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Journal of Organometallic Chemistry 632 (2001) 11–16

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Experimental and theoretical study of the interaction of molybdenocene dichloride (Cp_2MoCl_2) with β-cyclodextrin

Susana S. Braga [a], Isabel S. Gonçalves [a,*], Martyn Pillinger [a], Paulo Ribeiro-Claro [a,b], José J.C. Teixeira-Dias [a]

[a] *Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*
[b] *Química-Física Molecular, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-353 Coimbra, Portugal*

Received 15 February 2001; accepted 29 March 2001

Dedicated to Professor Dr Alberto Romão Dias on the occasion of his 60th birthday

Abstract

A crystalline 1:1 inclusion complex was isolated from the reaction of β-cyclodextrin (β-CD) with aqueous Cp_2MoCl_2. The existence of a true inclusion complex in the solid-state was confirmed by a combination of powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), FTIR and Raman spectroscopy, and magic-angle spinning (MAS) ^{13}C NMR spectroscopy. Ab initio calculations were carried out to generate the possible inclusion geometries and calculate the vibrational frequencies for Cp_2MoCl_2 in the 100–400 cm^{-1} region. The best organometallic–β-CD interaction geometry was found to be one with one Cp ligand inside the host cavity. The vibrational spectra support the existence of this structure and in addition confirm that the organometallic is included with the Mo–Cl bond intact. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclodextrins; Molybdenum; Molybdenocene; Host–guest chemistry; Solid-state structures

1. Introduction

The (bis)cyclopentadienyl fragment [Cp_2Mo] has featured prominently in the organometallic chemistry of molybdenum(IV) ever since the discovery of the dihydride Cp_2MoH_2 ($Cp = \eta^5$-C_5H_5) by Green et al. in 1961 [1]. Insertion of alkenes and alkynes into the Mo–H bond is just one example of the many key reaction steps known for this molecule. The corresponding neutral halide complexes Cp_2MoX_2 were soon obtained by treating the hydride with CHX_3 (X = Cl, Br) [2]. A large number of complexes $[Cp_2MoL_2]^{n+}$ ($n = 0,1,2$) have been subsequently prepared from Cp_2MoX_2 and their chemistry developed [3–6]. In the recent years some of us have directed our research towards finding new simple preparations of $[Cp_2MoL_2]^{n+}$ complexes and mixed-ring $[Cp'_2MoL_2]^{n+}$ analogues (Cp′ = Cp, indenyl, fluorenyl) [7].

Cp_2MoCl_2 is soluble in water but undergoes rapid and complete hydrolysis of the chloride ligands to yield aquated $Cp_2Mo(OH_2)_2^{2+}$ in acidic solution [8]. The Mo–Cp ligation is however hydrolytically stable even at neutral pH. These properties make aqueous Cp_2MoCl_2 amenable for phosphate coordination chemistry. It has been found that the aquated ion promotes the hydrolysis of activated phosphoesters such as 4-nitrophenyl phosphate [9a] and unactivated phosphoesters such as dimethyl phosphate [9b]. The latter is important because it mimics the diester functionality of DNA. The interaction of metallocene dichlorides with DNA is of special interest as these compounds exhibit antitumor activity for a wide range of murine and human tumors [10]. Indeed, titanocene dichloride has recently entered clinical trials.

The encapsulation of Cp_2TiCl_2 in β-cyclodextrin (β-CD) was recently reported [11]. Cyclodextrin (CD) inclusion complexes are interesting for pharmaceutical use owing to the increased aqueous solubility of the drugs, better oral absorption, and enhanced chemical and physical stability with respect to oxidation by air,

* Corresponding author. Fax: +351-234-370084.
E-mail address: igoncalves@dq.ua.pt (I.S. Gonçalves).

PII: S0022-328X(01)00836-1

sensitivity to light, rate of disproportionation or polymerization, and acidic conditions [12]. Complexation of the promising antitumor agent rhodium(II) citrate with hydroxypropyl-β-CD, e.g. improved the encapsulation and release kinetics from biodegradable polymer microspheres [13]. CDs are known to form stable inclusion compounds with a variety of organometallic species including ferrocene and its derivatives [14], and half-sandwich complexes of molybdenum [15]. In this article, we report on the interaction of β-CD with aqueous Cp_2MoCl_2. The inclusion compound formed was characterized in the solid-state by a range of techniques, and ab initio calculations were performed to calculate the vibrational spectra and possible host–guest inclusion geometries.

2. Results and discussion

2.1. Synthesis

An aqueous solution of β-CD was treated with Cp_2MoCl_2 (**1**) and the product β-CD·Cp_2MoCl_2 (**1a**) isolated by liophilization. Elemental analysis indicated that the β-CD/molybdenum ratio in compound **1a** was close to 1:1, suggesting the formation of a stoichiometric inclusion complex. The product was further characterized in the solid-state by powder XRD, TGA, Raman and FTIR spectroscopy, and MAS NMR (^{13}C).

2.2. Powder XRD and TGA

Compound **1a** is crystalline but its powder XRD pattern does not contain peaks corresponding either to that of pristine β-CD hydrate or pure non-included Cp_2MoCl_2 (Fig. 1). This can be taken as an initial indication for the occurrence of a true inclusion complex [16].

Fig. 2 shows the results of the thermogravimetric analysis of β-CD·Cp_2MoCl_2 (**1a**), the organometallic Cp_2MoCl_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 shows 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 is no further change until 260°C when the compound begins 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. Both compound **1a** and the physical mixture start decomposing at the lower temperature of 180°C. Thereafter, however, the behavior of **1a** is quite different from that of the mixture. A mass loss of 47% is recorded in the temperature range of 180–350°C. This is then followed by an abrupt mass loss of about 30%, characterized by a strong, sharp peak in the DTG profile at 358°C. The lower decomposing points of β-CD in **1a** and the mixture compared with that of pure β-CD are presumably because of the promoting effects of molybdenum on the decomposition of CD.

2.3. IR and Raman spectroscopy

The KBr IR spectrum of compound **1a** shows the typical bands reported earlier for bulk KBr spectra of β-CD [17], indicating no chemical modification of the CD host. In addition, a weak shoulder at 3110 cm^{-1} and a weak band at 840 cm^{-1} are attributed to ν(CH)

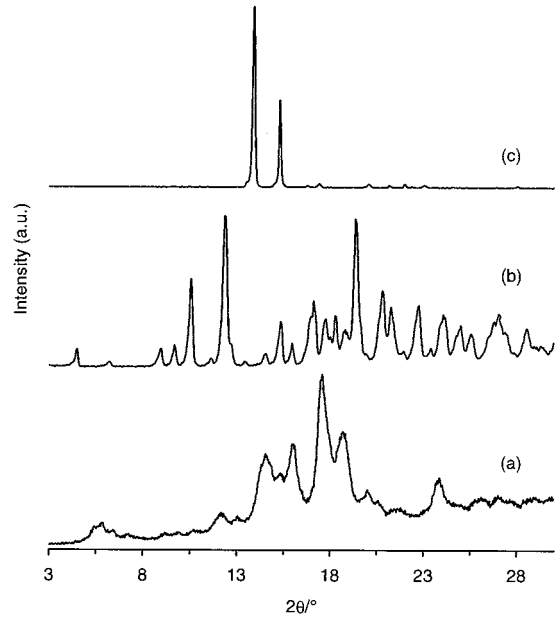

Fig. 1. Powder XRD of: (a) β-CD·Cp_2MoCl_2 (**1a**); (b) pristine β-CD hydrate; and (c) Cp_2MoCl_2 (**1**).

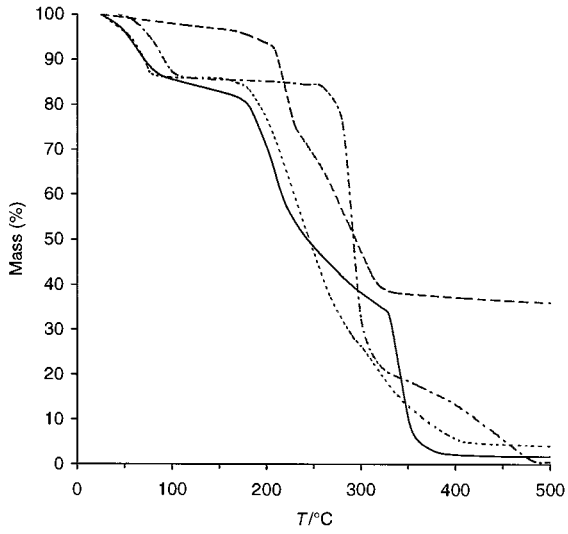

Fig. 2. TGA of β-CD·Cp_2MoCl_2 (**1a**) (—), Cp_2MoCl_2 (**1**) (– – –), pristine β-CD hydrate (–·–·–), and a physical mixture of β-CD and **1** in a 1:1 molar ratio (- - - -).

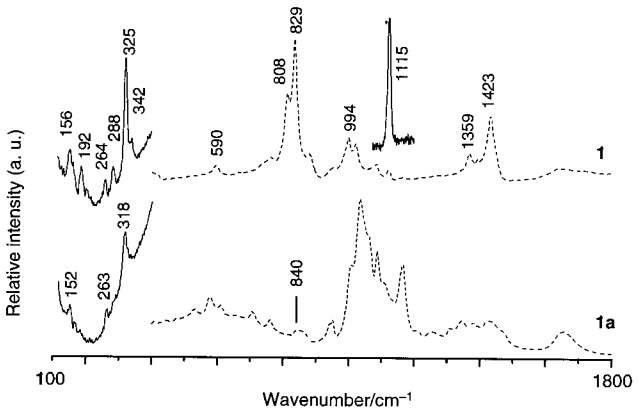

Fig. 3. Raman (solid lines) and FTIR (dashed lines) spectra of Cp_2MoCl_2 (**1**) and β-CD·Cp_2MoCl_2 (**1a**) in the region 100-1800 cm^{-1}.

Table 1
Calculated and observed wavenumbers (cm^{-1}) for Cp_2MoCl_2 (**1**) and β-CD·Cp_2MoCl_2 (**1a**) in the 100–400 cm^{-1} region

Calculated (**1**)	Observed (Raman)		Approximate description
	1	**1a**	
343	342		Cp-ring tilt
302	325	318	Mo–Cp symmetric stretch
284	288		Mo–Cp asymmetric stretch
269	264	263	Mo–Cl symmetric stretch
184	192		Mo–Cp bending mode
160	156	152	Mo–Cp bending mode

and π(CH) vibrations, respectively, of the included guest molecule (cf. 3097 and 829 cm^{-1} for the KBr spectrum of the pure non-included organometallic **1**). Blue-shifts of ν(CH) and π(CH) modes in similar metal–cyclopentadienyl complexes have been previously associated with an increase in the covalency of the Cp–M bond [18]. However, more recent vibrational studies discard this hypothesis in favor of an increase in the electron density in the Cp ring [19]. Unfortunately, the broadness of the vibrational spectra does not allow a deeper analysis of this structural issue.

Several low wavenumber bands of Cp_2MoCl_2 (**1**) are identified in the Raman spectrum, assigned to Mo–Cp and Mo–Cl modes (Fig. 3, Table 1). The assignments are based on the ab initio calculations described below and are in agreement with those reported in a systematic vibrational study of η^5-C_5H_5 metal complexes [19]. In what concerns the spectrum of the inclusion compound **1a**, only the strongest bands of the organometallic fragment could be identified off the broad background. The most relevant observation in this spectral region arises from the effect of the inclusion process on the metal–ligand stretching modes: while the ν(Mo–Cl) mode is nearly insensitive to the inclusion, the ν(Mo–Cp) mode presents a red-shift of ca. 8 cm^{-1} from **1** to **1a**. This behavior can be related with the preferential inclusion geometry, as discussed below.

2.4. ^{13}C solid-state NMR spectroscopy

The solid-state ^{13}C CP MAS NMR spectra of β-CD·Cp_2MoCl_2 (**1a**), pristine β-CD hydrate and Cp_2MoCl_2 (**1**) are shown in Fig. 4. The spectrum of β-CD hydrate is similar to that reported previously and exhibits multiple resonances for each type of carbon atom [20]. This has been mainly correlated with different torsion angles about the (1→4) linkages for C-1 and C-4 [20a,20b], and with torsion angles describing the orientation of the hydroxyl groups [20c]. 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). Contrastingly, the corresponding β-CD carbons for complex **1a** are observed as single broad peaks at 103.4, 81.0, 72.9 and 59.9 ppm, respectively. This is a clear indication that the organometallic molecule Cp_2MoCl_2 is included in the cavities of β-CD, as it implies that β-CD adopts a more symmetrical conformation in the complex, with each glucose unit in a similar environment [21]. Similar spectra have been reported for β-CD adducts of the [1]ferrocenophane [Fe{(η^5-C_5H_4)$_2$$SiMe_2$}] [14d] and the half-sandwich molybdenum complexes Cp′Mo(η^3-C_3H_5)$(CO)_2$ (Cp′ =

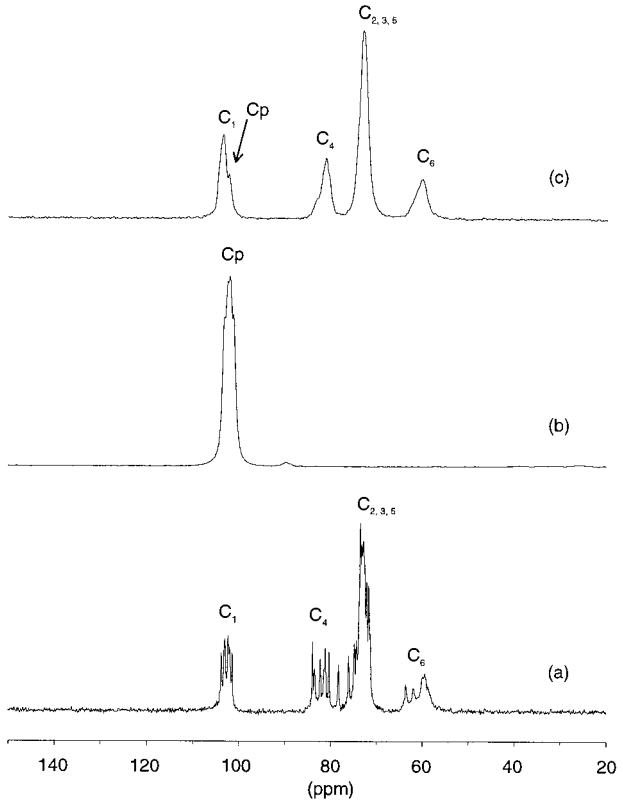

Fig. 4. Solid-state ^{13}C CP MAS NMR spectra of: (a) pristine β-CD·hydrate; (b) Cp_2MoCl_2 (**1**); and (c) β-CD·Cp_2MoCl_2 (**1a**).

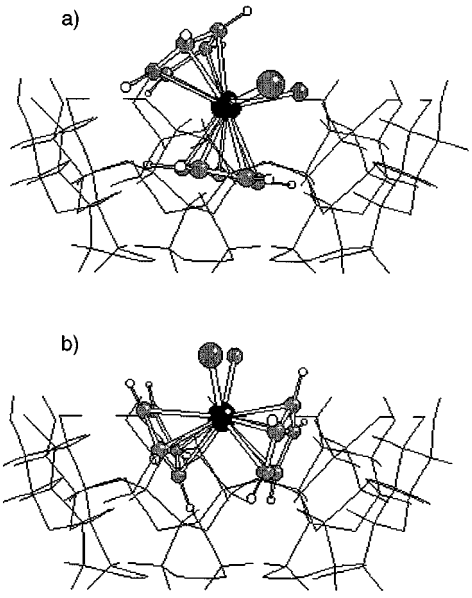

Fig. 5. Ab initio structures of the lowest energy inclusion geometries for β-CD·Cp_2MoCl_2 (**1a**).

Cp, Ind) [15a]. The peak at 103.4 ppm exhibits a resolved shoulder at 102.2 ppm that is assigned to the cyclopentadienyl carbons of the guest molecule. The preferred model for the incorporation of Cp_2MoCl_2 in β-CD (see below) places one Cp group inside the cavity and one outside, and therefore one might expect more than one ^{13}C signal for the guest molecule. It is possible that a second peak exists but is obscured by the broad β-CD C-1 signal.

2.5. Ab initio calculations

The lowest energy minimum found for the free organometallic **1** has a nearly C_s symmetry, with the Cp rings in a staggered conformation, in agreement with the available X-ray structure [22]. Calculated bond lengths (r_e values) are generally 3% longer than the experimental r_0 counterparts (e.g. average Mo–C distance is $r_e = 237$ pm while $r_0 \approx 230$ pm [22]). The calculated ligand–Mo–ligand angles are 83° for chloro and 137° for Cp centroids, and compare well with the experimental values of 82 and ca. 135° [22], respectively.

The best organometallic–β-CD interaction geometry for **1a** was found to be the one with one Cp ligand inside the cavity, similar to that proposed for several ferrocene derivatives [23] (Fig. 5(a)). This structure is < 1 kJ mol^{-1} more stable than the structure with a shallow penetration of both the Cp ligands (Fig. 5(b)) suggested previously for the β-CD inclusion compound of Cp_2TiCl_2 (solution ^1H NMR evidence) [11]. Although it is conceivable that both structures can compete at room temperature, the experimental data seems to be in favor of structure (a). In fact, the vibrational spectra present a red-shift of the Mo–Cp symmetric stretching upon inclusion, while a blue-shift would be expected in the case of structure (b) owing to confinement (steric) effects. The red-shift can be more easily explained in the case of structure (a) in terms of mass effects, assuming there is no significant change in the relevant force constant.

3. Conclusion

Complex formation between β-CD and Cp_2TiCl_2 has been previously proven in solution [11]. However, to date, no detailed studies have been carried out in the solid-state for inclusion compounds formed between CDs and cyclopentadienyl compounds of the type Cp_2MX_2. In this work, a stoichiometric well-defined crystalline material was isolated from the reaction of β-CD with aqueous Cp_2MoCl_2. The evidence suggests that Cp_2MoCl_2 is the species incorporated in the CD cavity, rather than the hydrolysis products $Cp_2Mo(H_2O)Cl^+$ or $Cp_2Mo(H_2O)_2^{2+}$. By using a combination of solid-state physical methods and ab initio calculations, the formation of a true inclusion complex in the solid-state can be confirmed and, further, possible inclusion geometries can be presented.

4. Experimental

4.1. Materials and methods

Microanalyses were performed at the TU Munich by Barth and co-workers. The IR spectra were recorded on a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets. Raman spectra were recorded on a Jobin-Yvon t64000 Raman system, using an Ar + laser (50 mW at the sample position) and a non-intensified CCD detector, with samples sealed in glass capillary tubes. 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). Room-temperature solid-state ^{13}C CP MAS NMR spectra were recorded at 100.62 MHz on a (9.4 T) Bruker MSL 400P spectrometer, with a 4.5 μs ^1H 90° pulse, 2 ms contact time, spinning rate 9 kHz and 12 s recycle delays. Chemical shifts are quoted in parts per million from TMS.

β-CD was obtained from Wacker Chemie (München) and recrystallized before use. Cp_2MoCl_2 was prepared as described recently in Ref. [24]. ^{13}C CP MAS NMR of Cp_2MoCl_2 (**1**): $\delta = 102.3$ (Cp).

4.2. Synthesis of inclusion compound β-CD·Cp_2MoCl_2 (1a)

Cp_2MoCl_2 (67.8 mg, 0.23 mmol) was added to a solution of β-CD (300 mg, 0.26 mmol) in water (20 ml). The resulting solution was stirred at room temperature (r.t.) for 10 min, then frozen and dried under vacuo. The voluminous solid product obtained was rehydrated by exposure to water vapor for 1 h. Yield: 0.35 g (96%). Anal. Found: C, 38.48; H, 6.14; Mo, 6.12. Calc. for $(C_{10}H_{10}Cl_2Mo)\cdot(C_{42}H_{70}O_{35})\cdot 10H_2O$: C, 38.74; H, 6.25; Mo, 5.95%. IR (KBr, cm^{-1}): 3389vs, 3110sh, 2928m, 1640m, 1415m, 1368m, 1334m, 1300m, 1243m, 1200m, 1156s, 1099sh, 1079s, 1053sh, 1028vs, 1003sh, 945m, 857m, 840m, 756m, 704m, 650w, 609m, 577m, 531m. ^{13}C CPMAS NMR: $\delta = 103.4$ (br, β-CD, C-1), 102.2 (Cp), 81.0 (br, β-CD, C-4), 72.9 (br, β-CD, C-2,3,5), 59.9 (br, β-CD, C-6).

4.3. Ab initio calculations

Ab initio calculations were carried out using the GAUSSIAN98W program package [25] 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 [26] and the Los Alamos Effective Core Potentials plus double-zeta [27] for the Mo atom (LanL2DZ option of GAUSSIAN98). Harmonic vibrational frequencies were calculated at the same level, using analytic second derivatives. For the comparison with the experimental values, calculated wavenumbers were scaled by a factor of 0.98.

In what concerns the inclusion compounds, several possible inclusion geometries were tested by single-point calculations using the two-layer approximation of Morokuma et al. [28] (ONIOM keyword of GAUSSIAN98). 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 Potentials minimal basis [29].

Acknowledgements

The authors are grateful to Professor Dr João Rocha for his generous support. We thank PRAXIS XXI for the partial funding. We also wish to thank Paula Esculcas for assistance in the NMR experiments.

References

[1] M.L.H. Green, J.A. McClaverty, L. Pratt, G. Wilkinson, J. Chem. Soc. (1961) 4854.
[2] R.L. Cooper, M.L.H. Green, J. Chem. Soc. A (1967) 1155.
[3] A.R. Dias, M.L.H. Green, J. Chem. Soc. A (1971) 1951.
[4] T. Aviles, M.L.H. Green, A.R. Dias, C. Romão, J. Chem. Soc. Dalton Trans. (1979) 1367.
[5] M.J. Calhorda, M.A.A.F de C.T. Carrondo, A.R. Dias, A.M.T. Domingos, M.T.L.S. Duarte, M.H. Garcia, C.C. Romão, J. Organomet. Chem. 320 (1987) 63.
[6] M.J. Calhorda, A.R. Dias, M.T. Duarte, A.M. Martins, P.M. Matias, C.C. Romão, J. Organomet. Chem. 440 (1992) 119.
[7] (a) C.C. Romão, Appl. Organomet. Chem. 14 (2000) 539 (and references cited therein);
(b) M.G.B. Drew, V. Félix, I.S. Gonçalves, C.C. Romão, B. Royo, Organometallics 17 (1998) 5782.
[8] L.Y. Kuo, M.G. Kanatzidis, M. Sabat, A.L. Tipton, T.J. Marks, J. Am. Chem. Soc. 113 (1991) 9027.
[9] (a) L.Y. Kuo, S. Kuhn, D. Ly, Inorg. Chem. 34 (1995) 5341;
(b) L.Y. Kuo, L.A. Barnes, Inorg. Chem. 38 (1999) 814.
[10] (a) P. Köpf-Maier, H. Köpf, Drugs Future 11 (1986) 297;
(b) M.L. McLaughlin, J.M. Cronan Jr., T.R. Schaller, R.D. Snelling, J. Am. Chem. Soc. 112 (1990) 8949;
(c) M.M. Harding, G. Mokdsi, J.P. Mackay, M. Prodigalidad, S.W. Lucas, Inorg. Chem. 37 (1998) 2432;
(d) G. Mokdsi, M.M. Harding, J. Organomet. Chem. 565 (1998) 29;
(e) M.M. Harding, G.J. Harden, L.D. Field, FEBS Lett. 322 (1993) 291.
[11] I. Turel, A. Demsar, J. Kosmrlj, J. Mol. Recognit. Macro. Chem. 35 (1999) 595.
[12] E. Fenyvesi, L. Szente, N.R. Russel, M. McNamara, in: J.L. Atwood, J.E.D Davies, D.D. MacNicol, F. Vögtle, J.-M. Lehn, J. Szejtli, T. Osa (Eds.), Comprehensive Supramolecular Chemistry, vol. 3, Pergamon, Oxford, 1996 (chap. 10).
[13] R.D. Sinisterra, V.P. Shastri, R. Najjar, R. Langer, J. Pharm. Sci. 88 (1999) 574.
[14] (a) A. Harada, S. Takahashi, J. Chem. Soc. Chem. Commun. (1984) 645;
(b) A. Harada, Y. Hu, S. Yamamoto, S. Takahashi, J. Chem. Soc. Dalton Trans. (1988) 729;
(c) Y. Odagaki, K. Hirotsu, T. Higuchi, A. Harada, S. Takahashi, J. Chem. Soc. Perkin Trans. 1 (1990) 1230;
(d) P. Ferreira, I.S. Gonçalves, M. Pillinger, J. Rocha, P. Santos, J.J.C. Teixeira-Dias, Organometallics 19 (2000) 1455.
[15] (a) S.S. Braga, I.S. Gonçalves, A.D. Lopes, M. Pillinger, J. Rocha, C.C. Romão, J.J.C. Teixeira-Dias, J. Chem. Soc. Dalton Trans. (2000) 2964;
(b) S. Lima, I.S. Gonçalves, P. Ribeiro-Claro, M. Pillinger, A.D. Lopes, P. Ferreira, J.J.C. Teixeira-Dias, J. Rocha, C.C. Romão, Organometallics (2001) in press.
[16] W. Saenger, Angew. Chem. Int. Ed. Engl. 19 (1980) 344.
[17] R.C. Sabapathy, S. Bhattacharyya, W.E. Cleland, C.L. Hussey, Langmuir 14 (1998) 3797.
[18] H.P. Fritz, Adv. Organomet. Chem. 1 (1964) 239.
[19] E. Diana, R. Rossetti, P.L. Stanghellini, S.F.A. Kettle, Inorg. Chem. 36 (1997) 382.
[20] (a) M.J. Gidley, S.M. Bociek, J. Am. Chem. Soc. 110 (1988) 3820;
(b) S.J. Heyes, N.J. Clayden, C.M. Dobson, Carbohydr. Res. 233 (1992) 1;
(c) R.P. Veregin, C.A. Fyfe, R.H. Marcessault, M.G. Tayler, Carbohydr. Res. 160 (1987) 41.
[21] J. Li, A. Harada, M. Kamachi, Bull. Chem. Soc. Jpn. 67 (1994) 2808.

[22] K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton, G.V. Rees, Acta Crystallogr. B 30 (1974) 2290.
[23] (a) L.A. Godínez, S. Patel, C.M. Criss, A.E. Kaifer, J. Phys. Chem. 99 (1995) 17449;
(b) R. Isnin, C. Salam, A.E. Kaifer, J. Org. Chem. 56 (1991) 35.
[24] (a) I.S. Gonçalves, E. Herdtweck, C.C. Romao, B. Royo, J. Organomet. Chem. 580 (1998) 169;
(b) M.G.B. Drew, V. Felix, I.S. Gonçalves, F.E. Kühn, A.D. Lopes, C.C. Romão, Polyhedron 17 (1998) 1091.
[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98 (Revision A.1), Gaussian, Inc., Pittsburgh, PA, 1998.
[26] T.H. Dunning Jr., P.J. Hay, in: H.F. Schaefer (Ed.), Modern Theoretical Chemistry, vol. 3, Plenum Press, New York, 1976, p. 1.
[27] W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284.
[28] (a) S. Humbel, S. Sieber, K. Morokuma, J. Chem. Phys. 105 (1996) 1959;
(b) T. Matsubara, S. Sieber, K. Morokuma, J. Quantum Chem. 60 (1996) 1101;
(c) M. Svensson, S. Humbel, R.D.J. Froese, T. Matsubara, S. Sieber, K. Morokuma, J. Phys. Chem. 100 (1996) 19357.
[29] (a) W. Stevens, H. Basch, J. Krauss, J. Chem. Phys. 81 (1984) 6026;
(b) W.J. Stevens, M. Krauss, H. Basch, P.G. Jasien, Can. J. Chem. 70 (1992) 612.