

# Some additional aspects of versatile starting compounds for cationic organoiron complexes: molecular structure of the aqua complex $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Fe}(\text{CO})_2(\text{OH}_2)]\text{BF}_4$ and solution behavior of the THF complex $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2(\text{THF})]\text{BF}_4$

Munetaka Akita \*, Masako Terada, Masako Tanaka, Yoshihiko Morooka \*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

Received 19 July 1995; in revised form 13 September 1995

## Abstract

The structures of the versatile starting compounds for organoiron complexes, the cationic aqua complex  $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Fe}(\text{CO})_2(\text{OH}_2)]\text{BF}_4$  (**1b**) and the halide complexes  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{-I}$  (**2a**),  $(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Fe}(\text{CO})_2\text{-I}$  (**2b**) and  $(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Fe}(\text{CO})_2\text{-Cl}$  (**3b**), are characterized by X-ray crystallography. Complex **1b** [Fe–O: 2.022(8) Å and 2.043(9) Å, two independent molecules] is the first structurally characterized example of organoiron aqua complexes. Details of the synthetic procedures for the above complexes and the labile cationic THF complexes  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2(\text{THF})]\text{BF}_4$  (**4**) are disclosed, and the dissociation equilibrium of **4** is confirmed by means of variable temperature  $^1\text{H-NMR}$  as well as saturation transfer experiment.

**Keywords:** Iron; Carbonyl; Crystal structure; Halide; Water

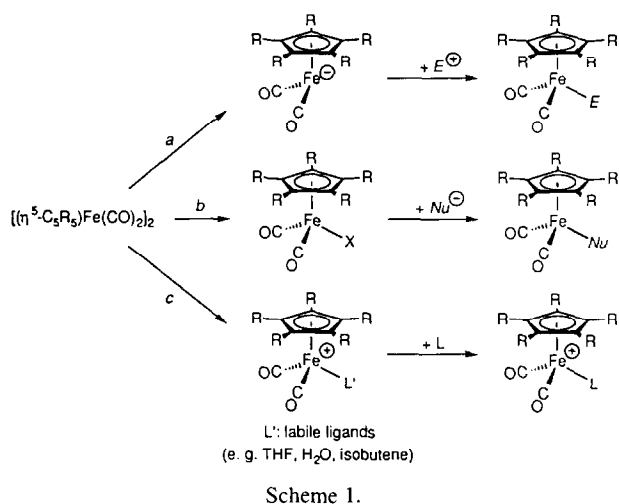
## 1. Introduction

Compounds containing an iron fragment  $\text{CpFe}(\text{CO})_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), which is isolobal with a methyl group, have been studied extensively since the infancy of organometallic chemistry [1]. The compounds exhibit considerable stability toward air, moisture and temperature, and their so-called half-sandwich or piano-stool type structure can be characterized readily by simple spectroscopic features such as two strong  $\nu(\text{C}\equiv\text{O})$  absorptions and a single Cp resonance (NMR). The ring-substituted derivatives  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2(\text{L})$  ( $\text{R} = \text{alkyl, phenyl, silyl, halide, ester, etc.}$ ) have also been studied in order to investigate the electronic and steric effect of the Cp ligand [2]. In particular, pentamethylcyclopentadienyl derivatives ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) have been used by many researchers in this field following the pioneering work of King and coworkers [3]. The ligand increases the solubility of compounds, and im-

parts considerable stability to compounds by steric shielding of the iron center. In addition, good single crystals are obtained frequently owing to resolution of the disorder problem of the Cp ring.

The  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{-L}$  type compounds have been prepared by various methods, analogous to those employed for the Cp derivatives ( $\text{R} = \text{H}$ ; Scheme 1), starting from the dimer complex  $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ . Typical methods involve nucleophilic substitution by the ferrate  $[\text{Cp}^*\text{Fe}(\text{CO})_2]^-$  (path a) [3a,4] and functionalization of  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{-X}$  ( $\text{X} = \text{halide}$ ) with nucleophiles (path b). Cationic complexes are prepared by displacement reaction of the labile O-ligated complexes  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{THF})]^+$  [4] or  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{OH}_2)]^+$  [5,6]. By using these precursors most of the  $\text{Cp}^*$ -version of the previously reported  $\text{CpFe}(\text{CO})_2\text{-L}$  type compounds have been prepared successfully (Scheme 1). For example, we reported synthesis of iron acetylide complexes  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{-C}\equiv\text{C-R}$  by reaction of  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{-I}$  with lithium acetylide (path b), and further treatment with the cation  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{THF})]\text{BF}_4$  afforded dinuclear bridging acetylide complexes  $[(\text{Cp}^*\text{Fe}(\text{CO})_2)_2(\mu\text{-C}\equiv\text{C-R})]\text{BF}_4$  (path c) [7].

\* Corresponding authors.



In this paper we report the molecular structures of the  $\eta^5\text{-C}_5\text{Me}_5$  ( $\text{Cp}^*$ ) or  $\eta^5\text{-C}_5\text{Me}_4\text{Et}$  ( $\text{Cp}^\#$ ) derivative of the versatile starting compounds,  $[\text{Cp}^\# \text{Fe}(\text{CO})_2(\text{OH}_2)]\text{BF}_4$  (**1b**),  $\text{Cp}^* \text{Fe}(\text{CO})_2\text{-I}$  (**2a**),  $\text{Cp}^\# \text{Fe}(\text{CO})_2\text{-I}$  (**2b**), and  $\text{Cp}^\# \text{Fe}(\text{CO})_2\text{-Cl}$  (**3b**), and solution behavior of  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2(\text{THF})]\text{BF}_4$  (**4**) [8].

## 2. Results and discussion

### 2.1. Synthesis of the organoiron precursors

The synthetic routes to the organoiron precursors are summarized in Scheme 2. Both the  $\text{Cp}^*$  and  $\text{Cp}^\#$  derivatives are prepared in essentially the same way as reported for the Cp complexes [9]. The dimer complex **5** was obtained by treatment of  $\text{C}_5\text{Me}_4\text{R(H)}$  with  $\text{Fe}(\text{CO})_5$  in refluxing xylenes [4]. Purification of the  $\text{Cp}^*$  derivative **5a** was rather troublesome because of the low solubility in organic solvents, but the solid residue containing iron fine powders [10] could be subjected to iodination (**5**  $\rightarrow$  **2**) without further purification. Treat-

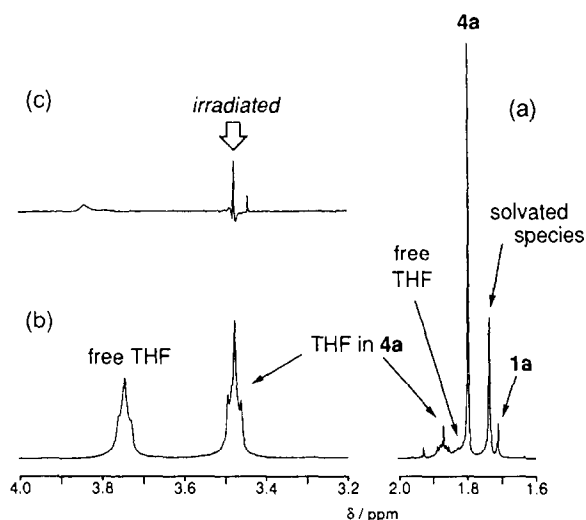
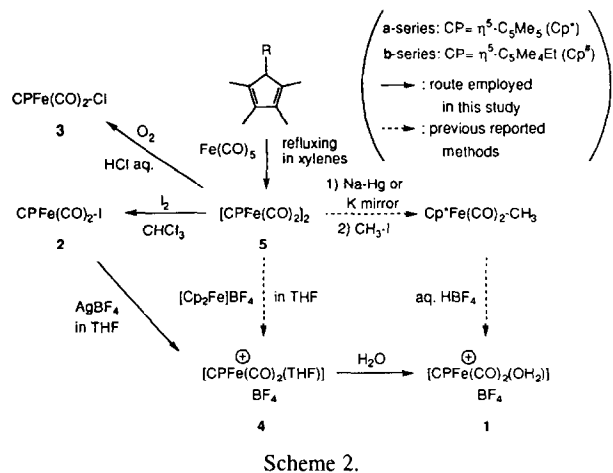
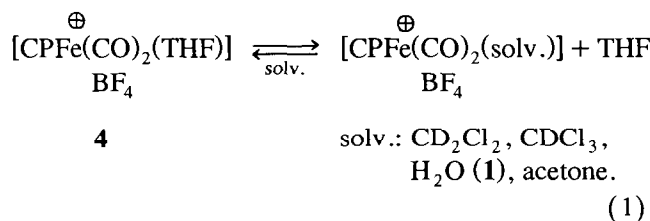


Fig. 1.  $^1\text{H-NMR}$  spectra of **4a** observed in  $\text{CDCl}_3$  (400 MHz; at room temperature). (a)  $\text{Cp}^*$  region; (b)  $\text{O}(\text{CH}_2)_2$  region (THF); (c) saturation transfer experiment (the irradiated site is indicated by an arrow).

ment of the resulting iodide complex **2** with  $\text{AgBF}_4$  in THF gave the labile cationic complex **4** coordinated by THF. Addition of an equimolar amount of water to a  $\text{CH}_2\text{Cl}_2$  solution of **4** resulted in instantaneous color change from deep red to light orange red, and the aqua complex **1** was recovered from the solution.

Synthesis of the  $\text{Cp}^*$  derivatives of the THF complex **4a** and the aqua complex **1a** via different routes have already been reported by Astruc and coworkers [4] and Lapinte and coworkers [5] respectively. Oxidative cleavage of the Fe–Fe bond in **5a**, effected by the action of the ferrocenium cation  $[\text{Cp}_2\text{Fe}]^+$  in THF, afforded **4a**. In Ref. [4] it is also reported that **4a** served as a versatile starting compound for cationic complexes through displacement of the labile THF ligand.

The high lability of **4a** was also demonstrated by the observation of dissociation equilibrium (Eq. (1)) [11]. The  $^1\text{H-NMR}$  spectrum of **4a** recorded in  $\text{CDCl}_3$  (at 400 MHz) contained a couple of  $\text{Cp}^*$  signals (Fig. 1). The major peak at  $\delta$  1.80 was



assigned to **4a** on the basis of comparison of its intensity with that of the coordinated THF signal [ $\delta(\text{O}(\text{CH}_2)_2) \sim 3.47$ ], which appeared in a higher field than that of free THF ( $\delta \sim 3.74$ ). The minor component ( $\delta$  1.75) was then assigned to a solvent-stabilized cationic species  $[\text{Cp}^* \text{Fe}(\text{CO})_2(\text{CDCl}_3)]^+$  [12] or a  $\text{BF}_4^-$

coordinated species  $\text{Cp}^* \text{Fe}(\text{CO})_2(\text{BF}_4)$  [13,14]. Upon lowering the temperature to  $-90^\circ\text{C}$ , the equilibrium ratio of the two species in  $\text{CD}_2\text{Cl}_2$  was changed from 1/0.33 to 1/0.22 (**4a**/the solvated species). Furthermore, the dissociation equilibrium was confirmed by a saturation transfer experiment (Fig. 1(c)). When the  $\text{CH}_2\text{O}$  signal of the coordinated THF in **4a** was irradiated, the intensity of the  $\text{CH}_2\text{O}$  signal of free THF decreased. Therefore the coordinated THF was found to be exchanged with free THF at a rate slower than the NMR time scale. In the case of the Cp derivative, dissociation was not observed on the NMR time scale. (Only a single species was detected at ambient temperature.) The weakest signal ( $\delta$  1.73), whose intensity varied depending on samples, was due to **1a** arising from hydrolysis of **4a** by moisture [15]. The sensitivity of **4** towards moisture was demonstrated by recovery of **1** after repeated recrystallization of **4**. Addition of  $\text{D}_2\text{O}$  caused instantaneous replacement of the signals of **4a** and  $[\text{Cp}^* \text{Fe}(\text{CO})_2(\text{CDCl}_3)]^+$  by that of **1a-d**<sub>2</sub> and free THF. The  $\text{Cp}^\#$  derivative **4b** showed NMR features similar to those of **4a**.

Astruc and coworkers [4] also pointed out that alkene (and alkyne) complexes were not obtained from **4a**. However, this difficulty was overcome by the more labile aqua complex **1a** which was prepared by protonolysis of the methyl complex  $\text{Cp}^* \text{Fe}(\text{CO})_2\text{-CH}_3$  by aqueous  $\text{HBF}_4$  at low temperature as reported by Lapinte and coworkers [5] (Scheme 2). The aqua complex **1a** was converted readily to a variety of  $\eta^2$ -alkene and -alkyne complexes by heating in the presence of substrates. Although the ruthenium analogue (**6**) of **1a** was characterized crystallographically, neither the X-ray structure of the iron cation **1a** nor of its derivatives has been reported so far.

## 2.2. Molecular structures of the cationic aqua complex **1b** and the halide complexes **2a,b** and **3b**

Molecular structures of **1b**, **2a,b** and **3b** are reproduced in Figs. 2 and 3, and the crystallographic data and selected structural parameters are summarized in Tables 1 and 2. All the complexes adopt a typical three-legged piano-stool structure.

The aqua complex **1b** is, to our knowledge, the first structurally characterized example of organoiron aqua complexes [16]. The unit cell contains two independent molecules with different orientation of the  $\text{Cp}^\#$  ring (see below). The  $\text{Fe-OH}_2$  distances [2.022(8) and 2.043(9) Å] are comparable with those found in aqua coordination compounds of iron [2.0–2.2 Å], which have recently attracted increasing attention as synthetic models for the active sites of metalloenzymes such as methane monooxygenase [17]. In the case of the ruthenium triflate analogue  $[\text{Cp}^* \text{Ru}(\text{CO})_2(\text{OH}_2)]\text{OSO}_2\text{CF}_3$  (**6**) [5], a hydrogen-bonding interaction between the

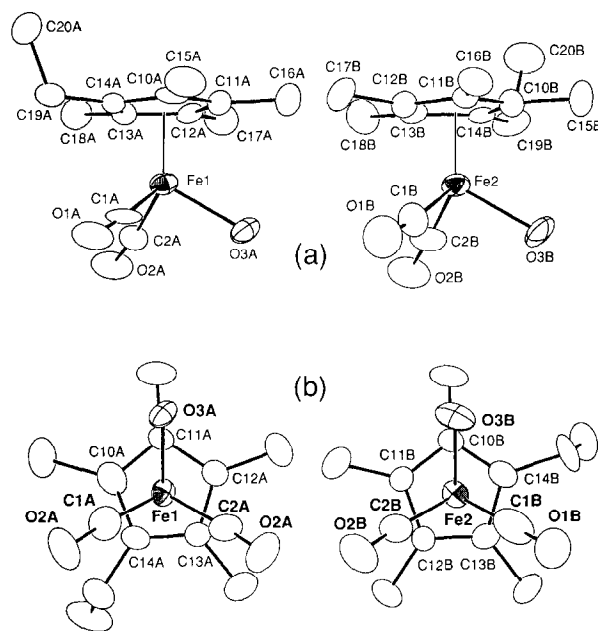


Fig. 2. Molecular structure of the two independent molecules of the aqua complex **1b** drawn at the 30% probability level. (The  $\text{BF}_4$  anions are omitted for clarity.) (a) Top views; (b) bottom views.

$\text{OH}_2$  atom and the  $\text{OSO}_2\text{CF}_3$  atom was revealed by X-ray crystallography ( $\text{H} \cdots \text{O}$ : 1.94 and 2.04 Å). Similar H-bonding is proposed for the  $\text{BF}_4$  salt of the iron cation **1a** on the basis of the  $\nu(\text{O-H})$  vibration ( $2720 \text{ cm}^{-1}$ ) appearing in low energy [5], and a very weak absorption assignable to  $\nu(\text{O-H})$  was also observed for **1b**. The rather short  $\text{H}_2\text{O}(3) \cdots \text{F}(\text{BF}_3)$  distances (around

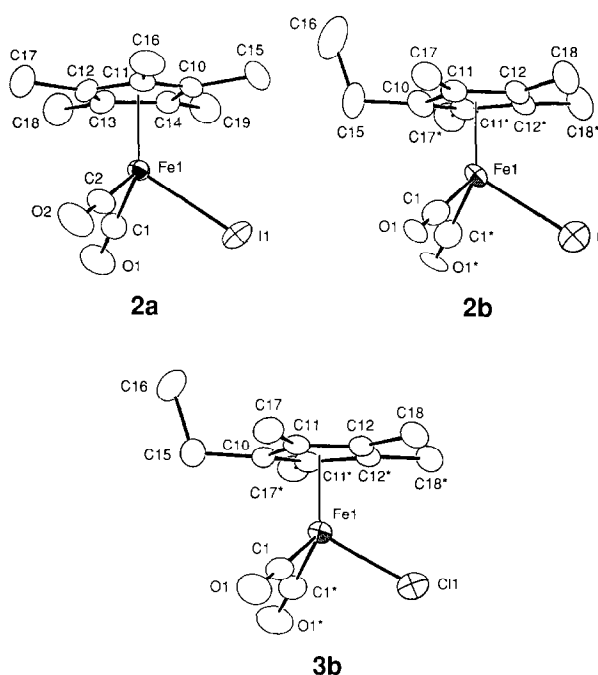


Fig. 3. Molecular structure of **2a,b** and **3b** drawn at the 30% probability level.

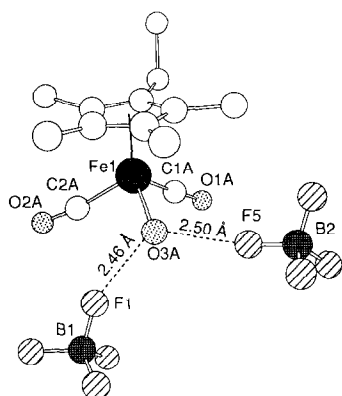


Fig. 4. Examples of short  $\text{H}_2\text{O} \cdots \text{F}$  distances in **1b** (molecule 1) suggesting hydrogen-bonding interaction.

2.5 Å) in **1b**, as typically exemplified in Fig. 4, suggest similar H-bonding interaction [16]. However, because the aqua hydrogen atoms could not be located and the highly disordered  $\text{BF}_4$  groups are refined using rigid groups (see Section 3), the interaction could not be characterized definitely by X-ray analysis. When the structure of the  $\text{Cp}^*\text{Fe}(\text{CO})_2$  parts are closed up in detail, the two Fe–CO distances in a molecule are considerably different [Fe–Cl < Fe–C2: 1.72(1) vs. 1.86(2) Å and 1.74(2) vs. 1.82(2) Å]. The structures of the  $\text{Cp}^*$  complexes, including those previously reported by us [7,18], and the iodide complex **2a**, which is also a versatile starting compound (Scheme 1), are essentially symmetrical with respect to the plane bisecting the  $\text{Fe}(\text{CO})_2\text{X}$  part (difference in the Fe–CO lengths less

Table 1  
Crystallographic data for **1b**, **2a,b**, and **3b**

	Complex			
	<b>1b</b>	<b>2a</b>	<b>2b</b>	<b>3b</b>
Formula	$\text{C}_{13}\text{H}_{17}\text{O}_3\text{BF}_4\text{Fe}$	$\text{C}_{12}\text{H}_{15}\text{O}_2\text{FeI}$	$\text{C}_{13}\text{H}_{17}\text{O}_2\text{FeI}$	$\text{C}_{13}\text{H}_{17}\text{O}_2\text{FeCl}$
Formula weight	363.9	374.0	388.0	261.1
Space group	$P2_1/c$	$P2_1/n$	$P2_1/m$	$P2_1/m$
<i>a</i> (Å)	16.82(2)	7.314(3)	6.991(2)	6.7166(9)
<i>b</i> (Å)	11.597(4)	14.444(2)	11.801(5)	11.334(2)
<i>c</i> (Å)	17.168(5)	13.142(3)	9.213(2)	9.2123(9)
$\beta$ (°)	90.86(5)	92.48(2)	93.85(2)	96.084(9)
<i>V</i> (Å <sup>3</sup> )	3348(3)	1386.9(6)	758.4(4)	697.3(1)
<i>Z</i>	8	4	2	2
$d_{\text{calc}}$ (g cm <sup>-3</sup> )	1.44	1.79	1.70	1.24
$\mu$ (cm <sup>-1</sup> )	9.5	33.0	30.0	10.6
$2\theta$ (°)	5–50	5–55	5–55	5–50
No. of data collected	6442	6808	2310	1412
No. of data with $I > 3\sigma(I)$	2681	2544	851	1075
No. of parameters refined	339	145	85	85
<i>R</i>	0.091	0.035	0.059	0.042
<i>R<sub>w</sub></i>	0.068	0.034	0.059	0.042

Table 2  
Selected interatomic distances (Å) and bond angles (°) for **1b**, **2a,b**, and **3b**

	Complex			
	<b>1b</b> <sup>a</sup>	<b>2a</b>	<b>2b</b> <sup>b</sup>	<b>3b</b> <sup>b</sup>
Fe–X	2.022(8)	2.043(9)	2.6077(9)	2.587(3)
Fe–C1	1.72(1)	1.74(2)	1.773(5)	1.88(2)
Fe–C2	1.86(2)	1.82(2)	1.775(5)	1.88(2)
Fe–C10–14	2.07–2.14(1)	2.08–2.14(1)	2.083–2.151(4)	2.06–2.11(2)
C–C(C10–14)	1.37–1.43(2)	1.40–1.46(2)	1.392–1.434(6)	1.38–1.43(2)
C–Me,Et	1.48–1.59(2)	1.48–1.54(2)	1.496–1.508(7)	1.49–1.51(2)
C1–O1	1.19(2)	1.09(2)	1.132(5)	0.90(2)
C2–O2	1.09(2)	1.12(2)	1.128(5)	0.90(2)
X–Fe–C1	94.7(5)	94.9(6)	89.4(2)	91.1(5)
X–Fe–C2	95.5(5)	95.2(6)	90.4(2)	91.1(5)
C1–Fe–C2	95.9(7)	95.5(8)	95.7(2)	91(1)
Fe–C1–O1	175(1)	177(2)	177.5(5)	178(2)
Fe–C2–O2	174(1)	173(1)	176.6(5)	178(2)

<sup>a</sup> Contains two independent molecules; <sup>b</sup> lies on a crystallographic mirror plane.

than 0.01 Å). Apparently, the different Fe–CO lengths may be attributed to unsymmetrical orientation of the Cp<sup>#</sup> ring with respect to the plane passing through the Fe and X atoms and the centroid of the η<sup>5</sup>-C<sub>5</sub> ring. In fact, the Et group of the Cp<sup>#</sup> ligand in the two independent molecules occupies different sites which are not the site on the mirror plane, as can be seen from the bottom views of **1b** (Fig. 2(b)). However, the pentagonal C<sub>5</sub> ring of the Cp\* and Cp<sup>#</sup> ligands are laid virtually symmetrically with respect to the mirror plane. The C10A–C12A [2.11–2.12(1) Å] and C14A–C13A [2.07(1) Å] atom pairs are located equidistant from the iron center, although the C<sub>5</sub> plane is slightly tilted away from the OH<sub>2</sub> ligand presumably owing to the different π-accepting ability of the CO and OH<sub>2</sub> ligands. In order to further consider the effect of the orientation of the Cp<sup>#</sup> ligand, the molecular structures of the iodide (**2b**) and chloride (**3b**) complexes have also been determined by X-ray crystallography (Fig. 3). However, because both **2b** and **3b** have crystallographic mirror symmetry [19], no definite conclusion could be deduced from the X-ray study. Thus the orientation of the Cp<sup>#</sup> ligand might not be the reason for the different Fe–CO lengths, and the problem should be attributed to unsymmetrical crystal packing caused by the Cp<sup>#</sup> ligand.

As for other structural parameters of the halide complexes **2a,b** and **3b**, the Fe–I lengths [2.6077(9) Å (**2a**), 2.587(3) Å (**2b**)] are comparable with those of the previously reported cyclopentadienyl iron iodide complexes [2.599(2) Å, (η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>MePh)Fe(CO)(PPh<sub>3</sub>)–I; 2.654(4) Å, CpFe(–)–DIOP–I] [20]. The molecular structure of the chloride complex **3b** is essentially the same as that of the Cp derivative [Fe–Cl, 2.288(2) Å; Fe–CO, 1.774(5), 1.767(6) Å; CO, 1.123(7), 1.126(8) Å] reported by Weiss and coworker [21].

### 3. Experimental section

#### 3.1. General

All manipulations were carried out under an argon atmosphere by using standard Schlenk tube techniques. Ether, THF and hexanes (Na–K alloy) and CH<sub>2</sub>Cl<sub>2</sub> (P<sub>2</sub>O<sub>5</sub>) were treated with appropriate drying agents, distilled, and stored under Ar. Pentamethyl- and tetramethylethylcyclopentadiene were prepared by the method reported in Ref. [22]. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a JEOL EX-400 spectrometer (<sup>1</sup>H: 400 MHz; <sup>13</sup>C: 100 MHz). Solvents for NMR measurements containing 1% TMS were dried over molecular sieves and distilled under reduced pressure. IR spectra were recorded on a JASCO FT/IR 5300 spectrometer.

Both the Cp\* and Cp<sup>#</sup> complexes were prepared by the method shown below. As typical examples, the

experimental procedures for the Cp<sup>#</sup> complexes are described in detail.

#### 3.2. Preparation of [Cp<sup>#</sup>Fe(CO)<sub>2</sub>]<sub>2</sub> (**5b**)

A mixture of tetramethylethylcyclopentadiene (19.0 g, 0.13 mol) and Fe(CO)<sub>5</sub> (34 ml, 0.26 mmol) was refluxed in xylenes (70 ml) for 20 h. Then the flask was cooled in a refrigerator (–20°C) overnight. The supernatant was removed by a syringe, and the residue was washed with hexanes (60 ml × 3) and then dried in vacuo [10]. **5b** (black purple crystals, 22.1 g, 42 mmol, 65% crude yield) <sup>1</sup>H-NMR (in CDCl<sub>3</sub>): δ 0.99 (3H, t, *J* = 7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.62, 1.72 (6H × 2, s, C<sub>5</sub>Me<sub>4</sub>Et), 2.19 (2H, q, *J* = 7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>), <sup>13</sup>C-NMR (in CDCl<sub>3</sub>): δ 8.4, 8.5 (q × 2, *J* = 129 Hz, C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.9 (q, *J* = 127 Hz, C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>), 17.2 (t, *J* = 130 Hz, C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>), 96.8, 98.5, 102.9 (s × 3, C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>), CO signals could not be located at room temperature probably owing to the exchange process of the terminal and bridging CO ligands [23]. IR ν(CO) (KBr) 1925, 1741; (CH<sub>2</sub>Cl<sub>2</sub>) 1922, 1749 cm<sup>-1</sup>. Anal. Found: C, 59.10; H, 6.21. C<sub>26</sub>H<sub>34</sub>O<sub>4</sub>Fe<sub>2</sub>. Calc.: C, 59.83; H, 6.51. **5b** could be purified by crystallization from CH<sub>2</sub>Cl<sub>2</sub>–hexanes.

#### 3.3. Preparation of Cp<sup>#</sup>Fe(CO)<sub>2</sub>–I (**2b**)

To a CHCl<sub>3</sub> solution (45 ml) of **5b** (4.52 g, 8.7 mmol; crude sample) was added I<sub>2</sub> (2.86 g, 11.3 mmol) in portions. An exothermic reaction took place immediately, and the mixture was further stirred at ambient temperature for 1 h. After the consumption of **5b** was checked by TLC, the content was poured into aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution in a separation funnel. The organic layer was washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution until the excess I<sub>2</sub> was decomposed completely. Then the organic layer was washed thrice with water, dried over MgSO<sub>4</sub>, and then filtered. The filtrate was evaporated and the residue was extracted with ether and filtered through an alumina plug [activity II–IV (Merck Art. 1097)]. Concentration and cooling afforded **2b** (5.90 g, 15.2 mmol, 88% yield based on crude **5b**) as black crystals. **2b** <sup>1</sup>H-NMR (in CDCl<sub>3</sub>): δ 1.06 (3H, t, *J* = 7.6 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.99, 2.00 (6H × 2, s, C<sub>5</sub>Me<sub>4</sub>Et), 2.33 (2H, q, *J* = 7.6 Hz, CH<sub>2</sub>CH<sub>3</sub>), <sup>13</sup>C-NMR (in CDCl<sub>3</sub>): δ 10.2, 10.5 (q × 2, *J* = 129 Hz, C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>), 14.5 (qt, *J* = 127 and 5 Hz, C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>), 18.7 (tq, *J* = 130 and 5 Hz, C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>), 95.2, 96.7, 99.9 (s × 3, C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>), 215.2 (s, CO). IR (KBr) 2066, 1955 (CH<sub>2</sub>Cl<sub>2</sub>); 2019, 1971 cm<sup>-1</sup>. Anal. Found: C, 39.99; H, 4.53. C<sub>13</sub>H<sub>17</sub>O<sub>2</sub>FeI. Calc.: C, 40.25; H, 4.38.

#### 3.4. Preparation of [Cp<sup>#</sup>Fe(CO)<sub>2</sub>(THF)]BF<sub>4</sub> (**4b**)

**2b** (1.40 g, 3.6 mmol) and AgBF<sub>4</sub> (0.68 g, 3.5 mmol) were weighed in a Schlenk tube under argon. Then THF

(15 ml) was added to the mixture, which was stirred overnight in the dark. The volatiles were removed under reduced pressure, and the red product was extracted with  $\text{CH}_2\text{Cl}_2$ , filtered through a Celite plug, and precipitated by addition of ether followed by cooling at  $-20^\circ\text{C}$ . **4b** (red powders, 1.24 g, 2.9 mmol, 81% yield)  $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ ):  $\delta$  1.11 (3H, t,  $J = 7.6$  Hz,  $\text{CH}_2\text{CH}_3$ ), 1.79, 1.87 (6H  $\times$  2, s,  $\text{C}_5\text{Me}_4\text{Et}$ ), 1.87 (m,  $\text{OCH}_2\text{CH}_2\text{CH}_2$  in THF), 2.26 (2H, q,  $J = 7.6$  Hz,  $\text{CH}_2\text{CH}_3$ ),  $\sim 3.48$  (4H, m,  $\text{O}(\text{CH}_2)_2$  in THF).  $^{13}\text{C-NMR}$  (in  $\text{CDCl}_3$ ):  $\delta$  9.1, 9.4, 13.1 (q  $\times$  3,  $J = 129$  Hz,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 17.7 (t,  $J = 131$  Hz,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 26.1 (t,  $J = 136$  Hz,  $\text{O}(\text{CH}_2)_2$  in THF), 80.8 (t,  $J = 152$  Hz, the other methylene carbon atoms in THF), 98.0, 99.6, 100.1 (s  $\times$  3,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 210.5 (s, CO). IR  $\nu(\text{CO})$  (KBr) 2008, 1954; ( $\text{CH}_2\text{Cl}_2$ ) 2046, 1997  $\text{cm}^{-1}$ . Anal. Found: C, 49.15; H, 6.23.  $\text{C}_{17}\text{H}_{25}\text{O}_3\text{FeBF}_4$ . Calc.: C, 48.63; H, 5.95.  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CDCl}_3)]^+$   $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ ):  $\delta$  1.08 (3H, t,  $J = 7.6$  Hz,  $\text{CH}_2\text{CH}_3$ ), 1.69, 1.78 (6H  $\times$  2, s,  $\text{C}_5\text{Me}_4\text{Et}$ ), 2.22 (2H, q,  $J = 7.6$  Hz,  $\text{CH}_2\text{CH}_3$ ),  $\sim 3.74$  (4H, m,  $\text{O}(\text{CH}_2)_2$  in free THF).

### 3.5. Preparation of $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{OH}_2)]\text{BF}_4$ (**1b**)

To a  $\text{CH}_2\text{Cl}_2$  solution (4 ml) of **4b** (154 mg, 0.37 mmol) was added water (7  $\mu\text{l}$ ). After the mixture was stirred overnight, the resulting orange  $\text{CH}_2\text{Cl}_2$  solution was concentrated and the product was isolated by addition of ether followed by cooling at  $-20^\circ\text{C}$ . **3b** (orange solids, 118 mg, 0.32 mmol, 88% yield)  $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ ):  $\delta$  1.05 (3H, t,  $J = 7.3$  Hz,  $\text{CH}_2\text{CH}_3$ ), 1.71, 1.77 (6H  $\times$  2, s,  $\text{C}_5\text{Me}_4\text{Et}$ ), 2.21 (2H, q,  $J = 7.3$  Hz,  $\text{CH}_2\text{CH}_3$ ), 2.35 (2H, s,  $\text{OH}_2$ ).  $^{13}\text{C-NMR}$  (in  $\text{CDCl}_3$ ):  $\delta$  8.8, 9.0 (q  $\times$  2,  $J = 128$  Hz,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 13.3 (q,  $J = 128$  Hz,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 17.4 (t,  $J = 128$  Hz,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 96.6, 98.8, 98.9 (s  $\times$  3,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 210.5 (s, CO). IR  $\nu(\text{CO})$  (KBr) 2012, 1956; ( $\text{CH}_2\text{Cl}_2$ ) 2028, 1977  $\text{cm}^{-1}$ . Anal. Found: C, 42.28; H, 5.18.  $\text{C}_{13}\text{H}_{19}\text{O}_3\text{FeBF}_4$ . Calc.: C, 42.68; H, 5.19.

### 3.6. Preparation of $\text{Cp}^*\text{Fe}(\text{CO})_2\text{Cl}$ (**3b**)

To a  $\text{CHCl}_3$  solution of **5b** (1.00 g, 1.92 mmol) was added EtOH (9 ml) and 2M HCl aqueous solution (9 ml), and then 1 ml of conc. HCl. The two-phase solution was stirred vigorously with bubbling air, until **5b** was consumed completely (1 h). The aqueous phase was removed and the organic layer was dried over  $\text{MgSO}_4$ . Filtration through an alumina plug followed by crystallization by addition of ether gave **3b** as deep red crystals (690 mg, 2.3 mmol, 60% yield).  $^1\text{H-NMR}$  (in  $\text{CDCl}_3$ ):  $\delta$  1.06 (3H, t,  $J = 6.8$  Hz,  $\text{CH}_2\text{CH}_3$ ), 1.76,

1.77 (6H  $\times$  2, s,  $\text{C}_5\text{Me}_4\text{Et}$ ), 2.22 (2H, q,  $J = 6.8$  Hz,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (in  $\text{CDCl}_3$ ):  $\delta$  9.3, 9.4 (q  $\times$  2,  $J = 129$  Hz,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 13.8 (q,  $J = 127$  Hz,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 17.9 (t,  $J = 130$  Hz,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 95.7, 97.9, 99.5 (s  $\times$  3,  $\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_3$ ), 213.8 (s, CO). IR  $\nu(\text{CO})$  (KBr) 2013, 1957; ( $\text{CH}_2\text{Cl}_2$ ) 2028, 1977  $\text{cm}^{-1}$ . Anal. Found: C, 52.68; H, 5.88.  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{-FeCl}$ . Calc.: C, 52.67; H, 5.73.

### 3.7. X-ray crystallography of **1b**, **2a,b** and **3b**

The complexes were recrystallized from  $\text{CH}_2\text{Cl}_2$ -ether (**1b**), ether-hexanes (**2a,b**), and  $\text{CH}_2\text{Cl}_2$ -hexanes (**3b**), and suitable crystals were sealed in a glass capillary (**1b**) or mounted on glass fibers (**2a,b**, **3b**). Diffraction measurements were made on a Rigaku AFC-5R automated four-circle diffractometer by using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). The unit cell was determined and refined by a least-squares method using 20–24 independent reflections. Data were collected with an  $\omega$ - $2\theta$  scan technique. If  $\sigma(F)/F$  was more than 0.1, a scan was repeated up to three times and the results were added to the first scan. Three standard reflections were monitored at every 150 measurements. The data processing was performed on a Micro Vax II computer (data collection) and an IRIS Indigo computer (structure analysis) by using the teXsan structure-solving program system obtained from the Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard source [24]. In the reduction of data, Lorentz, polarization, and empirical absorption corrections ( $\Psi$  scan) were made.

Structures of the compounds were solved by a combination of the direct method and Fourier synthesis (SAPI 91 & DIRDIF). All the non-hydrogen atoms except the  $\text{BF}_4$  anions of **1b** were refined anisotropically and the hydrogen atoms of the  $\text{Cp}^*$  and  $\text{Cp}^\#$  ligands were located at the calculated positions ( $\text{C-H} = 0.95$  Å) and were not refined. The unit cell of **1b** contained two independent molecules, and during the refinement it was found that the  $\text{BF}_4$  parts were disordered. Then the  $\text{BF}_4$  parts were refined by using rigid tetrahedral  $\text{BF}_4$  models (B-F: 1.36 Å), and the occupancy was determined to be B(1)F(1–4): B(2)F(5–8) = 0.553:0.447 and B(3)F(9–12): B(4)F(13–16) = 0.523:0.477.

### Acknowledgment

Financial support from the Ministry of Education, Science, Sports and Culture of the Japanese Government (Grants-in-Aids for Scientific Research on Priority Area, Nos. 04241105 and 05236103) is gratefully acknowledged.

## References and notes

- [1] See for example: (a) T.S. Piper, F.A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1** (1955) 165; (b) T.S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3** (1956) 104; (c) M. Rosenblum, *J. Organomet. Chem.*, **300** (1986) 191.
- [2] D.W. Macomber, W.P. Hart and M.D. Rausch, *Adv. Organomet. Chem.*, **21** (1982) 1.
- [3] (a) R.B. King and M.B. Bisnette, *J. Organomet. Chem.*, **8** (1967) 287; (b) R.B. King and A. Efraty, *J. Am. Chem. Soc.*, **93** (1971) 4950; (c) R.B. King and A. Efraty, *J. Am. Chem. Soc.*, **94** (1972) 3773; (d) R.B. King, W.M. Douglass and A. Efraty, *J. Organomet. Chem.*, **69** (1974) 131.
- [4] (a) D. Cathline and D. Astruc, *Organometallics*, **3** (1984) 1094; (b) J.-R. Hamon and D. Astruc, *Organometallics*, **8** (1989) 2243.
- [5] A. Tahiri, V. Guerschais, L. Toupet and C. Lapinte, *J. Organomet. Chem.*, **381** (1990) C47.
- [6] For a leading reference of organometallic Lewis acids, see W. Beck and K. Sünkel, *Chem. Rev.*, **88** (1988) 1405.
- [7] M. Akita, M. Terada, S. Oyama and Y. Moro-oka, *Organometallics*, **9** (1990) 816.
- [8] Throughout this paper the  $\eta^5\text{-C}_5\text{Me}_5$  and  $\eta^5\text{-C}_5\text{Me}_4\text{Et}$  ligands are abbreviated as Cp\* and Cp<sup>#</sup> respectively, and CP is used as a general term for the  $\eta^5\text{-C}_5\text{R}_5$  ligands.
- [9] Synthesis of the Cp derivatives. The dimer: Ref. [1a]; The iodide: T.S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2** (1956) 38; The THF cation: D.C. Reger and C. Coleman, *J. Organomet. Chem.*, **131** (1977) 153; The aqua cation: B.D. Dombek and R. Angelici, *Inorg. Chim. Acta*, **7** (1973) 345 and references cited therein.
- [10] The crude sample of **5** containing iron fine powders should be kept under inert atmosphere, otherwise exothermic oxidation of the iron powders takes place.
- [11] Astruc and coworker [4] reported NMR spectra of **4a** measured in acetone-*d*<sub>6</sub>. The  $\delta_{\text{C}}(\text{CH}_2\text{O})$  value (68.3) reported for **4a** is close to that of free THF ( $\delta_{\text{C}}$  67.8 in CDCl<sub>3</sub>) rather than the signal observed in CDCl<sub>3</sub> ( $\delta_{\text{C}}$  80.7). These observations lead us to the conclusion that the species observed in acetone-*d*<sub>6</sub> is [Cp\*Fe(CO)<sub>2</sub>(acetone-*d*<sub>6</sub>)]<sup>+</sup>. NMR data for **4a** (in CDCl<sub>3</sub>; see also Fig. 1) <sup>1</sup>H-NMR:  $\delta$  1.80 (15H, s, Cp\*),  $\sim$  3.47 (4H, m, O(CH<sub>2</sub>)<sub>2</sub> in THF). <sup>13</sup>C-NMR:  $\delta$  9.4 (q, *J* = 129 Hz, C<sub>5</sub>Me<sub>5</sub>), 26.1 (t, *J* = 132 Hz, O(CH<sub>2</sub>)<sub>2</sub> in THF), 80.7 (t, *J* = 149 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> in THF), 98.5 (s, C<sub>5</sub>Me<sub>5</sub>), 210.7 (s, CO). [Cp\*Fe(CO)<sub>2</sub>(CDCl<sub>3</sub>)]<sup>+</sup> <sup>1</sup>H-NMR (in CDCl<sub>3</sub>):  $\delta$  1.75 (15H, s, Cp\*),  $\sim$  3.74 (4H, m, O(CH<sub>2</sub>)<sub>2</sub> in free THF). <sup>13</sup>C-NMR (in CDCl<sub>3</sub>)  $\delta$  9.0 (q, *J* = 129 Hz, C<sub>5</sub>Me<sub>5</sub>), 97.4 (s, C<sub>5</sub>Me<sub>5</sub>), 210.8 (s, CO).
- [12] Complexes coordinated by alkyl halide were isolated. (a) C.H. Winter, W.R. Veal, C.M. Garner, A.M. Arif and J.A. Gladysz, *J. Am. Chem. Soc.*, **111** (1989) 4766. See also (b) J.S. Fernández and J.A. Gladysz, *Inorg. Chem.*, **25** (1986) 2674; (c) J.S. Fernández and J.A. Gladysz, *Organometallics*, **8** (1989) 207.
- [13] The coordination of the F atom in the BF<sub>4</sub> group was characterized for the tungsten analog CpW(CO)<sub>3</sub>(BF<sub>4</sub>). K. Sünkel, G. Urban and W. Beck, *J. Organomet. Chem.*, **252** (1983) 187.
- [14] Because the labile ligand coordinated to the iron atom, CDCl<sub>3</sub> or BF<sub>4</sub> could not be determined by means of NMR techniques, the species was tentatively assigned to [( $\eta^5\text{-C}_5\text{R}_5$ )Fe(CO)<sub>2</sub>(solvent)]<sup>+</sup>.
- [15] The reviewers raised a question concerning the relative lability of the THF complex **4** and the aqua complex **1**. The successful ligand displacement of **1** suggests that **1** may be more labile than **4**, however, the main product obtained from the reaction of **4** with unsaturated hydrocarbons is the tricarbonyl complex [CpFe<sup>+</sup>(CO)<sub>3</sub>] arising from a complicated ligand disproportionation reaction. Therefore the reason for the failure in conversion of **4** into alkene and alkyne complexes [4] is not its lower lability, and some different mechanisms may operate for the reactions of these related species. Judging from the NMR experiments (e.g. Fig. 1), the small aqua ligand appears to be bound to the iron center more tightly than THF does. Anyway, a sample of the THF complex **4** containing the aqua complex **1** can be used for subsequent transformations as it is.
- [16] For organometallic aqua complexes, see references cited in Ref. [5]. See also X.-L. Luo, G.K. Schulte and R.H. Crabtree, *Inorg. Chem.*, **29** (1990) 682.
- [17] (a) Y. Dong, H. Fujii, M.P. Hendrich, R.A. Leising, G. Pan, C.R. Randall, E.C. Wilkinson, Y. Zang, L. Que, Jr., B.G. Fox, R. Kauffmann and E. Münck, *J. Am. Chem. Soc.*, **117** (1995) 2778; (b) W. Micklitz and S.J. Lippard, *Inorg. Chem.*, **27** (1988) 3067. See also (c) A.L. Feig and S.J. Lippard, *Chem. Rev.*, **94** (1994) 759.
- [18] (a) M. Akita, A. Kondoh and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, (1989) 1083; (b) M. Akita, N. Ishii, A. Takabuchi, M. Tanaka and Y. Moro-oka, *Organometallics*, **13** (1994) 258.
- [19] Refinement according to the acentric space group *P*2<sub>1</sub> was unsuccessful.
- [20] (a) T.G. Attig, R.G. Teller, S.-M. Wu, R. Bau and A. Wojcicki, *J. Am. Chem. Soc.*, **101** (1979) 619; (b) G. Balavoine, S. Brunie and H.B. Kagan, *J. Organomet. Chem.*, **187** (1980) 125.
- [21] K.-J. von Jens and E. Weiss, *Acta Crystallogr.*, **C41** (1985) 895.
- [22] R.S. Threlkel and J.E. Bercaw, *J. Organomet. Chem.*, **136** (1977) 1.
- [23] O.A. Gansow, A.R. Burke and W.D. Vernon, *J. Am. Chem. Soc.*, **98** (1976) 5817.
- [24] *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch, UK, 1975.