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DYNAMICS AND STRUCTURE OF SOME TRICARBONYLFERROLE—IRON TRICARBONYL DERIVATIVES

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Summary

A series of compounds of the formula $Fe_2(CO)_{6-x}(PR_3)_x(R'C_2R'')_2$ ($x = 0$, R' and R'' = Ph, R' and R'' = H, R' = Ph and R'' = H; $x = 1$, R = Ph or n-Bu, and R' and R'' = Ph) were studied by ^{13}C NMR to observe their solution properties. The tricarbonylferrole unit was found to be static from —125 to +95° C, while the π-$Fe(CO)_3$ group appeared to be fluxional over the same temperature range. Definite assignments of the carbonyl carbon and ferrole ring carbon resonances have been made. A low temperature single crystal X-ray study of $Fe_2(CO)_5PPh_3(PhC_2Ph)_2$ demonstrated that the phosphine ligand was attached to the ferrole iron contrary to previous belief based on chemical evidence.

Introduction

Some years ago Reppe reported the isolation of metal complexes of the general formula $Fe_2(CO)_6(RC_2OH)_2$ from the reaction of an alkaline solution of iron carbonyl hydride and acetylenes [1,2]. A single crystal X-ray study by Hock and Mills [3] revealed the tricarbonylferrole—iron tricarbonyl structure illustrated in Fig. 1. More recently Hubel [4] and King [5] have found that reaction of iron carbonyl derivatives with acetylenes in chemically inert organic solvents form binuclear species with the same general structure [6]. Mössbauer spectra in glassy n-butylbenzene matrices at —188° C of several tricarbonylferrole—iron tricarbonyl derivatives resolved the two nonequivalent iron atoms in each structure [7]. A ^{13}C NMR study of several of these binuclear complexes was undertaken to investigate the solution properties of this rather general class of compounds. This work led to a structural study of $Fe_2(CO)_5PPh_3(PhC_2Ph)_2$.

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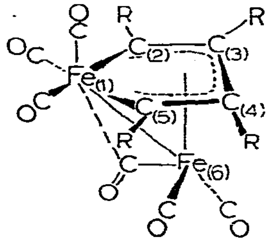

Fig. 1. The structure and numbering system for the tricarbonylferrole—iron tricarbonyl derivatives.

Experimental

Instrumentation and ^{13}C NMR procedures

The ^{13}C NMR spectra were obtained with a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 25.1 MHz. The instrument is equipped with a Transform Technology, Inc. pulse unit which delivers a 90° pulse in 15 μsec and a 36K Nicolet 1089 Computer system with disc. The ^{13}C chemical shifts were measured relative to an internal solvent peak and reported relative to tetramethylsilane. The conversion factors used are $\delta(TMS) = \delta(CH_2Cl_2) + 53.89$ ppm and $\delta(TMS) = \delta(\text{dioxane}) + 67.38$ ppm. To reduce T_1 relaxation times tris(acetylacetonato)chromium(III) (about 0.05 *M*) was added to each NMR sample [8].

Materials

The compounds $Fe_2(CO)_6(PhC_2Ph)_2$ [4], $Fe_2(CO)_6(PhC_2H)_2$ [4] (phenyl groups on the 2,5-carbons), $Fe_2(CO)_6(HC_2H)_2$ [9], and $Fe_2(CO)_5PPh_3(PhC_2Ph)_2$ [10], were prepared according to methods described in the literature. $Fe_2(CO)_5P(n\text{-}Bu)_3(PhC_2Ph)_2$ was prepared in 55% yield by the same procedure [10] employed for $Fe_2(CO)_5PPh_3(PhC_2Ph)_2$, m.p. = 142—144°C. (Analysis: Found: C, 64.00; H, 6.29. $C_{31}H_{37}Fe_2O_5P$ calcd.: C, 64.02; H, 6.31%.)

Diphenylacetylene, carbon-13 enriched, ($Ph—C^{13}{\equiv}C—Ph$) was prepared as described previously [11].

Single crystal X-ray study of $Fe_2(CO)_5PPh_3(PhC_2Ph)_2$ (IV)

Crystals of IV occurred as several different morphological types, with no apparent external symmetry. Preliminary precession photographs indicated a triclinic lattice with no extinctions, in agreement with a previous study [12]. Triclinic symmetry was confirmed by a systematic hemispherical search of reciprocal space [13] on the Picker FACS-1 diffractometer used for data collection. The intensity distribution suggested the centric space group $P\bar{1}$ (No. 2, C_i^1), which was confirmed by the solution of the structure (vide infra). A well formed crystal of approximate dimensions 0.25 × 0.30 × 0.35 mm was mounted with silicone grease on a glass fiber and cooled to —160 ± 5°C utilizing a gas flow cooling system [13]. No phase transition was apparent during cooling. Cell dimensions (at —160°C), based on a least squares fit of angular data from 13 reflections centered in $\pm 2\theta$ are $a = 12.868(9)$, $b = 11.667(8)$, $c = 13.867(9)$ Å, $\alpha = 85.98(3)$, $\beta = 90.35(3)$, and $\gamma = 83.36(3)°$. The volume of 2062.9 Å^3 gives a calculated density of 1.401 g cm^{-3} for $Z = 2$. The linear absorption coefficient for Mo-K_α radiation (λ = 0.71069 Å) is 8.12 cm^{-1}.

Data were collected using the moving-crystal moving-counter technique for reflections with $2\theta \leqslant 40°$ and $-h \pm k \pm l$. A limited set of redundant data were collected for $+h \pm k \pm l$ to check equivalent intensities. A 2° min^{-1} scan speed over a range of 1.5° plus a dispersion correction (to account for the $K_{\alpha 1}$-$K_{\alpha 2}$ splitting) was employed with 10 sec background counts at each extreme of the scan. A highly oriented graphite monochromator (002 reflection) and molybdenum radiation were utilized. Three reflections, chosen as standards, indicated only random fluctuations with an average standard deviation of 1.3%. A total of 4080 reflections, including redundancies, were collected, and reduced to 3822 unique intensities, of which 3453 were greater than their standard error, based on counting statistics. An ignorance factor of 0.05 was used in the data reduction formula which is given elsewhere [14].

Normalized structure factors were calculated and statistical distribution of the E's indicated a centrosymmetric space group. Considerable difficulty was encountered in finding the correct solution to the structure. Both MULTAN and LSAM [15] located the proper relative positions of the iron atoms, but an improper origin. A Fourier synthesis [16] assuming space group $P1$, and Patterson methods were able to correctly fix the origin. Initial attempts to phase data with limited $\sin\theta/\lambda$ led to an incorrect location of the phosphorus atom and no further peaks. The correct position was finally located by phasing on the largest 1000 E's. Standard Fourier techniques were then used to locate all remaining non-hydrogen atoms.

Full matrix least squares refinement [16] was terminated when the largest Δ/σ reduced to 0.015. The goodness of fit of the last cycle was 2.4, indicating the errors had been underestimated. Final residuals were $R(F) = 0.092$ and $Rw(F) = 0.092$. The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = 1/\sigma(F)^2$. Only those 3453 data with $I \geqslant \sigma(I)$ (based on counting statistics) were used in the refinement, leading to a ratio of 14.6:1 for observations to parameters. No absorption or extinction corrections were performed. Minimum and maximum transmission coefficients are estimated at 79 and 84% respectively. Because of the size of the problem, only isotropic refinement was utilized *. A final difference Fourier synthesis was essentially featureless, the largest peak (of intensity 0.84 e^{-1} Å^{-3}) was located approximately 0.5 Å from Fe(1). 12 of the 20 largest peaks could be assigned hydrogen coordinates. Scattering factors and anomalous dispersion terms were from ref. [17].

Final positional and thermal parameters are listed in Table 1. Structure factors and more extensive tables of crystallographic results are available. **

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* It is the author's experience that the precision lost by not utilizing anisotropic refinement is more than made up for by the use of data collected at low temperatures. In general the thermal parameters tend to be more nearly isotropic at —160° C, and the increase in the number of "observed" data more than compensates for the lack of costly anisotropic refinement.

** A complete summary of crystallographic data for $Fe_2(CO)_5PPh_3(PhC_2Ph)_2$ is available in microfiche form only for $2.50 from the Chemistry Library, Indiana University, Bloomington, Indiana 47401. Request Molecular Structure Center Report No. 7512.

TABLE 1. FINAL FRACTIONAL COORDINATES AND ISOTHERMAL PARAMETERS [a]

Atom	10^4x	10^4y	10^4z	10^2B
Fe(1)	2243(1)	2099(1)	1616(1)	263(4)
Fe(6)	2990(1)	3966(1)	2288(1)	311(4)
P(11)	1621(2)	251(2)	2098(2)	270(6)
C(2)	1500(7)	2983(8)	2520(7)	257(19)
C(3)	1970(7)	3144(8)	3438(7)	252(19)
C(4)	2982(7)	2762(8)	3518(7)	249(19)
C(5)	3293(7)	2255(8)	2672(7)	286(20)
C(7)	1329(8)	2335(8)	671(7)	324(21)
C(9)	3092(8)	1713(9)	736(8)	366(22)
C(12)	2832(8)	4076(9)	1028(8)	425(24)
C(14)	2677(9)	5328(10)	2521(8)	450(25)
C(16)	4291(10)	4512(11)	2204(9)	536(28)
C(18)	448(7)	3388(8)	2278(7)	266(20)
C(19)	371(8)	4438(9)	1697(8)	402(24)
C(20)	—627(9)	4770(10)	1445(8)	442(25)
C(21)	—1512(9)	4092(10)	1756(8)	480(26)
C(22)	—1464(8)	3043(9)	2318(8)	416(24)
C(23)	—464(8)	2711(9)	2563(7)	348(22)
C(24)	1509(7)	3688(8)	4269(7)	279(20)
C(25)	2068(8)	4609(9)	4716(8)	408(24)
C(26)	1683(9)	5003(10)	5584(8)	457(25)
C(27)	748(9)	4454(10)	5986(8)	442(25)
C(28)	182(8)	3538(9)	5541(8)	405(23)
C(29)	560(7)	3150(8)	4679(7)	316(21)
C(30)	3641(7)	2852(8)	4425(7)	279(20)
C(31)	4670(8)	3352(9)	4368(8)	408(24)
C(32)	5288(9)	3418(10)	5238(9)	532(28)
C(33)	4857(9)	3002(10)	6123(9)	514(27)
C(34)	3820(9)	2507(10)	6160(8)	486(26)
C(35)	3201(8)	2436(9)	5304(8)	385(23)
C(36)	4286(7)	1769(8)	2692(7)	316(21)
C(37)	5042(8)	1936(9)	1945(7)	365(22)
C(38)	5938(9)	1320(10)	1977(8)	466(26)
C(39)	6054(9)	500(11)	2715(9)	529(28)
C(40)	5333(9)	272(10)	3462(8)	440(25)
C(41)	4443(8)	892(9)	3449(7)	333(21)
C(42)	1827(7)	—214(8)	3377(7)	265(19)
C(43)	1325(8)	346(8)	4053(7)	329(21)
C(44)	1390(8)	—8(9)	5058(8)	423(24)
C(45)	1986(9)	—892(10)	5330(9)	490(26)
C(46)	2468(9)	—1448(10)	4664(8)	484(26)
C(47)	2404(8)	—1119(9)	3646(8)	377(23)
C(48)	231(7)	—250(8)	1999(7)	289(20)
C(49)	9571(8)	274(9)	1351(8)	392(23)
C(50)	—1493(9)	—211(10)	1238(8)	449(25)
C(51)	—1885(8)	—1206(9)	1774(8)	405(24)
C(52)	—1236(9)	—1746(10)	2432(8)	471(26)
C(53)	9822(8)	8738(9)	2553(8)	417(24)
C(54)	2219(8)	—831(8)	1437(7)	309(21)
C(55)	3292(8)	—810(9)	1454(8)	409(24)
C(56)	3777(10)	8351(11)	966(9)	561(29)
C(57)	3148(9)	—2463(10)	462(9)	521(28)
C(58)	2085(9)	—2493(10)	459(8)	498(27)
C(59)	1583(8)	—1669(9)	949(8)	400(23)
O(8)	797(5)	2570(6)	19(5)	437(16)
O(10)	3599(6)	1533(6)	81(5)	474(17)
O(13)	2854(6)	4431(7)	209(6)	600(20)
O(15)	2462(7)	6233(8)	2707(7)	699(22)
O(17)	5182(8)	4906(8)	2075(7)	747(23)

[a] Numbers in parentheses represent estimated errors in the least significant digits.

Results and discussion

The ferrole ring carbon resonances

The ^{13}C shielding values of $Fe_2(CO)_6(PhC_2Ph)_2$ (I) and other substituted derivatives of this type are presented in Table 2. The two ferrole ring carbon resonances were located by synthesis of I containing ^{13}C-enriched $Ph{-}^{13}C{\equiv}C{-}Ph$ as a reagent [11]. These two signals occur at 172.3 and 147.6 ppm. The more deshielded signal is assigned to the ring carbon atom adjacent to the iron [C(2,5)]. This assignment is confirmed by the phosphorus—carbon coupling associated with this resonance in the ^{13}C NMR spectrum of $Fe_2(CO)_5PPh_3(PhC_2Ph)_2$ (vide infra). The isomer obtained from phenylacetylene, $Fe_2(CO)_6(PhC_2H)_2$ (II), m.p. 178—180°C (dec.) [4] has the ring carbon signals at 174.9 and 111.4 ppm. Thus the phenyl groups appear to be attached to C(2,5) of the ferrole ring in this isomer. A single frequency off resonance measurement demonstrated proton coupling to the 111.4 ppm signal of II. The ring carbon signals of $Fe_2(CO)_6(HC_2H)_2$ (III) occur at 154.9 and 110.6 ppm as haş been previously reported [18]. As expected, phenyl substitution results in a deshielding of the ferrole ring carbon signals relative to III.

The carbonyl carbon resonances

Consideration of the various X-ray structure determinations of tricarbonylferrole—iron tricarbonyl derivatives [3,6,19—21], including that of I [12], suggests that the static molecule should exhibit 4 carbonyl resonances with relative areas of 2:2:1:1.

The ^{13}C NMR spectrum of I at room temperature exhibits three resonances at 214.7, 210.6 and 203.2 ppm with relative areas of 3:1:2 respectively. This pattern of carbonyl carbon signals is constant from —125° to +95°C. The area three resonance is due to either a coincidental overlap of two signals or to a very low energy carbonyl permutation process.

Treatment of I with PPh_3 in refluxing toluene generated $Fe_2(CO)_5PPh_3$-$(PhC_2Ph)_2$ (IV) [10]. Previously it had been reported that reaction of IV with bromine formed $Fe(CO)_2PPh_3$ (tetraphenylcyclopentadieneone) [10]. This led to the conclusion that the triphenylphosphine ligand was attached to Fe(6) in IV. In order to distinguish between the carbon ligands on Fe(1) and Fe(6) the ^{13}C NMR spectrum of IV as well as that of $Fe_2(CO)_5P(n\text{-}Bu)_3(PhC_2Ph)_2$ (V) were obtained and these data are presented in Table 2. Phosphorus—carbon coupling is observed on only one of the two ferrole ring carbon signals in these compounds. However, coupling to both ferrole ring carbon signals would be expected if the phosphine were attached to the π-bonded Fe(6) unit. This problem has been resolved by the single crystal X-ray study of IV (vide infra) which demonstrates that the triphenylphosphine ligand is substituted in place of the unique carbonyl on Fe(1). With this type of structure, one would expect stronger phosphorus—carbon coupling to the adjacent C(2,5) ring atoms than to C(3,4) as was observed. Compound IV exhibits two carbonyl carbon signals at 217.7 ppm (area 3) and 209.5 ppm (area 2) with phosphorus—carbon coupling observable on the smaller peak. The resonance for the two equivalent carbonyls on Fe(1) has changed from 203.2 ppm for I to 209.5 ppm for IV. It has been observed in many previous studies [22] that substitution of a phosphine ligand for a car-

(continued on p. 174)

TABLE 2

^{13}C NMR DATA OF TRICARBONYLFERROLE—IRON TRICARBONYL DERIVATIVES

Compound	δ_c,[a] (ppm)				
	Carbonyls on Fe(6)	Unique carbonyl on Fe(1)	Equivalent carbonyls on Fe(1)	Ferrole ring	
				C(2,5)	C(3,4)
$Fe_2(CO)_6(PhC_2Ph)_2$ (I)	214.7	210.6	203.2	172.3	147.6
$Fe_2(CO)_6(PhC_2H)_2$ (II)	212.3	209.2	204.5	174.9	111.4
$Fe_2(CO)_6(HC_2H)_2$ (III)	211.1 [b]	209.0 [b]	206.9 [b]	154.9	110.6
$Fe_2(CO)_5PPh_3(PhC_2Ph)_2$ (IV)	217.7		209.5 [J(P—C) 13.1 Hz]	176.6 [J(P—C) 12.4 Hz]	149.3
$Fe_2(CO)_5P(n\text{-}Bu)_3(PhC_2Ph)_2$ (V)	220.9		208.3 [J(P—C) 15.5 Hz]	172.1 [J(P—C) 15.8 Hz]	148.3

[a] See Fig. 1 for numbering system. [b] Only one carbonyl carbon signal (211.5 ppm) was observed for this compound in a previous report [18].

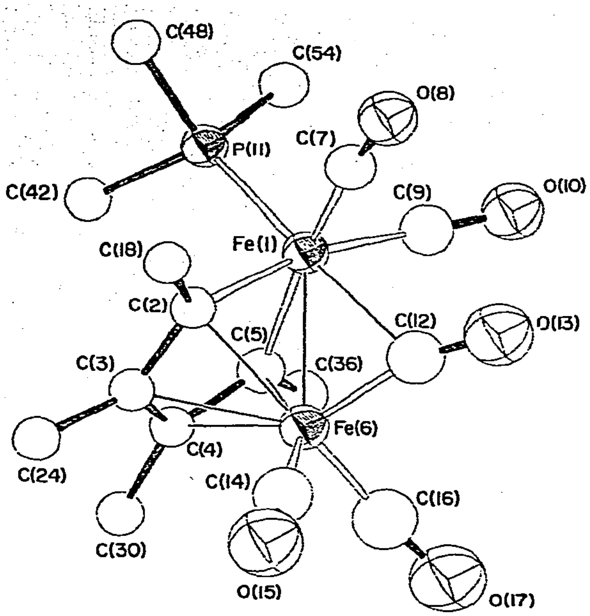

Fig. 2. ORTEP drawing of the molecule with phenyl rings removed for clarity. Phenyl carbons are numbered consecutively from the carbon shown in the figure.

TABLE 3

IMPORTANT INTRAMOLECULAR DISTANCES (Å) IN THE MOLECULE [a]

Fe(1)—Fe(6)	2.515(2)
Fe(1)—P(11)	2.267(3)
Fe(1)—C(2)	1.993(9)
Fe(1)—C(3)	2.921(9)
Fe(1)—C(4)	2.923(9)
Fe(1)—C(5)	1.990(9)
Fe(1)—C(7)	1.783(10)
Fe(1)—C(9)	1.759(11)
Fe(1)—C(12)	2.429(11)
Fe(6)—C(2)	2.131(9)
Fe(6)—C(3)	2.169(9)
Fe(6)—C(4)	2.132(9)
Fe(6)—C(5)	2.109(9)
Fe(6)—C(12)	1.755(12)
Fe(6)—C(14)	1.736(12)
Fe(6)—C(16)	1.723(13)
P(11)—C(42)	1.845(10)
P(11)—C(48)	1.824(10)
P(11)—C(54)	1.851(10)
O(8)—C(7)	1.166(10)
O(10)—C(9)	1.167(11)
O(13)—C(12)	1.180(12)
O(15)—C(14)	1.168(12)
O(17)—C(16)	1.195(13)
C(2)—C(3)	1.422(12)
C(2)—C(18)	1.512(12)
C(3)—C(4)	1.426(12)
C(3)—C(24)	1.510(13)
C(4)—C(5)	1.430(13)
C(4)—C(30)	1.515(13)
C(5)—C(36)	1.497(13)

[a] Phenyl ring carbon—carbon distances vary from 1.364 Å to 1.442 Å with estimated standard errors of ±0.014 Å.

bonyl results in a substantial deshielding of the resonance or resonances of other carbonyl groups attached to that metal center. The 217.7 ppm carbonyl resonance of IV remained as a sharp peak even at —125° C. Thus the question of the fluxionality of the carbonyls on Fe(6) or the accidental coincidence of these carbonyl carbon signals has not been completely answered. It seems probable that the Fe(6) iron tricarbonyl group with a partially bridging carbonyl (vide infra) has similar low energy site exchange properties to that of other normal π-bonded $Fe(CO)_3$ units [23,24].

TABLE 4

IMPORTANT ANGLES (°) IN THE MOLECULE

Fe(6)—Fe(1)—P(11)	141.1(1)
Fe(6)—Fe(1)—C(2)	55.0(3)
Fe(6)—Fe(1)—C(5)	54.3(3)
Fe(6)—Fe(1)—C(7)	111.6(3)
Fe(6)—Fe(1)—C(9)	109.9(3)
P(11)—Fe(1)—C(2)	101.4(3)
P(11)—Fe(1)—C(5)	94.5(3)
P(11)—Fe(1)—C(7)	98.4(3)
P(11)—Fe(1)—C(9)	94.8(3)
C(2)—Fe(1)—C(5)	79.7(4)
C(2)—Fe(1)—C(7)	92.1(4)
C(2)—Fe(1)—C(9)	163.5(4)
C(5)—Fe(1)—C(7)	166.0(4)
C(5)—Fe(1)—C(9)	96.7(4)
C(7)—Fe(1)—C(9)	87.9(5)
Fe(1)—Fe(6)—C(12)	66.6(4)
Fe(1)—Fe(6)—C(14)	142.3(4)
Fe(1)—Fe(6)—C(16)	123.8(4)
C(12)—Fe(6)—C(14)	98.1(5)
C(12)—Fe(6)—C(16)	92.4(5)
C(14)—Fe(6)—C(16)	89.6(6)
Fe(1)—P(11)—C(42)	116.6(6)
Fe(1)—P(11)—C(48)	120.6(3)
Fe(1)—P(11)—C(54)	113.1(3)
C(42)—P(11)—C(48)	99.3(4)
C(42)—P(11)—C(54)	103.1(4)
C(48)—P(11)—C(54)	101.6(4)
Fe(1)—C(2)—C(3)	116.6(6)
Fe(1)—C(2)—C(18)	122.1(6)
C(3)—C(2)—C(18)	121.1(8)
C(2)—C(3)—C(4)	113.3(8)
C(2)—C(3)—C(24)	126.2(8)
C(4)—C(3)—C(24)	120.5(8)
C(3)—C(4)—C(5)	113.3(8)
C(3)—C(4)—C(30)	123.0(8)
C(5)—C(4)—C(30)	123.7(8)
Fe(1)—C(5)—C(4)	116.5(7)
Fe(1)—C(5)—C(36)	123.6(7)
C(4)—C(5)—C(36)	119.0(8)
Fe(1)—C(7)—O(8)	173.9(9)
Fe(1)—C(9)—O(10)	172.6(9)
Fe(1)—C(12)—O(13)	125.3(9)
Fe(6)—C(12)—O(13)	162.7(10)
Fe(6)—C(14)—O(15)	177.9(11)
Fe(6)—C(16)—O(17)	175.2(11)

TABLE 5

LEAST SQUARES PLANE DATA FOR THE FERRACYCLOPENTADIENE RING [a]

Atom	Distance from plane (Å)
Fe(1) [b]	−0.043
C(2) [b]	0.053
C(3) [b]	−0.036
C(4) [b]	−0.014
C(5) [b]	0.040
Fe(6)	1.718
P(11)	−2.284
C(7)	0.250
O(8)	0.561
C(9)	0.367
O(10)	0.722
C(18)	0.112
C(24)	−0.110
C(30)	−0.085
C(36)	−0.080

[a] Equation of plane is: $4.184x + 9.475y - 4.774z = 2.199$ (based on crystal axes). [b] Atoms defining least squares plane.

Single crystal X-ray study of $Fe_2(CO)_5PPh_3(PhC_2Ph)_2$

The structure of IV is presented in Figure 2 [25] and important distances and angles are given in Tables 3 and 4. In general the bond distances and angles are comparable to those found by X-ray methods for other members of this class [3,6,19—21]. The Fe(1)—C(12) distance of the partially bridging carbonyl has been observed to vary from 2.80 Å [19] to 2.32 Å [20] in different derivatives of this structural class. The Fe(1)—C(12) distance (2.43 Å) of IV is found to be somewhat longer than the corresponding distance in I (2.374(9) Å) [12]. The shortness of this bonding interaction in I may be a manifestation of the better electron withdrawing capability of the *trans* carbonyl on Fe(1) in I as compared to that of the PPh_3 ligand in IV.

The least squares plane data for the ferracyclopentadiene ring are given in Table 5. The two carbonyls, C(7)—O(8) and C(9)—O(10), are bent out of the least squares plane by 15.4° and 17.7° respectively. This is probably a consequence of the steric requirements of the PPh_3 group.

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