxyl groups. The different carbon resonances are assigned to C-1 (δ 101–104), C-4 (78–84), C-2,3,5 (71–76) and C-6 (57–65). By contrast, the β-CD carbons C-1, C-2,3,5 and C-6 for complex **3a** were observed as single peaks at δ 104, 73 and 61 respectively. This is a common occurrence for cyclodextrin inclusion compounds and indicates that β-CD adopts a symmetrical conformation in the complex, with each glucose unit in a similar environment.[17,19] In addition to the resonances for the β-CD carbons, the spectrum of **3a** exhibits several resonances that can be assigned to the carbon atoms of the guest molecule. A single resonance is observed for the carbonyl group at δ 236.8, shifted upfield compared to that of the free organometallic (240.1) and close to that reported for the solution spectrum (δ 237.5, $CDCl_3$[13]). The carbon resonances for the η^5-indenyl ring appear at δ 124.2 ($C^{5/8}$, $C^{6/7}$), 112.2 ($C^{4/9}$) and 89.00 (C^2); the resonance for $C^{1/3}$ overlaps with the resonances for the β-CD C-4 carbons and cannot be assigned individually. The presence of the symmetrically co-ordinated allyl group is confirmed by the presence of two broad peaks at δ 54.3 (C_b) and 48.1 ($C_{a/c}$).

Compound β-CD/MoCp(η^3-C_3H_5)$(CO)_2$ **1a** gave a very similar ^{13}C CP MAS NMR spectrum to that of **3a** concerning the resonances for the β-CD carbons. In addition, a single resonance was observed for the carbonyl group of the guest molecule at δ 236.0, again shifted upfield compared to that of the free organometallic (238.9) and closer to that reported for the solution spectrum (δ 237.1, $CDCl_3$[13]). Two peaks were observed for the cyclopentadienyl carbons at δ 92.3 and 90.4 of approximately equal area. The former chemical shift value is close to that observed for the free organometallic **1**. Two broad overlapping peaks were also observed for the allyl $C_{1/3}$ carbons at δ 39.3 and 35.8. However, the presence of bulk organometallic **1** in compound **1a** was not sustained by powder XRD, TGA or FTIR studies. A possible explanation is that there are two complexed forms of $MoCp(\eta^3\text{-}C_3H_5)(CO)_2$ in **1a**. Compound β-CD/$Mo(C_5H_4SiMe_3)(\eta^3\text{-}C_3H_5)(CO)_2$ **2a** gave a different ^{13}C MAS NMR spectrum to **1a** and **3a** in that the resonances attributed to the carbon atoms of the host matched much more closely with those of free β-CD hydrate, *i.e.* several peaks were observed for each type of carbon atom. The only difference was that the peaks in the spectrum of **2a** were considerably broader. A weak peak was also observed at δ 2.5, ascribed to the methyl carbons of the trimethylsilyl substituent. This result, coupled with the powder XRD studies, indicates that the arrangement of the cyclodextrin molecules in **2a** should be similar to that in free β-CD hydrate.

Concluding remarks

A range of techniques have been used to characterise the solid-state structures of 1:1 inclusion compounds formed between β-CD and half-sandwich complexes of molybdenum. The crystalline products precipitated at the interface between a solution of β-CD in water and a solution of the organometallic in dichloromethane. This method seems to be generally applicable to the preparation of inclusion compounds between organometallics and cyclodextrins.[14,17] The complexes $MoCp(\eta^3\text{-}C_3H_5)(CO)_2$ and $Mo(C_9H_7)(\eta^3\text{-}C_3H_5)(CO)_2$ form channel-type structures with β-CD and it can be concluded that the molecules are fully enclosed within the CD cavity. A completely different result was obtained when a trimethylsilyl substituent was introduced on the Cp ligand. This indicates that the reaction is very selective regarding the geometry and the functional groups of the guest molecule. Theoretical studies are underway in our laboratories better to understand this behaviour.

Acknowledgements

We are grateful to PRAXIS XXI for partial funding and to Paula Esculcas for assistance in the NMR experiments.

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