DALTON
FULL PAPER

Intramolecular photo-substitution in the inclusion compound of mono[6-deoxy-6-(2-butenedinitrile-2,3-dimercapto sodium salt)]–β-cyclodextrin with cyclopentadienyl manganese tricarbonyl in DMF solution

Chang-Sheng Lu, Wen-Wei Zhang, Xiao-Ming Ren, Chuan-Jiang Hu, Hui-Zhen Zhu and Qing-Jin Meng *

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China. E-mail: MengQJ@netra.nju.edu.cn

Received 21st March 2001, Accepted 10th August 2001
First published as an Advance Article on the web 1st October 2001

A novel β-CD derivative, mono[6-deoxy-6-(2-butenedinitrile-2,3-dimercapto sodium salt)]–β-CD **1**, and its inclusion compound **2** with $\mathrm{CpMn^I(CO)_3}$ have been prepared and characterized by spectroscopic methods. The inclusion complexation significantly stabilized both the host and guest. Upon irradiation of inclusion compound **2** in DMF solution, an interesting intramolecular photo-substitution resulting in the formation of a self-stabilized compound mono[6-deoxy-6-(2-butenedinitrile-2,3-dimercapto sodium salt)]–β-CD–$\mathrm{Mn^{II}(DMF)_2Cp}$ **5** was observed. Based upon a double-recognition between the host and the organometallic guest, compound **5** became very stable in DMF solution.

Introduction

A great number of organometallic complexes have been synthesized and have attracted much attention as homogeneous catalysts in organic reactions.[1] To improve activities and selectivities of the catalysts, guest–host chemistry of organometallic compounds has become an important research field recently.[2] Cyclodextrins (CDs) can form inclusion compounds with a variety of guest compounds, including organometallic molecules, and modify properties of both guests and hosts effectively.[3] In our laboratory, we attempted to introduce the maleonitriledithiolate (mnt) group to β-CD, and obtained a well-defined species, mnt–β-CD. The species has both a hydrophobic β-CD cavity, and a nucleophilic mnt group which has been among the most extensively studied systems in its stacked structures and electrical conductivity, photoconductivity, photolysis of water catalyzed, long wave length optical absorption and magnetic coupling.[4] In this research we prepared the inclusion compound **2** of mono[6-deoxy-6-(2-butenedinitrile-2,3-dimercapto sodium salt)]–β-CD **1** (6-mnt–β-CD) with cyclopentadienyl manganese tricarbonyl ($\mathrm{CpMn^I(CO)_3}$). Our intention was to investigate whether the new species (mnt–β-CD) would exhibit a better guest-binding ability, and how the attached mnt group would work in inclusion compounds of mnt–β-CD with guest molecules.

Experimental

Physical measurements and materials

A Bruker IFS66V FT-IR spectrophotometer was used, and the measurements were made by the KBr disk method. The UV spectra were recorded on a Shimadzu UV-3100 spectrometer. The mass spectra were performed on a Finnigan MAT APISSQ-710 mass spectrometer. All ^{13}C-NMR and ^{1}H-NMR spectra were recorded on a Bruker AVANCE-300 spectrometer in DMSO-d$_6$ solution at 15 °C. Elemental analysis was determined by a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analysis curves were recorded on an American SDT-2960 thermal analyzer. The ESR spectrum was recorded using a (JEOL) JES-IXG spectrometer at 100 kHz modulation. $\mathrm{Mn^{2+}}$ in MgO was used as the standard sample. Ethanol and THF were of analytically pure grade. DMF was distilled under reduced pressure in a N_2 atmosphere before use. 2-Butenedinitrile-2,3-dimercapto disodium salt ($\mathrm{Na_2mnt}$) and mono-(6-*O*-tolylsulfonyl)–β-cyclodextrin (6-Ots–β-CD) were synthesized according to the methods described in the literature.[5,6]

Synthesis of 6-mnt–β-CD 1

To a solution of $\mathrm{Na_2mnt}$ (0.2 g, 1.08 mmol) in water (30 ml) was added 6-Ots–β-CD (0.5 g, 0.39 mmol), and the mixture was stirred at 65 °C for 3–4 h under a N_2 atmosphere. After cooling to room temperature, the yellow solution was concentrated under reduced pressure. The dark-red residue (about 3–4 ml) was then added dropwise to stirred ethanol (120 ml) to precipitate crude 6-mnt–β-CD (0.4 g, 80%) as yellow deposits. The crude product was dissolved in 1 ml of water, and was then added dropwise to stirred ethanol (10 ml). After standing overnight, the final product precipitated from the ethanol solution as a yellow powder (Found: C, 38.85; H, 6.21; N, 2.08%. $\mathrm{C_{46}H_{69}O_{34}N_2NaS_2\cdot 8H_2O}$ requires C, 38.76; H, 6.01; N, 1.97%); λ_{max}/nm (DMF) 385.5 (ε/dm^3 mol^{-1} cm^{-1} 9200); ν_{max}/cm^{-1} 2189.7; δ_C (DMSO-d$_6$) 59.94, 72.12, 72.49, 73.15, 80.94, 81.15, 81.62, 102.05, 118.38, 118.79; *m*/*z* 1258.0 ($[M - Na]^-$).

Preparation of inclusion compound 6-mnt–β-CD/CpMn^I(CO)$_3$ 2

The inclusion compound of 6-mnt–β-CD with $\mathrm{CpMn^I(CO)_3}$ was prepared by the co-precipitation method.[7] 0.53 mmol of 6-mnt–β-CD was dissolved in 50 ml of water, and then 1.06 mmol of $\mathrm{CpMn^I(CO)_3}$ was added. After stirring at 40 °C for 2 h, the solution was cooled to room temperature and a yellow solid precipitated, which was then collected by filtration and washed twice with water and THF. Finally, drying of this solid in air for 4 h gave the inclusion compound as a yellow powder (Found: C, 41.20; H, 5.50; N, 1.70%. $\mathrm{C_{54}H_{74}O_{37}N_2MnNaS_2\cdot 5H_2O}$ requires C, 41.17; H, 5.37; N, 1.78%). The pale yellow inclusion com-

Table 1 Spectroscopic and photophysical data for compounds **1** and **2**

Compound	UV[a] λ_{max}/nm	IR ν/cm^{-1}	^{1}H-NMR δ/ppm			
CpMn^I(CO)$_3$	325	2025.1 1939.0				
Na$_2$mnt	387.5	2194.9				
1	385.5	2189.7	4.82 (H-1) 3.55 (H-5)	3.31 (H-2) 3.63 (H-6)	3.63 (H-3)	3.35 (H-4)
β-CD/CpMn^I(CO)$_3$	325.5	2015.8 1944.8	4.83 (H-1) 3.56 (H-5)	3.30 (H-2) 3.63 (H-6)	3.63 (H-3) 5.05 (H-Cp)[b]	3.34 (H-4)
2	385	2012.2 1938.8 2186.4	4.83 (H-1) 3.56 (H-5)	3.30 (H-2) 3.64 (H-6)	3.64 (H-3) 5.05 (H-Cp)[b]	3.34 (H-4)

[a] In DMF. [b] Hydrogen atoms in the cyclopentadienyl ring of the organometallic guest.

Table 2 Partial ^{13}C-NMR spectroscopic data[a] for compounds **1**, **2** and **5**

Compound	C-1/ppm	C-2/ppm	C-3/ppm	C-4/ppm	C-5/ppm	C-6/ppm	C[b]/ppm	C[c]/ppm	C[d]/ppm
β-CD	102.05	72.15	73.16	81.63	72.50	60.02	—	—	—
1	102.05	72.12	73.15	81.62	72.49	59.95	—	81.04	—
2	101.98	72.07	73.06	81.55	72.41	59.90	83.96	81.05	225.61
5	101.78	71.86	72.88	81.36	72.23	59.74	82.98	83.72	—

[a] Spectra were recorded in DMSO-d$_6$ at 20 °C, and data were referenced to internal DMSO-d$_6$ (39.51 ppm); C-1 to C-6 refer to the carbon atoms of the β-CD structure. [b] Carbon atoms in the cyclopentadienyl ring of the organometallic guest. [c] Carbon atoms of the nitrile groups in mnt. [d] Carbon atoms of the carbonyl groups in the organometallic guest.

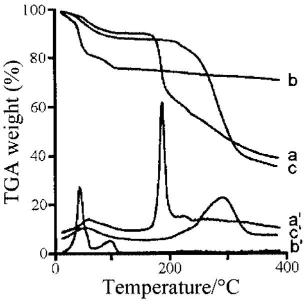


Fig. 1 TG and DTG curves of 6-Ots–β-CD (a, a′), Na$_2$mnt (b, b′) and 6-mnt–β-CD (c, c′).

pound β-CD/CpMn^I(CO)$_3$ was obtained in a similar way (Found: C, 40.61; H, 6.32%. $C_{50}H_{75}O_{38}Mn\cdot8H_2O$ requires C, 40.49; H, 6.18%).

Results and discussion

The new host 6-mnt–β-CD 1

Both the electronic and the IR analyses of 6-mnt–β-CD have shown the presence of the mnt group in the compound (see the Experimental section and Table 1). Moreover, electrospray MS provided structural evidence for mnt-modified β-CD (*m*/*z* 1258.0, see the Experimental section). In addition, the ^{13}C-NMR spectrum of the host molecule (6-mnt–β-CD) showed resonances due to one C=C bond at 118.38 and 118.79 ppm, and two nitrile groups at 80.94 and 81.15 ppm. Upfield shifts in the ^{13}C-NMR spectrum of 6-mnt–β-CD, compared with that of pure β-CD, were observed. These shifts were considered to result mainly from the introduction of an electron-rich mnt moiety onto the β-CD rim,[8] and the 6-substitution of β-CD could be confirmed by the most prominent change (−0.07 ppm) in C-6 (Table 2). Fig. 1 shows thermogravimetric (TG) and differential thermogravimetric (DTG) curves for 6-Ots–β-CD, Na$_2$mnt, and 6-mnt–β-CD. Two peaks were observed in the DTG curve of the hydrate 6-Ots–β-CD (curve a′). The first peak at around 59 °C corresponds to the dehydration process, and the other (at around 185 °C) is related to the degradation of the 6-Ots–β-CD structure. In the case of Na$_2$mnt (curve b′), peaks were clearly visible for the desolvation and decomposition (at around 48 and 98 °C, respectively). However in 6-mnt–β-CD (curve c′), no obvious signals were recorded near 98 or 185 °C. In addition to the dehydration occurring at around 53 °C, a new peak (at around 291 °C) was clearly visible, which could be assigned to the decomposition of the 6-mnt–β-CD structure.

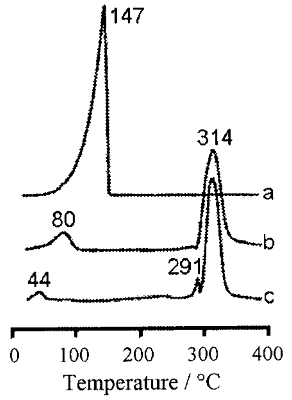


Fig. 2 DTG curves of pure CpMn^I(CO)$_3$ (a), pure β-CD hydrate (b) and inclusion compound β-CD/CpMn^I(CO)$_3$ (c).

The inclusion compound 6-mnt–β-CD/CpMn^I(CO)$_3$ 2

Electrospray MS spectra of inclusion compound 6-mnt–β-CD/CpMn^I(CO)$_3$ showed the presence of the 6-mnt–β-CD anion (*m*/*z* 1258.1). Spectroscopic data for inclusion compound **2** are collected in Table 1. The stoichiometry (1 : 1 molar ratio) of the inclusion compounds that were isolated as solid compounds was determined by comparison of peak areas of the host and guest molecules in the ^{1}H-NMR spectra.

Fig. 2 shows the DTG curves of pure CpMn^I(CO)$_3$ (a), pure β-CD hydrate (b) and the inclusion compound β-CD/CpMn^I(CO)$_3$ (c). In curve a, only one peak arose at 147 °C, which was attributed to the decomposition of pure CpMn^I(CO)$_3$. The two peaks at around 80 and 314 °C in curve b

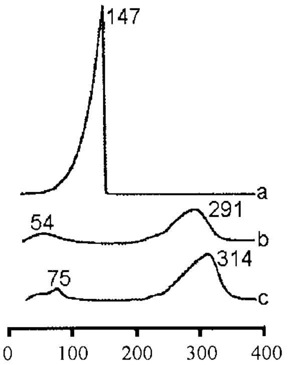


Fig. 3 DTG curves of pure CpMn^{I}(CO)$_3$ (a), pure 6-mnt–β-CD (b) and inclusion compound 6-mnt–β-CD/CpMn^{I}(CO)$_3$ **2** (c).

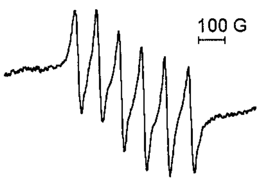


Fig. 4 ESR spectra of inclusion compound **2** in DMF solution upon irradiation in sunlight for 30 minutes.

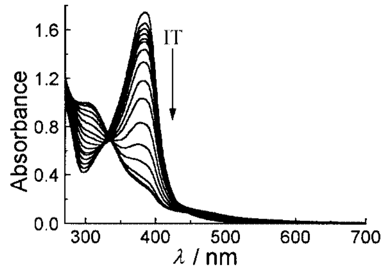


Fig. 5 Absorption spectra of inclusion compound **2** in DMF solution at various irradiation times (IT).

correspond to the dehydration and decomposition of pure β-CD hydrate, respectively. In curve c three peaks were observed. The peak at around 44 °C was assigned to the dehydration of inclusion compound β-CD/CpMn^{I}(CO)$_3$, and the decomposition peak of the bound host in inclusion compound β-CD/CpMn^{I}(CO)$_3$ was observed at around 314 °C. The third peak that appeared at 291 °C suggested the liberation and decomposition of the included guest in β-CD/CpMn^{I}(CO)$_3$. The decomposition temperature of the included guest was much higher than that of its free form, and the decomposition temperature difference between free guest and the included guest was +144 °C (ΔT_{guest}). As one would anticipate, inclusion complexation stabilized the organometallic guest dramatically.

DTG curves of pure CpMn^{I}(CO)$_3$ (a), pure 6-mnt–β-CD hydrate (b) and the inclusion compound 6-mnt–β-CD/CpMn^{I}(CO)$_3$ (c) are shown in Fig. 3. The effects of inclusion complexation upon the thermo-stability of the organometallic guest are clearly evident in curve c. The inclusion compound, 6-mnt–β-CD/CpMn^{I}(CO)$_3$, decomposed at around 314 °C and the decomposition temperature differences between free host and included host, and between free guest and included guest were +23 °C (ΔT_{host}) and +167 °C (ΔT_{guest}), respectively.[9] Obviously, thermo-stabilities of both the host and guest have been greatly improved after inclusion complexation in this sample.

Compared with β-CD, 6-mnt–β-CD has an mnt side-arm. After forming an inclusion compound with CpMn^{I}(CO)$_3$, the side-arm of 6-mnt–β-CD would interact with the included guest, and thereby help to prevent its liberation and subsequent decomposition, when the inclusion compound 6-mnt–β-CD/CpMn^{I}(CO)$_3$ was heated. Thus the additional interplay between host and guest in 6-mnt–β-CD/CpMn^{I}(CO)$_3$ results in a higher ΔT_{guest} compared to β-CD/CpMn^{I}(CO)$_3$. It is evident that a properly designed and well functionalized host could improve the thermo-stability of the inclusion compound even more effectively. However, it was interesting that the host 6-mnt–β-CD in 6-mnt–β-CD/CpMn^{I}(CO)$_3$ decomposed at a much higher temperature (ΔT_{host} = +23 °C) than its free form. This fact indicates that the inclusion of guest (CpMn^{I}(CO)$_3$) into 6-mnt–β-CD stabilizes not only the guest but also the host.

Intramolecular photo-substitution in the inclusion compound 6-mnt–β-CD/CpMn^{I}(CO)$_3$

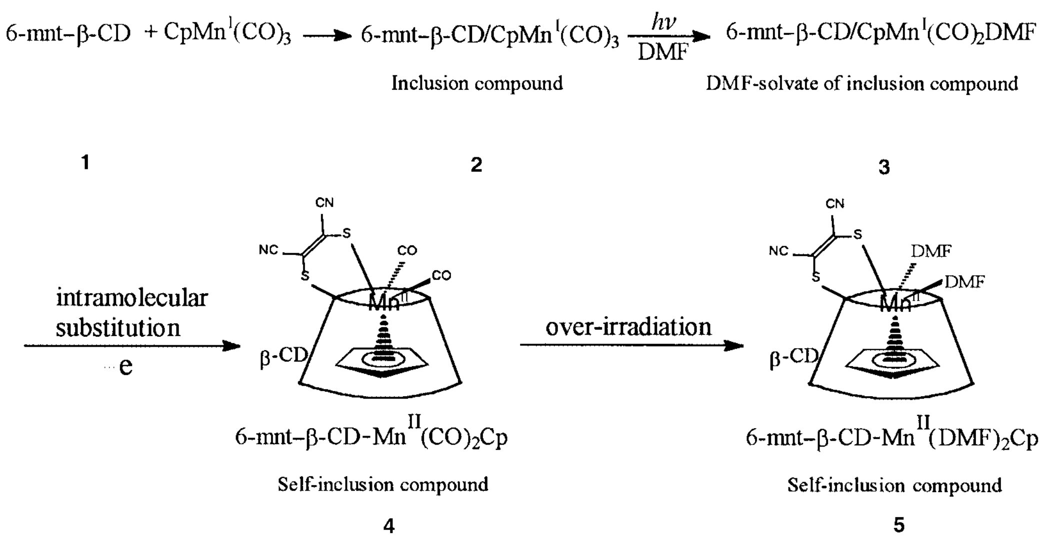
Upon irradiation under sunlight, a CpMn^{I}(CO)$_3$ solution in DMF readily undergoes photo-substitution of CO to precipitate substituted derivative. For both the inclusion compound β-CD/CpMn^{I}(CO)$_3$ and the mixture of Na$_2$mnt and CpMn^{I}(CO)$_3$ (1 : 1 molar ratio), similar results were obtained in our experiments. Also all of the known photochemistry of CpMn^{I}(CO)$_3$ in solution is consistent with the formation of CpMn^{I}(CO)$_2$X in the presence of an entering nucleophile (X) as the principal result, almost any entering nucleophile can be used. Some of the photosubstituted products, CpMn^{I}(CO)$_2$X, have been obtained as fine crystals.[10]

Upon irradiation of a solution of inclusion compound **2** in DMF, the color of the solution gradually turned brown, while a continuous release of CO from the solution was observed but no precipitates were found. Low-spin Mn^{II} signals were observed in the ESR spectrum of the brown solution (Fig. 4).

Moreover, electrochemical investigations of the substituted derivative, CpMn^{I}(CO)$_2$X, have shown that strong nucleophilic ligands can facilitate the one-electron oxidation of CpMn^{I}(CO)$_2$X (X = $^{-}$NR$_2$ and $^{-}$SR), and stabilize the Mn^{II} metal center effectively to yield CpMn^{II}(CO)$_2$X.[11] It is therefore postulated that the primary result of the photo-substitution of inclusion compound **2**, 6-mnt–β-CD/CpMn^{I}(CO)$_3$, in DMF solution is the dissociative loss of CO and the formation of DMF-solvate, 6-mnt–β-CD/CpMn^{I}(CO)$_2$DMF **3** (Scheme 1).[12] Furthermore, the coordinated DMF in the DMF-solvate **3** is substituted by the strong nucleophilic mnt group attached to the host to yield the intramolecular photo-substituted product 6-mnt–β-CD–Mn^{I}(CO)$_2$Cp. Finally, the photochemically generated 6-mnt–β-CD–Mn^{I}(CO)$_2$Cp undergoes one-electron oxidation to give the product 6-mnt–β-CD–Mn^{II}(CO)$_2$Cp **4**. The release of CO from the DMF solution of inclusion compound **1** (*vide supra*) was observed after several minutes of irradiation and the transformation from Mn^{I} to Mn^{II} was confirmed by ESR spectroscopy (Fig. 4). Further evidence in favor of this intramolecular photo-substitution was provided from electronic spectra (*vide infra*).

Fig. 5 shows the absorption spectra of inclusion compound **2** in DMF solution as a function of irradiation time (IT). The peak at around 385 nm, which can be assigned to the 3p⟶π* transition of the mnt group,[13] decreased gradually with increasing irradiation time. Later, a new absorption maximum situated at about 306 nm rose after 3 hours irradiation, which can be assigned to the LMCT[13] transition. These results indicate the formation of an S–Mn bond upon irradiation, thus supporting the previous conclusion of the intramolecular photo-substitution reaction: Cp(CO)$_3$Mn^{I} ⟶ 6-mnt–β-CD–Mn^{I}(CO)$_2$Cp.

Over-irradiation of the solution of inclusion compound **2** in DMF resulted in the disappearance of CO signals in ^{13}C-NMR spectra, which suggested a total release of CO from the mono-substituted product 6-mnt–β-CD–Mn^{II}(CO)$_2$Cp.[13] The over-irradiated solution **5** was brown and very stable in air for more than one year. Concentration of this solution under reduced pressure gave a dark-brown powder, which was soluble in water.



Scheme 1 Proposed mechanism of the intramolecular photo-substitution.

The IR spectrum of the powder showed no CO signals at all whilst the ^{1}H-NMR spectrum of the powder showed three additional hydrogen atoms at 2.87 (6H), 3.03 (6H) and 7.95 (2H) ppm, compared to inclusion compound **2**. This result suggested the formation of a DMF-solvate 6-mnt–β-CD–Mn^{II}-(DMF)$_2$Cp **5** upon over-irradiation that greatly encouraged the previously-described intramolecular photo-substitution process. However, the comparison of peak areas of the cyclopentadienyl ring and the host molecule in the powder suggested the liberation, in part, of the cyclopentadienyl moiety from **5** upon concentration. In compound **5**, the metal coordination recognition brings about the binding of mnt to the Mn^{II} center, and the hydrophobic recognition brings about the inclusion of organomanganese fragment within the β-CD cavity. The double recognition led to the self-stabilization of compound **5** in solution.

Table 2 shows ^{13}C-NMR data of compound **1**, inclusion compound **2**, and the self-stabilized compound **5**. ^{13}C-NMR signals of carbons in the β-CD moiety of compound **2** appeared upfield compared with those of compound **1**. For example, after inclusion of the organometallic guest, the signals for C-3 in the β-CD structure shifted from 73.15 (in compound **1**) to 73.06 ppm (in compound **2**). For the over-irradiated solution **5**, upfield shifts of carbons in both the β-CD moiety and the cyclopentadienyl ring of the guest were observed. Downfield shifts were also observed for carbons in the nitrile groups of the mnt moiety. For example, the signals of C-3 shifted from 73.06 (in compound **2**) to 72.88 ppm (in compound **5**), the signals of carbons in the cyclopentadienyl ring shifted from 83.96 (in compound **2**) to 82.98 ppm (in compound **5**), and the signals of carbons of the nitrile groups shifted from 81.05 (in compound **2**) to 83.72 ppm (in compound **5**). This revealed the charge transfer from the attached mnt group to the organometallic fragment in the β-CD cavity, which could be interpreted as the formation of S–Mn bonding as mentioned above.

Conclusion

We prepared a new β-CD derivative, 6-mnt–β-CD, and its inclusion compound with an organometallic guest, CpMn(CO)$_3$. The mnt-modified β-CD in the inclusion compound 6-mnt–β-CD/CpMn(CO)$_3$ exhibited better guest-binding ability, and gave better thermal protection to the included guest than pure β-CD. In addition, intramolecular photo-substitution in the inclusion compound 6-mnt–β-CD/CpMn(CO)$_3$ in DMF solution was explored. This intramolecular photo-substitution finally brought about a double-recognition between the host and the organometallic guest.

Acknowledgements

This work was supported by the RFDP (No. 96028426), the National Natural Science Foundation (No. 29771017 and No. 29831010) and the State Education Commission of China.

References

1 (*a*) A. Harada, Y. Hu, S. Yamamoto and S. Takahashi, *J. Chem. Soc., Dalton Trans.*, 1988, 729; (*b*) Y. Maeda, N. Ogawa and Y. Takashima, *J. Chem. Soc., Dalton Trans.*, 1987, 627.
2 H. M. Colquhoun, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 487.
3 (*a*) M. L. Bender and M. Komiyami, *Cyclodextrin Chemistry*, Springer, New York, 1977; (*b*) A. Harada and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1984, 645; (*c*) A. Harada, K. Saeki and S. Takahashi, *Chem. Lett.*, 1985, 1157; (*d*) M. Shimada, Y. Morimoto and S. Takahashi, *J. Organomet. Chem.*, 1993, **443**, C8; (*e*) L. Song, Q. Meng and X. You, *J. Organomet. Chem.*, 1995, **498**, C1.
4 (*a*) U. Ammon, C. Chiorboli, W. Dümler, G. Grampp, F. Scandola and H. Kisch, *J. Phys. Chem. A*, 1997, **101**, 6876; (*b*) W. Reith, K. Polborn and E. Amberger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 699; (*c*) M. Uruichi, K. Yakushi, Y. Yamashita and J. Qin, *J. Mater. Chem.*, 1998, **8**, 141; (*d*) V. Gama, R. T. Henriques, G. Bonfait, L. C. Pereira, J. Cwaerenbogh, I. C. Santos, M. T. Duarte, J. M. P. Cabral and M. Almeida, *Inorg. Chem.*, 1992, **31**, 2598; (*e*) P. I. Clemenson, *Coord. Chem. Rev.*, 1990, **106**, 171.
5 G. Bähr and G. Schleitzer, *Chem. Ber.*, 1957, **90**, 438.
6 M. Yoshihisa and O. Akihiko, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3030.
7 C. S. Lu, C. J. Hu, Y. Yu and Q. J. Meng, *Chem. Pharm. Bull.*, 2000, **48**, 56.
8 L. X. Song, Q. J. Meng and X. Z. You, *J. Organomet. Chem.*, 1995, **498**, C1.
9 V. T. Yilmaz, A. Karadag and H. Icbudak, *Thermochim. Acta*, 1995, **261**, 107.
10 (*a*) P. J. Giordano and M. S. Wrighton, *Inorg. Chem.*, 1977, **16**, 160; (*b*) M. S. Wrighton, *Chem. Rev.*, 1974, **74**, 401; (*c*) W. A. Herrmann, R. Serrano and J. Weichmann, *J. Organomet. Chem.*, 1983, **246**, C57.
11 R. Gross and W. Kaim, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 856.
12 (*a*) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams and H. B. Gray, *J. Am. Chem. Soc.*, 1964, **86**, 4594; (*b*) R. Eisenberg, J. A. Ibers, R. J. H. Clark and H. B. Gray, *J. Am. Chem. Soc.*, 1964, **86**, 113; (*c*) A. R. Latham, V. C. Hascall and H. B. Gray, *Inorg. Chem.*, 1965, **4**, 788.
13 R. B. King, W. C. Zipperer and M. Ishaq, *Inorg. Chem.*, 1972, **11**, 1361.