

## Reaction of a $\pi$ -vinylcarbeneiron complex with aromatic diamines: formation and structure of ferracyclopentenone(diamine) complexes

Ken-ichi Fujita, Kenji Ito, Teruyuki Kondo, Take-aki Mitsudo \*

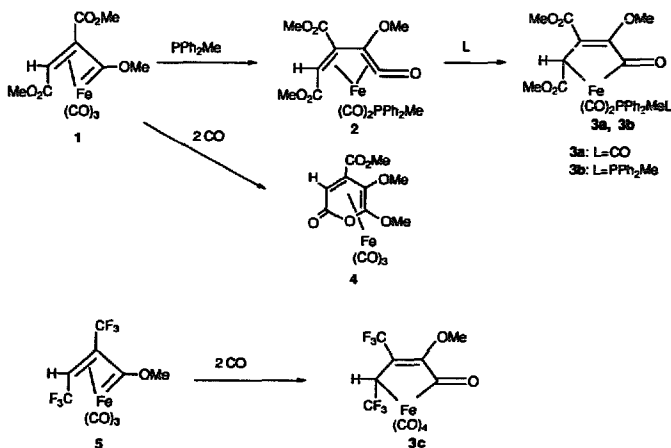
Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Received 28 August 1996; revised 9 October 1996

### Abstract

[1-3- $\eta$ -1-Methoxy-*anti*-2,3-bis(methoxycarbonyl)-prop-2-en-1-ylidene]tricarbonyliron (1) reacts with 2,2'-bipyridyl or 1,10-phenanthroline to give corresponding 2-ferracyclopent-4-en-1-one derivatives, 3d and 3e, in 45 and 80% yields respectively. Complex 3d crystallizes in the triclinic space group *P*1 with  $a = 13.526(10)$ ,  $b = 15.71(2)$ ,  $c = 11.06(1)$  Å,  $\alpha = 91.51(10)^\circ$ ,  $\beta = 108.50(6)^\circ$ ,  $\gamma = 103.26(7)^\circ$ , and  $Z = 4$ . Complex 3d has octahedral Fe(II) and two carbonyl groups are in *cis* configuration; the acyl group and one of the bipyridyl nitrogen are in *trans* configuration.

**Keywords:** Amine; Carbene; Carbonyl; Iron; Carbonylation; Metallacycle



Scheme 1.

\* Corresponding author.

## 1. Introduction

$\eta^3$ -Vinylcarbene (or  $\pi$ -vinylcarbene) transition metal complexes [1–11] have received much attention, especially because of their role in the Dötz reaction [12], and a theoretical study of the  $\pi$ -vinylcarbene complexes was performed [13]. However, the reactivity of  $\pi$ -vinylcarbene complexes has not been fully clarified. We previously reported carbonylation reactions of ( $\pi$ -vinylcarbene)tricarbonyliron induced by the coordination of tertiary phosphines and/or carbon monoxide [9,10]. Products of these reactions were  $\eta^4$ -vinylketene (or  $\eta^3$ : $\eta^1$ -allylacyl) **2**, ferracyclopentenones **3a**, **3b** [9] and **3c** [10] or  $\eta^5$ -pyrone complex **4** [9], depending on substrates and reaction conditions (Scheme 1).

In the course of our study on the reactivity of  $\pi$ -vinylcarbene complexes with tertiary amines, we found that ( $\pi$ -vinylcarbene)tricarbonyliron (**1**) reacts with

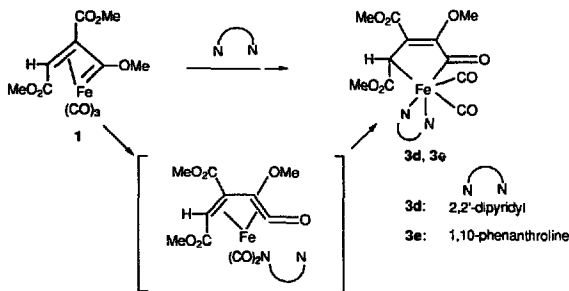
bidentate aromatic amines to give ferracyclopentenone complexes, **3d** and **3e**.

## 2. Results and discussion

### 2.1. Synthesis of the complexes **3d** and **3e**

[1-3- $\eta^1$ -Methoxy-*anti*-2,3-bis(methoxycarbonyl)-prop-2-en-1-ylidene]tricarbonyliron (**1**) reacted with 2,2'-bipyridyl or 1,10-phenanthroline under ambient reaction conditions to give the corresponding ferracyclopentenone derivatives, **3d** and **3e**, in 45 and 80% yields respectively (Scheme 2).

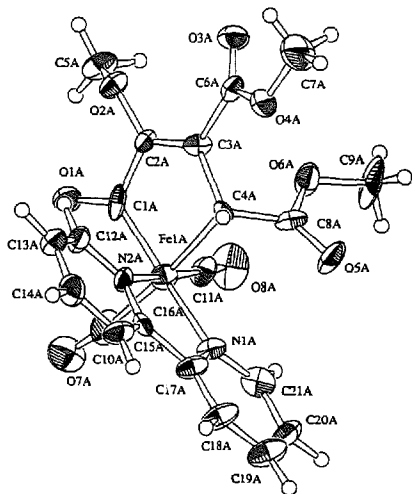
The complexes **3d** and **3e** were isolated as orange crystals which were stable in air for several hours. Spectral data for these complexes are summarized in Table 1. The IR spectrum of **3d** showed  $\nu$ (C=O) of an



Scheme 2.

Table 1  
Spectral data for **3d** and **3e**

	IR (KBr/cm <sup>-1</sup> )	<sup>1</sup> H NMR ( $\delta$ /ppm in CDCl <sub>3</sub> )	<sup>13</sup> C NMR ( $\delta$ /ppm in CDCl <sub>3</sub> )
<b>3d</b>	2008, 1946 (vs. $\nu$ FeCO) 1728 (m, $\nu$ COester) 1682 (m, $\nu$ COacyl) 1595 (m, $\nu$ C=C)	1.79 (s, 1H, CH) 3.41 (s, 3H, OMe) 3.65 (s, 3H, CO <sub>2</sub> Me) 3.94 (s, 3H, CO <sub>2</sub> Me) 7.42–8.75 (m, 8H, bipy.)	45.6 (d, CH, <sup>1</sup> J <sub>CH</sub> = 140.9 Hz) 49.9, 51.1 (q, CO <sub>2</sub> Me, <sup>1</sup> J <sub>CH</sub> = 146.7 Hz) 60.1 (q, OMe, <sup>1</sup> J <sub>CH</sub> = 146.7 Hz) 120.8–153.7 (m, bipy.) 137.7 (s, CCO <sub>2</sub> Me) 164.9, 167.4 (s, CO <sub>2</sub> Me) 179.9 (s, COMe) 204.4, 213.4 (s, FeCO) 270.2 (s, FeC=O)
<b>3e</b>	2019, 1942 (vs. $\nu$ FeCO) 1701, 1685 (m, $\nu$ COester) 1680 (m, $\nu$ COacyl) 1593 (m, $\nu$ C=C)	1.73 (s, 1H, CH) 3.42 (s, 3H, OMe) 3.60 (s, 3H, CO <sub>2</sub> Me) 3.99 (s, 3H, CO <sub>2</sub> Me) 7.66–9.20 (m, 8H, phen.)	44.5 (d, CH, <sup>1</sup> J <sub>CH</sub> = 137.9 Hz) 50.3 (q, CO <sub>2</sub> Me, <sup>1</sup> J <sub>CH</sub> = 143.8 Hz) 51.4 (q, CO <sub>2</sub> Me, <sup>1</sup> J <sub>CH</sub> = 146.7 Hz) 60.1 (q, OMe, <sup>1</sup> J <sub>CH</sub> = 146.7 Hz) 124.6–156.7 (m, phen.) 138.6 (s, CCO <sub>2</sub> Me) 164.4, 167.3 (s, CO <sub>2</sub> Me) 179.9 (s, COMe) 204.8, 213.7 (s, FeCO) 269.9 (s, FeC=O)

Fig. 1. ORTEP view of **3d** (molecule A).

acyl carbonyl at  $1682\text{ cm}^{-1}$  and  $\nu(\text{C}=\text{C})$  at  $1595\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR signal at high field,  $\delta$  1.79 ppm, and  $^{13}\text{C}$  NMR signal at  $\delta$  45.6 ppm ( $J_{\text{CH}} = 140.9\text{ Hz}$ ) showed that **3d** has a HC–Fe group. The  $^{13}\text{C}$  NMR spectrum exhibited a characteristic signal for an acyl group at  $\delta$  270.2 ppm and olefinic signals at  $\delta$  137.7 and 179.9 ppm. Spectral data for **3e** were similar to those for

Table 2  
Crystallographic data for **3d**

Formula	$\text{C}_{21}\text{H}_{10}\text{O}_8\text{N}_2\text{Fe}$
Formula weight	482.23
Crystal system	triclinic
Space group	$P\bar{1}$
$a$ (Å)	13.526(10)
$b$ (Å)	15.71(2)
$c$ (Å)	11.06(1)
$\alpha$ (deg)	91.51(10)
$\beta$ (deg)	108.50(6)
$\gamma$ (deg)	103.26(7)
$V$ (Å <sup>3</sup> )	2157(3)
$Z$	4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.484
Crystal dimensions (mm <sup>3</sup> )	$0.20 \times 0.10 \times 0.20$
Radiation	Mo K $\alpha$
Monochromator	graphite
$2\theta$ limits (deg)	55
No. of reflections measured	8263
No. of unique data	7844
No. of $I > 2.5\sigma(I)$	2338
$R$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	7.49
$R_w$	0.069
$R_w$	0.053
GOF	1.45

Table 3  
Atomic coordinates and  $B_{\text{eq}}$  /  $B_{\text{eq}}$  for **3d**

Atom	$x$	$y$	$z$	$B_{\text{eq}}$
Fe(1A)	0.2219(2)	0.3383(2)	0.6047(2)	3.00(7)
Fe(1B)	0.7548(2)	0.1751(1)	0.8891(2)	2.66(7)
O(1A)	0.3907(7)	0.2716(7)	0.5666(10)	4.2(3)
O(1B)	0.9776(8)	0.2451(7)	0.920(1)	4.3(3)
O(2A)	0.5341(7)	0.4337(6)	0.6004(9)	3.6(3)
O(2B)	1.0234(7)	0.0836(7)	0.894(1)	4.7(3)
O(3A)	0.5677(8)	0.6049(6)	0.7287(9)	4.2(3)
O(3B)	0.9066(9)	-0.0962(7)	0.802(1)	5.6(4)
O(4A)	0.4113(7)	0.6409(6)	0.6439(9)	4.0(3)
O(4B)	0.7702(7)	-0.1264(6)	0.8810(9)	4.0(3)
O(5A)	0.2075(8)	0.5271(7)	0.7934(9)	4.6(3)
O(5B)	0.5505(7)	-0.0266(6)	0.7204(9)	4.1(3)
O(6A)	0.3757(8)	0.5145(7)	0.876(1)	4.3(3)
O(6B)	0.6857(8)	-0.0126(7)	0.641(1)	4.3(3)
O(7A)	0.1523(9)	0.1477(8)	0.532(1)	5.9(4)
O(7B)	0.8194(8)	0.3666(7)	0.943(1)	5.0(3)
O(8A)	0.309(1)	0.3084(9)	0.873(1)	6.6(4)
O(8B)	0.7088(10)	0.1883(8)	0.618(1)	5.6(4)
N(1A)	0.0762(9)	0.3571(8)	0.594(1)	3.0(4)
N(1B)	0.6050(9)	0.1552(8)	0.898(1)	2.9(4)
N(2A)	0.1671(9)	0.3691(7)	0.424(1)	2.5(3)
N(2B)	0.7821(9)	0.1225(7)	1.075(1)	2.7(3)
C(1A)	0.361(1)	0.336(1)	0.594(1)	3.2(5)
C(1B)	0.903(1)	0.179(1)	0.899(1)	3.3(5)
C(2A)	0.437(1)	0.424(1)	0.619(1)	2.3(4)
C(2B)	0.920(1)	0.090(1)	0.882(1)	3.4(5)
C(3A)	0.405(1)	0.4907(10)	0.649(1)	2.3(4)
C(3B)	0.838(1)	0.0204(9)	0.864(1)	2.2(4)
C(4A)	0.291(1)	0.4719(9)	0.652(1)	2.3(4)
C(4B)	0.733(1)	0.0406(10)	0.854(1)	2.6(4)
C(5A)	0.606(1)	0.388(1)	0.675(1)	4.2(5)
C(5B)	1.053(1)	0.100(1)	0.782(2)	7.3(7)
C(6A)	0.472(1)	0.584(1)	0.679(1)	2.9(4)
C(6B)	0.846(1)	-0.071(1)	0.844(2)	3.9(5)
C(7A)	0.469(1)	0.731(1)	0.668(2)	6.1(5)
C(7B)	0.769(1)	-0.218(2)	0.869(2)	6.6(5)
C(8A)	0.284(1)	0.5062(9)	0.776(2)	3.1(4)
C(8B)	0.644(1)	-0.0043(9)	0.737(2)	2.6(4)
C(9A)	0.380(1)	0.546(1)	1.000(2)	8.4(7)
C(9B)	0.613(1)	-0.059(1)	0.524(2)	6.0(5)
C(10A)	0.173(1)	0.222(1)	0.558(2)	4.8(5)
C(10B)	0.790(1)	0.2919(10)	0.924(1)	2.7(4)
C(11A)	0.274(1)	0.319(1)	0.768(2)	3.4(5)
C(11B)	0.726(1)	0.180(1)	0.726(2)	4.2(6)
C(12A)	0.220(1)	0.3794(10)	0.340(1)	3.3(4)
C(12B)	0.513(1)	0.1567(9)	0.802(1)	3.2(4)
C(13A)	0.180(1)	0.4033(10)	0.218(1)	3.2(4)
C(13B)	0.413(1)	0.141(1)	0.812(2)	3.8(5)
C(14A)	0.077(1)	0.412(1)	0.176(1)	4.4(5)
C(14B)	0.404(1)	0.1175(10)	0.928(2)	3.8(5)
C(15A)	0.020(1)	0.402(1)	0.262(2)	4.2(5)
C(15B)	0.493(1)	0.1148(10)	1.032(1)	3.7(4)
C(16A)	0.069(1)	0.3810(9)	0.385(1)	2.7(4)
C(16B)	0.592(1)	0.1329(9)	1.012(1)	3.0(4)
C(17A)	0.013(1)	0.3712(9)	0.481(2)	3.3(4)
C(17B)	0.694(1)	0.1333(8)	1.115(1)	2.1(4)
C(18A)	-0.088(1)	0.3814(10)	0.462(1)	4.2(5)
C(18B)	0.701(1)	0.1106(10)	1.237(1)	3.7(4)
C(19A)	-0.132(1)	0.375(1)	0.559(2)	4.7(5)
C(19B)	0.799(1)	0.115(1)	1.322(2)	5.5(5)
C(20A)	-0.068(1)	0.359(1)	0.674(2)	4.5(5)
C(20B)	0.888(1)	0.137(1)	1.287(2)	5.8(5)
C(21A)	0.037(1)	0.3515(10)	0.691(1)	3.9(5)
C(21B)	0.877(1)	0.156(1)	1.162(2)	4.1(5)

3d. Comparing these spectral data with those reported [9,10], 3d and 3e were deduced to be (dicarbonyl)(diamine)-2-ferracyclopent-4-en-1-one.

## 2.2. Structure of the complex 3d

To elucidate the precise structure of the (dicarbonyl)(diamine)-2-ferracyclopent-4-en-1-one, X-ray analysis of 3d was performed. The molecular geometry and atom numbering system of 3d (molecule A) are shown in Fig. 1, and Tables 2–4 summarize the results obtained. The crystal contains two independent molecules (A and B) in a unit cell, however, there are no major differences in their conformation other than a small rotation of the methoxy group on C(2). The results indicate that the insertion of carbon monoxide surely occurred between the carbene carbon and the iron atom in 1. The structure of 3d was a 2-ferracyclopent-4-en-1-one with octahedral iron(II) as expected from the spectral data. The five atoms of the ferracyclopentenone ring lie on a plane, with the mean deviation from the least-squares plane being 0.0085 (molecule A) and

0.0204 Å (molecule B) respectively. The Fe(1)–C(1), C(1)–C(2), C(2)–C(3), C(3)–C(4) and Fe(1)–C(4) lengths for A and B are 1.93(1) and 1.95(1), 1.48(2) and 1.48(2), 1.30(2) and 1.33(2), 1.50(2) and 1.50(2), 2.07(1) and 2.07(1) Å respectively. The short C(2)–C(3) bond lengths show that the  $\pi$ -electrons are localized on C(2) = C(3). The acyl group and one of the bipyridyl nitrogen were in *trans* configuration. The two carbonyl groups were in *cis* configuration and the planes of the cyclopentenone and the 2,2'-bipyridyl were perpendicular. 2,2'-Bipyridyl coordinated to the iron avoiding the steric hindrance between the methoxycarbonyl group.

## 2.3. General discussion

In the reaction of 1 with tertiary phosphines and/or carbon monoxide, a  $\eta^4$ -vinylketene (or  $\eta^3$ : $\eta^1$ -allylacyl) complex was formed in the first stage and further reaction of the  $\eta^4$ -vinylketene complex with tertiary phosphine or carbon monoxide gave ferracyclopentenone complexes (Scheme 1) [9,10].

Although the corresponding intermediate  $\eta^4$ -

Table 4  
Selected bond lengths (Å) and angles (deg) for 3d

Fe(1A)–N(1A)	2.03(1)	Fe(1B)–N(1B)	2.01(1)
Fe(1A)–N(2A)	2.01(1)	Fe(1B)–N(2B)	2.02(1)
Fe(1A)–C(1A)	1.93(1)	Fe(1B)–C(1B)	1.95(1)
Fe(1A)–C(4A)	2.07(1)	Fe(1B)–C(4B)	2.07(1)
Fe(1A)–C(10A)	1.79(2)	Fe(1B)–C(10B)	1.79(1)
Fe(1A)–C(11A)	1.78(2)	Fe(1B)–C(11B)	1.73(2)
C(1A)–C(2A)	1.48(2)	C(1B)–C(2B)	1.48(2)
C(2A)–C(3A)	1.30(2)	C(2B)–C(3B)	1.33(2)
C(3A)–C(4A)	1.50(2)	C(3B)–C(4B)	1.50(2)
C(1A)–O(1A)	1.23(1)	C(1B)–O(1B)	1.23(2)
C(10A)–O(7A)	1.15(2)	C(10B)–O(7B)	1.14(1)
C(11A)–O(8A)	1.14(2)	C(11B)–O(8B)	1.16(2)
N(1A)–Fe(1A)–N(2A)	78.0(5)	N(1B)–Fe(1B)–N(2B)	79.3(5)
N(1A)–Fe(1A)–C(1A)	169.9(6)	N(1B)–Fe(1B)–C(1B)	170.6(6)
N(1A)–Fe(1A)–C(4A)	90.6(5)	N(1B)–Fe(1B)–C(4B)	90.2(5)
N(1A)–Fe(1A)–C(10A)	94.7(6)	N(1B)–Fe(1B)–C(10B)	96.0(5)
N(1A)–Fe(1A)–C(11A)	101.9(6)	N(1B)–Fe(1B)–C(11B)	99.4(7)
N(2A)–Fe(1A)–C(1A)	93.3(5)	N(2B)–Fe(1B)–C(1B)	93.3(6)
N(2A)–Fe(1A)–C(4A)	85.2(5)	N(2B)–Fe(1B)–C(4B)	85.6(5)
N(2A)–Fe(1A)–C(10A)	93.7(7)	N(2B)–Fe(1B)–C(10B)	93.6(6)
N(2A)–Fe(1A)–C(11A)	176.2(7)	N(2B)–Fe(1B)–C(11B)	172.9(7)
C(1A)–Fe(1A)–C(4A)	83.5(6)	C(1B)–Fe(1B)–C(4B)	83.4(6)
C(1A)–Fe(1A)–C(10A)	90.9(7)	C(1B)–Fe(1B)–C(10B)	90.3(7)
C(1A)–Fe(1A)–C(11A)	86.4(6)	C(1B)–Fe(1B)–C(11B)	87.1(7)
C(4A)–Fe(1A)–C(10A)	174.2(7)	C(4B)–Fe(1B)–C(10B)	173.5(6)
C(4A)–Fe(1A)–C(11A)	90.9(7)	C(4B)–Fe(1B)–C(11B)	87.5(7)
C(10A)–Fe(1A)–C(11A)	90.2(8)	C(10B)–Fe(1B)–C(11B)	93.4(8)
Fe(1A)–C(1A)–C(2A)	113.2(10)	Fe(1B)–C(1B)–C(2B)	112(1)
Fe(1A)–C(1A)–O(1A)	127(1)	Fe(1B)–C(1B)–O(1B)	126(1)
C(1A)–C(2A)–C(3A)	118(1)	C(1B)–C(2B)–C(3B)	118(1)
C(2A)–C(3A)–C(4A)	116(1)	C(2B)–C(3B)–C(4B)	115(1)
Fe(1A)–C(4A)–C(3A)	108.6(9)	Fe(1B)–C(4B)–C(3B)	109(1)
Fe(1A)–C(10A)–O(7A)	173(1)	Fe(1B)–C(10B)–O(7B)	174(1)
Fe(1A)–C(11A)–O(8A)	178(1)	Fe(1B)–C(11B)–O(8B)	175(1)

vinylketene complex could not be isolated, the reaction is reasonably explained to proceed via an unstable  $\eta^4$ -vinylketene complex with mono-coordinated bidentate amine (Scheme 2). The coordination of the amine to the iron as a bidentate ligand induces the dissociation of the olefinic group to give the 2-ferracyclopent-4-en-1-one complexes **3d** and **3e**.

Reaction of the complex **1** with monodentate aromatic amines such as pyridine was attempted. No reaction was observed even in the presence of an excess amount of pyridine. The complex **1** reacted with aliphatic tertiary amines, such as triethylamine and *N,N,N',N'*-tetramethylethylenediamine to give yellow products. The spectral data of the products showed that methylation of the amine occurred to give the ammonium salt of ( $\eta^3$ -acryloyl)tricarbonylironate [1]. The reaction of complex **1** with bidentate phosphines such as diphenylphosphinoethane gave a complicated mixture of several complexes.

The present results suggest that the coordination of one of the amino groups of the bidentate aromatic amine to the  $\pi$ -vinylcarbene complex induces the insertion of a carbonyl group between the carbene carbon and iron, and further coordination of the other amino group to form a chelate, and stabilizes the complex as 2-ferracyclopent-4-en-1-one.

### 3. Experimental section

#### 3.1. General comments

All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques. Dichloromethane and 1,2-dichloroethane were distilled from  $\text{CaCl}_2$ ; diethyl ether was distilled from benzophenone ketyl; *n*-hexane and toluene were distilled from sodium. A  $\pi$ -vinylcarbene iron complex **1** was prepared by the literature method [1]. Other reagents were used as obtained from commercial sources. Melting points were determined under air on a Yanagimoto micro-melting point apparatus. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer and calibrated with a polystyrene standard.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained on a JEOL GSX-270 or a JEOL EX-400 spectrometer.

#### 3.2. Synthesis of **3d**

To a solution of **1** (0.50 g, 1.5 mmol) in toluene (12 ml) was added 0.24 g (1.5 mmol) of 2,2'-bipyridyl, and then the mixture was stirred at room temperature for 4 h. After evaporation of the solvent, the residue was recrystallized from dichloromethane–diethyl ether (1:13) to give orange crystals of a ferracyclopentenone complex **3d** (0.33 g, 0.68 mmol, 45%). M.p. 154.5–155.0 °C.

IR (KBr):  $\nu(\text{FeCO})$  2008 (vs), 1946 (vs),  $\nu(\text{C}=\text{O}$  ester) 1728 (m),  $\nu(\text{C}=\text{O}$  acyl) 1682 (m),  $\nu(\text{C}=\text{C})$  1595 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.75–7.42 (m, 8H, bipy.), 3.94, 3.65 (s, 3H,  $\text{CO}_2\text{Me}$ ), 3.41 (s, 3H, OMe), 1.79 (s, 1H, CH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  270.2 (s,  $\text{FeC}=\text{O}$ ), 213.4, 204.4 (s,  $\text{FeCO}$ ), 179.9 (s, COMe), 167.4, 164.9 (s,  $\text{CO}_2\text{Me}$ ), 153.7–120.8 (m, bipy.), 137.7 (s,  $\text{CCO}_2\text{Me}$ ), 60.1 (q, OMe,  $^1J_{\text{CH}} = 146.7\text{ Hz}$ ), 51.1, 49.9 (q,  $\text{CO}_2\text{Me}$ ,  $^1J_{\text{CH}} = 146.7\text{ Hz}$ ), 45.6 (d, CH,  $^1J_{\text{CH}} = 140.9\text{ Hz}$ ). Anal. Found: C, 52.52; H, 3.76; N, 5.79.  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_4\text{Fe}$  Calc.: C, 52.31; H, 3.76; N, 5.81%.

#### 3.3. Synthesis of **3e**

To a solution of **1** (0.19 g, 0.58 mmol) in 1,2-dichloroethane (6 ml) was added 0.13 g (0.70 mmol) of 1,10-phenanthroline, and then the mixture was stirred at room temperature for 4 h. After evaporation of the solvent, the residue was recrystallized from 1,2-dichloroethane–*n*-hexane (1:10) to give orange crystals of a ferracyclopentenone complex **3e** (0.23 g, 0.46 mmol, 80%). M.p. 160–161 °C (decomp.). IR (KBr):  $\nu(\text{FeCO})$  2019 (vs), 1942 (vs),  $\nu(\text{C}=\text{O}$  ester) 1701 (m), 1685 (m),  $\nu(\text{C}=\text{O}$  acyl) 1680 (m),  $\nu(\text{C}=\text{C})$  1593 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  9.20–7.66 (m, 8H phen.),  $\delta$  3.99, 3.60 (s, 3H,  $\text{CO}_2\text{Me}$ ),  $\delta$  3.42 (s, 3H, OMe),  $\delta$  1.73 (s, 1H, CH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  269.9 (s,  $\text{FeC}=\text{O}$ ), 213.7, 204.8 (s,  $\text{FeCO}$ ), 179.9 (s, COMe), 167.3, 164.4 (s,  $\text{CO}_2\text{Me}$ ), 156.7–124.6 (m, phen.), 138.6 (s,  $\text{CCO}_2\text{Me}$ ), 60.1 (q, OMe,  $^1J_{\text{CH}} = 146.7\text{ Hz}$ ), 51.4 (q,  $\text{CO}_2\text{Me}$ ,  $^1J_{\text{CH}} = 146.7\text{ Hz}$ ), 50.3 (q,  $\text{CO}_2\text{Me}$ ,  $^1J_{\text{CH}} = 143.8\text{ Hz}$ ), 44.5 (d, CH,  $^1J_{\text{CH}} = 137.9\text{ Hz}$ ).

#### 3.4. X-ray structure determination of **3d**

The crystal data and experimental details for **3d** are summarized in Table 2. Diffraction data for **3d** were obtained with a Rigaku AFC-7R. The reflection intensities were monitored by three standard reflections every 150 measurements. Reflection data were corrected for Lorentz and polarization effects. Absorption corrections were empirically applied.

The structures were solved by direct methods using SIR88 [14], and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Hydrogen atoms were included, but their positions were not refined; isotropic *B* values were refined. Atomic scattering factors and anomalous dispersion terms were taken from the literature [15]. The final *R* and *R<sub>w</sub>* values were 0.069 and 0.053. The calculations were performed on an IRIS Indigo computer using the program system teXsan [16].

The final atomic parameters for non-hydrogen atoms are given in Table 3, and selected bond lengths and angles are summarized in Table 4.

## References

- [1] T. Mitsudo, H. Nakanishi, T. Inubushi, I. Morishima, Y. Watanabe and Y. Takegami, *J. Chem. Soc., Chem. Commun.*, (1976) 416; K. Nakatsu, T. Mitsudo, H. Nakanishi, Y. Watanabe and Y. Takegami, *Chem. Lett.*, (1977) 1447; T. Mitsudo, Y. Watanabe, H. Nakanishi, I. Morishima, T. Inubushi and Y. Takegami, *J. Chem. Soc., Dalton Trans.*, (1978) 1298.
- [2] J. Klimes and E. Weiss, *Angew. Chem.*, **94** (1982) 207; *Angew. Chem., Int. Ed. Engl.*, **21** (1982) 205; K.J. Jens and E. Weiss, *Chem. Ber.*, **117** (1984) 2469; T. Valeri, F. Meier and E. Weiss, *Chem. Ber.*, **121** (1988) 1093.
- [3] W.A. Herrmann, R.A. Fischer and E. Herdtweck, *Angew. Chem., Int. Ed. Engl.*, **26** (1987) 1284; R.A. Fischer, R.W. Fischer, W.A. Herrmann and E. Herdtweck, *Chem. Ber.*, **122** (1989) 2035.
- [4] A. Mayr, M.F. Asaro and T.J. Glines, *J. Am. Chem. Soc.*, **109** (1987) 2215; A. Mayr, M.F. Asaro, T.J. Glines, D.V. Engen and G.M. Tripp, *J. Am. Chem. Soc.*, **115** (1993) 8187.
- [5] K.E. Garrett, J.B. Sheridan, D.B. Pourteau, W.C. Feng, G.L. Geoffroy, D.L. Staley and A.L. Rheingold, *J. Am. Chem. Soc.*, **111** (1989) 8383.
- [6] S.G. Feng, A.S. Gamble and J.L. Templeton, *Organometallics*, **8** (1989) 2024.
- [7] J. Park, S. Kang, D. Whang and K. Kim, *Organometallics*, **11** (1992) 1738.
- [8] J. Barluenga, F. Aznar, A. Martín, S.G. Granda and E.P. Carrero, *J. Am. Chem. Soc.*, **116** (1994) 11191.
- [9] T. Mitsudo, H. Watanabe, T. Sasaki, Y. Takegami and Y. Watanabe, *Organometallics*, **8** (1989) 368.
- [10] T. Mitsudo, K. Fujita, S. Nagano, T. Suzuki, Y. Watanabe and H. Masuda, *Organometallics*, **14** (1995) 4228.
- [11] K. Fujita, Y. Watanabe and T. Mitsudo, *Chem. Lett.*, (1996) 513.
- [12] K.H. Dötz, *Angew. Chem., Int. Ed. Engl.*, **14** (1975) 644; *Pure Appl. Chem.*, **55** (1983) 1689; *Angew. Chem., Int. Ed. Engl.*, **23** (1984) 587; W.D. Wulff, P.C. Tang, K.S. Chan, J.S. McCallum, D.C. Yang and S.R. Gilbertson, *Tetrahedron*, **41** (1985) 5813; K.H. Dötz and M. Popall, *Tetrahedron*, **41** (1985) 5797; A. Yamashita, T. A. Scallill and A. Toy, *Tetrahedron Lett.*, **26** (1985) 2969; W.D. Wulff, S.R. Gilbertson and J.P. Springer, *J. Am. Chem. Soc.*, **108** (1986) 520; M.F. Semmelhack, R. Tamura, W. Schwaner and J.P. Springer, *J. Am. Chem. Soc.*, **106** (1984) 5363; M.F. Semmelhack and J. Park, *Organometallics*, **5** (1986) 2550; M.E. Bos, W.D. Wulff, R.A. Miller, S. Chamberlin and T.A. Brandvold, *J. Am. Chem. Soc.*, **113** (1991) 9293; W.D. Wulff, B.M. Bax, T.A. Brandvold, K.S. Chan, A.M. Gilbert, R.P. Hsung, J. Mitchell and J. Clardy, *Organometallics*, **13** (1994) 102.
- [13] P. Hofmann, M. Hämmerle and G. Unfried, *New J. Chem.*, **15** (1991) 769.
- [14] M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Cryst.*, **22** (1989) 389.
- [15] D.T. Cromer and G.T. Waber, *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974; J.A. Ibers and W.C. Hamilton, *Acta Crystallogr.*, **17** (1964) 781; D.C. Creagh and W.J. McAuley, *International Tables for X-Ray Crystallography*, Vol. C, Kluwer Academic, Boston, 1992; D.C. Creagh and J.H. Hubbell, *International Tables for X-Ray Crystallography*, Vol. C, Kluwer Academic, Boston, 1992.
- [16] teXsan, *Crystal Structure Analysis Package*, Molecular Structure Corp., 1985 and 1992.