

## Synthesis, characterization and molecular structure of an acyliron complex



Gene-Hsiang Lee, Shie-Ming Peng \*

*Department of Chemistry, National Taiwan University, Taipei, Taiwan*

Shie-Fu Lush and Rai-Shung Liu \*

*Department of Chemistry, National Tsing Hua University Hsinchu, Taiwan*

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### Abstract

The complexes  $\text{CpFe}(\text{CO})_2\text{CH}_2\text{CHCHCOOCOCHCHRCH}=\text{CH}$  (R = H (1), R = CH<sub>3</sub> (2)) undergo CO insertion in presence of excess PPh<sub>3</sub> to give the acyl complexes  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2\text{CHCHCOOCOCHCHRCH}=\text{CH})$  (R = H (3), R = CH<sub>3</sub> (4)) as two diastereoisomers *RR(SS)*, *RS(SR)* in good yield. These carbonylation products have been fully characterized from their IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra and their elemental analyses. The molecular structure of 4 has been determined by an X-ray diffraction study; crystallographic data: space group *C*<sub>2/c</sub>, *a* 25.568(4) Å, *b* 9.485(1) Å, *c* 25.34(2) Å, β 103.01(3)°, *Z* = 8, *R* 4.8%, *R*<sub>w</sub> 4.4%.

### Introduction

Recently, we have reported the synthesis of the transition-metal pentadienyl complexes  $\text{M}(\eta^1\text{-pentadienyl})$  (M = CpMo(CO)<sub>3</sub>, CpFe(CO)<sub>2</sub>, Mn(CO)<sub>5</sub>) [1–3]. These complexes were shown to undergo [4 + 2] cycloaddition with reactive alkenes such as tetracyanoethylene and maleic anhydride [4]. Previously, only the [4 + 2] cycloaddition and electrophilic reaction of pentadienylmetal complexes of main group compounds such as ( $\eta^1\text{-2,4-pentadienyl}$ )MMe<sub>3</sub> (M = Si, Sn) were studied [5,6]. Metal–carbon bonds of many transition metal complexes are known to undergo carbonylation and insertion with many unsaturated organic substrates, and thus can be of great value. In an attempt to expand the chemistry of transition-metal  $\eta^1\text{-pentadienyl}$  complexes here we report on the carbonylation of the [4 + 2] adducts  $\text{CpFe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CHCHCOOCOCHCHRCH}=\text{CH})$  (R = H (1); CH<sub>3</sub> (2)) and on

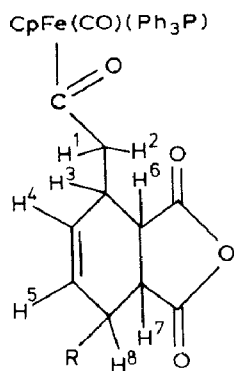
the structure resulting from this reaction. The preparation of **1** and **2** has been described previously [4].

## Results and discussion

Reflux of a benzene solution of **1** and **2** with excess  $\text{PPh}_3$  produced the acyl compounds **3** and **4** in high yields. Orange crystals of analytical purity were isolated from a saturated tetrahydrofuran solution at  $-25^\circ\text{C}$ . The structure depicted is consistent with its spectroscopic data. A single absorption band at  $1910\text{ cm}^{-1}$  was observed in the  $1800\text{--}2200\text{ cm}^{-1}$  region, indicative of a single terminal CO group [7]. The proton resonances of  $\text{H}^1$  and  $\text{H}^2$  show an ABX pattern within  $\delta\ 3.10\text{--}4.10$  ppm and the  $^{13}\text{C}$  NMR resonances of  $\text{CH}^1\text{H}^2$  were observed at  $\delta\ 65\text{--}66$  ppm. This suggests that CO has been inserted into the  $\sigma\text{-Fe-CH}^1\text{H}^2$  bond. The presence of an acyl group was further indicated by an IR absorption peak at  $1590\text{ cm}^{-1}$ , and  $^{13}\text{C}$  NMR resonances of a doublet at  $272\text{--}273$  ppm ( $J(\text{PC})\ 21$  Hz) [8,9]. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data reveal that these two acyl complexes exist as two diastereoisomers because of the chiral centers at Fe and  $\text{CH}^3$  carbon. The chiral center at the  $\text{CH}^3$  carbon has no significant effect on product diastereoselectivity and the intensities of the proton resonances of the two diastereoisomers are almost equal. Assignment of the  $RR(SS)$  and  $RS(SR)$  configurations to these proton NMR resonances is based on the X-ray crystallography carried out on the  $RR$  isomer. The dihedral angles  $\phi$  between the hydrogen positions  $\text{H}^1$ ,  $\text{H}^2$  and  $\text{H}^3$  along the  $\text{C}(7)\text{--C}(8)$  axis provide the coupling constants  $J(\text{H}^1\text{H}^3)$  and  $J(\text{H}^2\text{H}^3)$  derived from the Karplus equation [10]:

$$J(\text{HH}) = 7 - \cos \phi + 5 \cos 2\phi$$

The calculated values  $J_{13}\ 10.9\text{--}11.0$  Hz  $J_{23}\ 2.8\text{--}4.0$  Hz ( $\phi\ 002(6)^\circ$  and  $115(5)^\circ$ , respectively) are fairly consistent with the observed values  $J_{13}\ 10.0$  Hz and  $J_{23}\ 3.2$  Hz in the proton resonances of one of the isomers. The other isomer with  $J_{13}\ 7.1$  Hz and  $J_{23}\ 6.8$  Hz was therefore assigned to the  $RS(SR)$  configuration. For **3**, the major isomer was found to be the  $RR(SS)$  form with an intensity ratio,  $RR/RS$  of



(**3**:  $\text{R} = \text{H}^9$  ;  
**4**:  $\text{R} = \text{CH}_3$  )

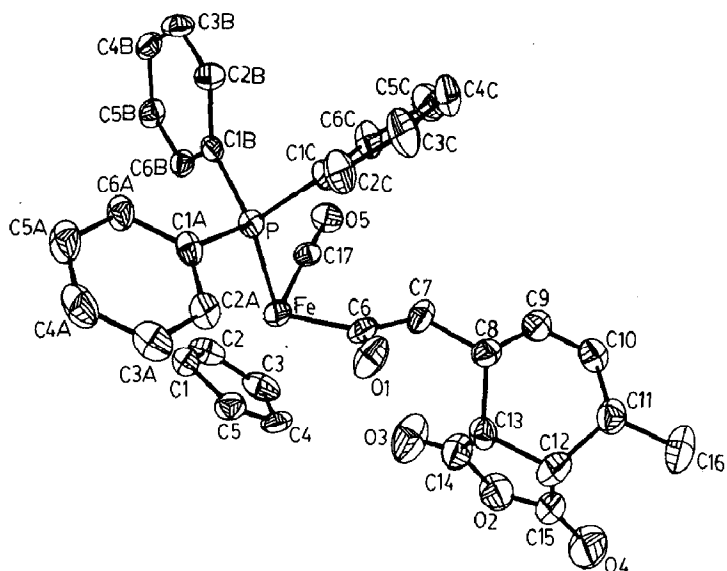


Fig. 1. Molecular structure of complex **4**.

52/48. However, for **4**, the major isomer was found to be the *RS(SR)* form with an intensity ratio of 55/45. For the *RR(SS)* forms of both **3** and **4**, the methylene protons  $\text{CH}^1\text{H}^2$  showed the greater separation in their chemical shifts, and the higher field hydrogen showed a smaller coupling constant with the methine proton than the lower field methylene proton. In contrast, the *RS(SR)* configuration, characterized by a smaller separation in the chemical shifts of the methylene protons, has a reversed magnitude of vicinal coupling constants to the higher and lower field methylene hydrogen. Attempts to separate the isomers by fractional crystallization and column chromatography were unsuccessful.

An X-ray diffraction study of **4** has been undertaken. The single crystals were grown from an ethereal solution containing nearly equal amounts of the two diastereoisomers. The ORTEP drawing is depicted in Fig. 1, and the bond distances, angles and atomic coordinates are given in Table 1 and 2 respectively. The configuration of the molecule is *RR*, with respect to the iron center and C(8) carbon. The coordination geometry about the iron atom is approximately a distorted tetrahedron with one carbonyl, one  $\alpha$ -carbon, one phosphine and a Cp group occupying the four coordination sites. The L–Fe–L angles are  $127.8(4)^\circ$ ,  $126.4(4)^\circ$ ,  $117.7(4)^\circ$ ,  $90.1(3)^\circ$ ,  $92.1(3)^\circ$ ,  $93.2(4)^\circ$  for Cp–Fe–P, Cp–Fe–C(17), Cp–Fe–C(6), P–Fe–C(17), P–Fe–C(6), C(17)–Fe–C(6), respectively, Cp is the centroid of the cyclopentadienyl group. The iron atom is in a site of  $C_1$  symmetry. The C(6)–O(1) bond lies in the position *endo* to the C(17)–O(5) bond. The Fe–C(6) bond (1.96(1) Å) is shorter than the Fe–C bond (2.062(3) Å) of the parent complex **2** [4], but the C(6)–O(1) bond length (1.216(11) Å) is consistent with the normal C=O bond distance [11]. In the bicyclic  $\text{C}_{10}\text{H}_{11}\text{O}_3$  group, three bonds, C(9)–C(10), C(14)–O(3) and C(15)–O(14) are double bonds (1.295(10), 1.191(14), 1.193(13) Å, respectively), and the rest are single bonds. The atoms C(8), C(9), C(10) and C(11) are coplanar with a maximum deviation of 0.018(14) Å. The atoms C(8), C(13), C(12) and C(11) also form a plane with a maximum deviation of 0.032(14) Å. The dihedral angles between various planes are listed in Table 3. The 6-membered ring of the cyclohe-

Table 1

Bond lengths (Å) and bond angles (°)

<i>Bond lengths (Å)</i>			
Fe–P	2.198(3)	C(3C)–C(4C)	1.361(15)
Fe–C(1)	2.124(10)	C(4C)–C(5C)	1.356(15)
Fe–C(2)	2.139(11)	C(5C)–C(6C)	1.383(14)
Fe–C(3)	2.086(9)	C(1)–C(2)	1.381(13)
Fe–C(4)	2.106(9)	C(1)–C(5)	1.405(14)
Fe–C(5)	2.088(9)	C(2)–C(3)	1.391(15)
Fe–C(6)	1.964(10)	C(3)–C(4)	1.393(15)
Fe–C(17)	1.705(9)	C(4)–C(5)	1.379(13)
P–C(1A)	1.825(8)	C(6)–C(7)	1.509(13)
P–C(1B)	1.815(9)	C(6)–O(1)	1.216(11)
P–C(1C)	1.836(9)	C(7)–C(8)	1.523(14)
C(1A)–C(2A)	1.378(12)	C(8)–C(9)	1.508(14)
C(1A)–C(6A)	1.404(12)	C(8)–C(13)	1.521(13)
C(2A)–C(3A)	1.372(13)	C(9)–C(10)	1.295(14)
C(3A)–C(4A)	1.366(15)	C(10)–C(11)	1.487(14)
C(4A)–C(5A)	1.364(15)	C(11)–C(12)	1.521(15)
C(5A)–C(6A)	1.406(13)	C(11)–C(16)	1.520(15)
C(1B)–C(2B)	1.379(12)	C(12)–C(13)	1.568(14)
C(1B)–C(6B)	1.393(13)	C(12)–C(15)	1.471(15)
C(2B)–C(3B)	1.367(13)	C(13)–C(14)	1.469(14)
C(3B)–C(4B)	1.366(14)	C(14)–O(2)	1.377(12)
C(4B)–C(5B)	1.386(13)	C(14)–O(3)	1.191(14)
C(5B)–C(6B)	1.365(13)	C(15)–O(2)	1.388(15)
C(1C)–C(2C)	1.398(13)	C(15)–O(4)	1.193(13)
C(1C)–C(6C)	1.340(12)	C(17)–O(5)	1.174(11)
C(2C)–C(3C)	1.368(14)		
<i>Bond angles (°)</i>			
P–Fe–C(1)	94.8(3)	P–C(1C)–C(2C)	122.6(7)
P–Fe–C(2)	118.0(3)	P–C(1C)–C(6C)	119.1(7)
P–Fe–C(3)	156.3(3)	C(2C)–C(1C)–C(6C)	118.3(8)
P–Fe–C(4)	142.7(3)	C(1C)–C(2C)–C(3C)	120.6(9)
P–Fe–C(5)	106.2(3)	C(2C)–C(3C)–C(4C)	119.9(9)
P–Fe–C(6)	92.1(3)	C(3C)–C(4C)–C(5C)	119.9(9)
P–Fe–C(17)	90.1(3)	C(4C)–C(5C)–C(6C)	120.2(9)
C(1)–Fe–C(2)	37.8(4)	C(1C)–C(6C)–C(5C)	121.1(9)
C(1)–Fe–C(3)	63.9(4)	Fe–C(1)–C(2)	71.7(6)
C(1)–Fe–C(4)	64.5(4)	Fe–C(1)–C(5)	69.2(6)
C(1)–Fe–C(5)	39.0(4)	C(2)–C(1)–C(5)	108.3(8)
C(1)–Fe–C(6)	135.2(4)	Fe–C(2)–C(1)	70.5(6)
C(1)–Fe–C(17)	130.9(4)	Fe–C(2)–C(3)	68.7(6)
C(2)–Fe–C(3)	38.4(4)	C(1)–C(2)–C(3)	106.9(9)
C(2)–Fe–C(4)	64.8(4)	Fe–C(3)–C(2)	72.8(6)
C(2)–Fe–C(5)	64.6(4)	Fe–C(3)–C(4)	71.4(6)
C(2)–Fe–C(6)	147.4(4)	C(2)–C(3)–C(4)	109.5(8)
C(2)–Fe–C(17)	98.5(4)	Fe–C(4)–C(3)	69.8(5)
C(3)–Fe–C(4)	38.8(4)	Fe–C(4)–C(5)	70.1(5)
C(3)–Fe–C(5)	64.5(4)	C(3)–C(4)–C(5)	106.9(8)
C(3)–Fe–C(6)	110.3(4)	Fe–C(5)–C(1)	71.9(5)
C(3)–Fe–C(17)	96.3(4)	Fe–C(5)–C(4)	71.5(5)
C(4)–Fe–C(5)	38.4(4)	C(1)–C(5)–C(4)	108.4(8)
C(4)–Fe–C(6)	83.9(4)	Fe–C(6)–C(7)	118.7(7)
C(4)–Fe–C(17)	127.1(4)	Fe–C(6)–O(1)	122.5(7)
C(5)–Fe–C(6)	96.8(4)	C(7)–C(6)–O(1)	118.6(9)

Table 1 (continued)

<i>Bond angles (°)</i>			
C(5)–Fe–C(17)	160.5(4)	C(6)–C(7)–C(8)	120.4(8)
C(6)–Fe–C(17)	93.2(4)	C(7)–C(8)–C(9)	113.4(8)
Fe–P–C(1A)	114.5(3)	C(7)–C(8)–C(13)	113.6(9)
Fe–P–C(1B)	115.5(3)	C(9)–C(8)–C(13)	108.8(7)
Fe–P–C(1C)	115.4(3)	C(8)–C(9)–C(10)	121.1(9)
C(1A)–P–C(1B)	103.2(4)	C(9)–C(10)–C(11)	117.3(9)
C(1A)–P–C(1C)	105.4(4)	C(10)–C(11)–C(12)	110.6(8)
C(1B)–P–C(1C)	101.2(4)	C(10)–C(11)–C(16)	110.8(9)
P–C(1A)–C(2A)	119.3(7)	C(12)–C(11)–C(16)	113.8(9)
P–C(1A)–C(6A)	121.3(7)	C(11)–C(12)–C(13)	113.9(8)
C(2A)–C(1A)–C(6A)	119.1(8)	C(11)–C(12)–C(15)	112.9(8)
C(1A)–C(2A)–C(3A)	122.3(9)	C(13)–C(12)–C(15)	103.2(8)
C(2A)–C(3A)–C(4A)	118.7(9)	C(8)–C(13)–C(12)	112.0(8)
C(3A)–C(4A)–C(5A)	120.9(9)	C(8)–C(13)–C(14)	113.7(8)
C(4A)–C(5A)–C(6A)	121.3(9)	C(12)–C(13)–C(14)	103.3(8)
C(1A)–C(6A)–C(5A)	117.6(9)	C(13)–C(14)–O(2)	112.5(9)
P–C(1B)–C(2B)	123.0(7)	C(13)–C(14)–O(3)	130.3(10)
P–C(1B)–C(6B)	120.0(6)	O(2)–C(14)–O(3)	117.2(10)
C(2B)–C(1B)–C(6B)	117.0(8)	C(12)–C(15)–O(2)	112.0(8)
C(1B)–C(2B)–C(3B)	121.7(9)	C(12)–C(15)–O(4)	130.5(11)
C(2B)–C(3B)–C(4B)	120.5(8)	O(2)–C(15)–O(4)	117.5(11)
C(3B)–C(4B)–C(5B)	119.3(8)	Fe–C(17)–O(5)	178.9(7)
C(4B)–C(5B)–C(6B)	119.8(9)	C(14)–O(2)–C(15)	108.6(8)
C(1B)–C(6B)–C(5B)	121.7(8)		

xene moiety is approximately in a boat configuration with the atoms C(9), C(10), C(13) and C(12) forming a basal plane with a maximum deviation of 0.034(14) Å. The C(8) and C(11) atoms lie 0.583(16) Å and 0.539(16) Å above this plane respectively. The C(8) and C(16) atoms occupy the two equatorial positions to avoid the steric hinderance that would be imposed at the two axial positions. The anhydride plane lies toward the C(9)–C(10) double bond and to *cis* to the C(7) and C(16) atoms.

Although carbon–hydrogen distances are underestimated by X-ray diffraction studies, fairly accurate angles involving hydrogen can be obtained [12]. In order to test the accuracy of predicting the hydrogen position from the skeletal carbon structure, the expected hydrogen positions were also calculated by use of the C–C–C angles on the assumption a H–C–H angle of 109.5°. The calculated positions only differed by an average of 0.17(9) Å from the refined positions. The latter was used for assignment of the absolute configuration of the diastereoisomers.

## Experimental

All reactions were carried out under dry nitrogen using Schlenk-tube techniques. The solvents diethyl ether, benzene, tetrahydrofuran and pentane were dried with sodiumbenzophenone and distilled before use. The synthesis of compounds **1** and **2** has been described previously [4]. NMR spectra were recorded on either a JEOL FX-100 or a Bruker AM-400 spectrometer. Microanalysis were performed by the microanalytic laboratory at the National Taiwan University, Taipei.

Table 2

Atomic parameters ( $x$ ,  $y$ ,  $z$ ) and  $B_{\text{iso}}$ . Esd's refer to the last digit

	$x$	$y$	$z$	$B_{\text{iso}}^a$
Fe	0.45927(5)	0.10870(16)	0.10509(5)	3.82(6)
P	0.37794(9)	0.1692(3)	0.06172(10)	3.27(12)
C(1A)	0.3247(3)	0.1099(10)	0.0938(4)	3.6(4)
C(2A)	0.3265(3)	0.1470(10)	0.1467(4)	4.1(5)
C(3A)	0.2892(4)	0.1002(12)	0.1741(4)	5.3(6)
C(4A)	0.2504(4)	0.0087(12)	0.1487(4)	5.7(6)
C(5A)	0.2477(4)	-0.0330(11)	0.0966(4)	5.6(6)
C(6A)	0.2843(3)	0.0178(10)	0.0672(4)	4.3(5)
C(1B)	0.3569(3)	0.1021(9)	-0.0069(3)	3.2(4)
C(2B)	0.3163(3)	0.1628(10)	-0.0454(4)	4.2(5)
C(3B)	0.2999(3)	0.1068(11)	-0.0961(4)	4.7(5)
C(4B)	0.3227(4)	-0.0139(11)	-0.1099(4)	4.6(5)
C(5B)	0.3642(4)	-0.0762(10)	-0.0725(4)	4.5(5)
C(6B)	0.3809(3)	-0.0184(10)	-0.0222(4)	3.8(5)
C(1C)	0.3668(3)	0.3592(9)	0.0505(3)	3.5(4)
C(2C)	0.3319(4)	0.4364(10)	0.0746(4)	5.3(6)
C(3C)	0.3261(4)	0.5787(11)	0.0665(5)	6.4(7)
C(4C)	0.3536(4)	0.6454(10)	0.0335(4)	5.9(6)
C(5C)	0.3880(4)	0.5716(11)	0.0105(4)	5.7(6)
C(6C)	0.3938(4)	0.4277(10)	0.0187(4)	4.7(6)
C(1)	0.4357(4)	-0.0896(11)	0.1310(4)	4.7(5)
C(2)	0.4798(4)	-0.1103(12)	0.1088(4)	5.7(6)
C(3)	0.5213(4)	-0.0293(12)	0.1389(4)	6.1(6)
C(4)	0.5039(4)	0.0380(11)	0.1807(4)	5.5(6)
C(5)	0.4505(4)	0.0035(11)	0.1750(4)	4.7(6)
C(6)	0.4732(3)	0.2965(11)	0.1379(3)	4.3(5)
C(7)	0.5173(4)	0.3850(12)	0.1241(4)	5.9(6)
C(8)	0.5436(4)	0.5023(11)	0.1620(4)	4.7(5)
C(9)	0.5814(4)	0.5925(12)	0.1386(4)	5.6(6)
C(10)	0.6108(4)	0.6880(11)	0.1675(4)	5.3(6)
C(11)	0.6033(4)	0.7111(11)	0.2233(4)	5.5(6)
C(12)	0.6042(4)	0.5714(12)	0.2531(4)	5.4(6)
C(13)	0.5730(4)	0.4499(10)	0.2174(4)	4.8(5)
C(14)	0.6151(4)	0.3459(12)	0.2155(4)	6.6(7)
C(15)	0.6587(5)	0.5132(13)	0.2712(4)	7.3(7)
C(16)	0.6432(5)	0.8187(13)	0.2532(5)	8.3(8)
C(17)	0.4834(3)	0.1534(10)	0.0499(3)	3.7(5)
O(1)	0.44995(25)	0.3407(8)	0.1714(3)	6.3(4)
O(2)	0.6644(3)	0.3858(9)	0.2460(3)	7.6(5)
O(3)	0.6124(3)	0.2346(9)	0.1933(4)	10.9(6)
O(4)	0.6971(3)	0.5592(10)	0.3020(4)	11.1(6)
O(5)	0.5009(3)	0.1844(7)	0.01244(25)	5.3(4)

<sup>a</sup>  $B_{\text{iso}}$  is the mean of the principal axes of the thermal ellipsoid.*Preparation of CpFe(CO)(PPh<sub>3</sub>)(COCH<sub>2</sub>CHCHCOOCOCHCH<sub>2</sub>CH=CH) (3)*

Triphenylphosphine (0.52 g, 0.20 mmol) was added to **2** (0.34 g, 0.10 mmol) in 20 ml benzene. The solution was then refluxed under argon for 4 h. After evaporation of the solvent, the residues were extracted with ether/tetrahydrofuran (5/1). The extract was reduced to a saturated solution and cooled at  $-25^\circ\text{C}$  to give an orange crystalline solid (0.46 g,  $7.6 \times 10^{-2}$  mmol). Found: C, 67.01; H, 4.40.  $\text{C}_{34}\text{H}_{29}\text{FePO}_5$

Table 3

Deviation from the least-squares plane

	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)
Plane 1	0.008(15)	-0.018(14)	0.016(13)	-0.008(15)		
Plane 2	-0.018(15)			0.017(15)	-0.032(14)	0.026(13)
Plane 3		-0.034(14)	0.013(14)		-0.028(15)	0.023(13)

Dihedral angles between plane A and B

Plane	A	B	Angle (°)
	1	2	49.0(6)
	1	3	25.4(5)
	2	3	23.7(5)

Equation of plane AX + BY + CZ = D

Plane	A	B	C	D
1	17.10(14)	-6.29(4)	4.49(19)	6.86(8)
2	23.09(6)	-2.40(6)	-13.71(15)	9.14(6)
3	22.32(8)	-4.62(5)	-5.26(13)	9.54(9)

calcd.: C, 67.55; H, 4.80%. IR (Nujol):  $\nu(\text{CO})$  1912(s), 1768(s), 1585(m)  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{C})$  1648  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ): major species,  $\delta$  1.28 (m, 1H,  $\text{H}^9$ ), 2.12 (m, 1H,  $\text{H}^8$ ), 2.21 (m, 1H,  $\text{H}^3$ ), 2.38 (dd, 1H,  $\text{H}^7$ ), 3.12 (dd, 1H,  $\text{H}^1$ ), 3.24 (dd, 1H,  $\text{H}^6$ ); 3.95 (dd, 1H,  $\text{H}^2$ ), 4.41 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.08 (m, 1H,  $\text{H}^5$ ), 5.35 (m, 1H,  $\text{H}^4$ ), 7.05, 7.70 (m, 15H,  $\text{P}(\text{C}_6\text{H}_5)_3$ ),  $J_{12}$  18.1 Hz,  $J_{13}$  10.4 Hz,  $J_{23}$  3.9 Hz,  $J_{67}$  8.7 Hz; minor species,  $\delta$  1.46 (m, 1H,  $\text{H}^9$ ), 2.21 (m, 1H,  $\text{H}^8$ ), 2.26 (m, 1H,  $\text{H}^3$ ), 2.28 (m, 1H,  $\text{H}^7$ ), 2.41 (m, 1H,  $\text{H}^6$ ), 3.45 (dd, 1H,  $\text{H}^1$ ), 3.71 (dd, 1H,  $\text{H}^2$ ), 4.17 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.38 (m, 1H,  $\text{H}^5$ ), 5.48 (m, 1H,  $\text{H}^4$ ),  $J_{12}$  17.9 Hz,  $J_{13}$  7.2 Hz,  $J_{23}$  6.4 Hz;  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ): major species, 24.0 ( $\text{CH}^8\text{H}^9$ ), 32.0 ( $\text{CH}^3$ ), 40.8, 43.4 ( $\text{CH}^6 + \text{CH}^7$ ), 65.9 (d,  $J(\text{PC})$  5 Hz,  $\text{CH}^1\text{H}^2$ ), 85.6 ( $\text{C}_5\text{H}_5$ ), 126.0, 129.3, 129.2, 132.5 ( $\text{PPh}_3$ ), 127.3, 134.2 ( $\text{CH}^4 + \text{CH}^5$ ), 174.5, 172.9 (COOCO), 221.1 (d,  $J(\text{CP})$  31 Hz, CO), 273.0 (d,  $J(\text{PC})$  20 Hz,  $\text{COCH}_2$ ).

*Synthesis of  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2\text{CHCHCOOCOCHCH}(\text{CH}_3)\text{CH}=\text{CH})$  (4)*

This complex was prepared similarly from refluxing a benzene solution of **2** with  $\text{PPh}_3$  under argon for 4 h. The yield is 56%. Found: C, 67.42; H, 4.84.  $\text{C}_{35}\text{H}_{31}\text{FePO}_5$  calcd.: C, 67.96; H, 5.10%. IR (Nujol):  $\nu(\text{CO})$  1918(s), 1769(s), 1592(s)  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{C})$  1652  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ): major species,  $\delta$  1.10 (d, 3H,  $\text{CH}_3$ ), 1.68 (m, 1H,  $\text{H}^8$ ), 2.13 (dd, 1H,  $\text{H}^7$ ), 2.30 (m, 1H,  $\text{H}^3$ ), 2.37 (dd, 1H,  $\text{H}^6$ ), 3.57 (dd, 1H,  $\text{H}^1$ ), 3.88 (dd, 1H,  $\text{H}^2$ ), 4.10 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.33 (m, 1H,  $\text{H}^4$ ), 5.55 (m, 1H,  $\text{H}^5$ ), 7.06, 7.17 (m, 15H,  $\text{PPh}_3$ ),  $J_{12}$  18.0 Hz,  $J_{13}$  7.1 Hz,  $J_{23}$  6.8 Hz,  $J_{36}$  3.5 Hz,  $J_{67}$  8.9 Hz,  $J_{8,\text{CH}_3}$  7.2 Hz; minor species,  $\delta$  1.12 (d, 3H,  $\text{CH}_3$ ), 1.47 (m, 1H,  $\text{H}^8$ ), 2.12 (m, 1H,  $\text{H}^3$ ), 2.22 (dd, 1H,  $\text{H}^7$ ), 3.25 (dd, 1H,  $\text{H}^6$ ), 3.25 (dd, 1H,  $\text{H}^2$ ), 4.04 (dd, 1H,  $\text{H}^1$ ), 4.40 (s,  $\text{C}_5\text{H}_5$ ), 5.10 (m, 1H,  $\text{H}^4$ ), 5.25 (m, 1H,  $\text{H}^5$ ), 7.00, 7.70 (m, 15H,  $\text{PPh}_3$ ),  $J_{12}$  16.5 Hz,  $J_{13}$  10.0 Hz,  $J_{23}$  3.2 Hz,  $J_{36}$  3.6 Hz,  $J_{67}$  9.0 Hz,  $J_{7,\text{CH}_3}$  7.0 Hz,  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , selected peaks): 65.90, 66.37 (d, d,  $J(\text{PC})$  5 Hz,  $\text{CH}^1\text{H}^2$ ), 171.4, 171.7, 172.6, 172.9 (COOCO), 220.8, 221.4 (d,d,  $J(\text{PC})$  31 Hz, CO), 272.1, 273.0 (d, d,  $J(\text{PC})$  20 Hz,  $\text{FeCOCH}_2$ ).

*Crystal data for*  $(C_5H_5)Fe(CO)(P(C_6H_5)_3)(COCH_2CHCHCOOCHCH(CH_3)CH=CH_2)$

$C_{35}H_{31}FePO_5$ , mol. wt. 618.23, monoclinic, space group  $C_{2/c}$ ,  $a$  25.568(4),  $b$  9.485(1),  $c$  25.34(2),  $\beta$  103.01(3)°,  $V$  5987 Å<sup>3</sup>,  $D_c$  1.372 g/cm<sup>3</sup>,  $\lambda(Mo-K_\alpha)$  0.7093 Å,  $\mu(Mo-K_\alpha) = 0.59$  mm<sup>-1</sup>,  $F(000) = 2575.66$ .

#### *Collection and reduction of X-ray data*

A yellow block-shaped crystal of dimensions 0.15 × 0.25 × 0.45 mm was coated with paraffin, sealed in a capillary tube, and used for data collection. Diffraction data were collected on a CAD4 diffractometer using graphite-monochromated Mo- $K_\alpha$  radiation. Unit cell dimensions were determined from a least-squares refinement of 25 carefully centered reflections ( $14^\circ < 2\theta < 28^\circ$ ). Intensity data within  $2\theta \leq 50^\circ$  were collected at various scan speeds of 20/15 to 20/3°/s by the  $\omega$ - $2\theta$  scan techniques, with a scan range calculated from the expression,  $0.7\theta + 0.35 \tan \theta$ . Stationary background measurements were taken before and after each scan for a period of time equal to a quarter of the scan time. The three intensity monitors were checked every 2 h and were fluctuated randomly within 2% over the entire data collection. After correction for background, the intensities were reduced to  $F$  and  $\sigma(F)$  according to counting statistics, and the weights were assigned as  $\omega = 1/\sigma^2(F) + 0.0001F^2$ . Of the 5260 total reflections, 1908 having  $I > 2\sigma(I)$ , were considered observed. Intensity data were correction for Lorentz polarization effects and elliptical absorption.

#### *Solution and refinement of the structure*

All calculations were carried out on a VAX-785 computer, using the NRCC-SDP-VAX package. The iron atom position was located from the Patterson map. Subsequent Fourier syntheses revealed the positions of all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at idealized positions and were included in the structure factor calculations. The final least-squares circle converged to  $R$  and  $R_w$ , respectively, at 4.8 and 4.4%. An attempt was made to refine the hydrogen atom position of the bicyclic  $C_{10}H_{11}O_3$  moiety. The difference between calculated and refined positions are small, on average 0.1–0.2 Å. The positional and isotropic thermal parameters of all the non-hydrogen atoms are given in Table 1. The bond distances and angles are listed in Table 2.

#### References

- 1 T.-W. Lee and R.-S. Liu, *J. Organomet. Chem.*, 320 (1987) 211.
- 2 S.-F. Lush and R.-S. Liu, *Organometallics*, 5 (1986) 1908.
- 3 G.-H. Lee, S.-M. Peng, T.-W. Lee and R.-S. Liu, *Organometallics*, 5 (1986) 2378.
- 4 G.-H. Lee, S.-M. Peng, S.-F. Lush, D. Muo and R.-S. Liu, *Organometallics*, in press.
- 5 D. Seyferth and J. Pomet, *J. Org. Chem.*, 45 (1980) 1721.
- 6 A. Hasomi, M. Saito and H. Sakurai, *Tetrahedron Lett.*, (1980) 3783.
- 7 M.L.H. Green and D.J. Westlake, *J. Chem. Soc. A*, (1971) 367.
- 8 I.S. Butler, F. Basolo and R.G. Pearson, *Inorg. Chem.*, 6 (1967) 2074.
- 9 L.J. Todd, J.R. Wilkinson, J.P. Hickey, D.L. Beach and K.W. Barnett, *J. Organomet. Chem.*, 74 (1974) C17.
- 10 A.B. Bothner-By, *Adv. Magn. Reson.*, 1 (1965) 195.
- 11 J.E. Huheey, *Inorganic Chemistry, Principle of Structures and Reactivity*, 3rd edition, 1983, Harper & Row, New York.
- 12 M.R. Churchill, *Inorg. Chem.*, 12 (1973) 1213.