TRIFERROCENYLPHOSPHINEIRON CARBONYLS BY SUBSTITUTION AND DISPROPORTIONATION PROCESSES *

GILBERT P. SOLLOTT *, DAVID L. DAUGHDRILL ** and WILLIAM R. PETERSON, Jr.

Chemistry Research Division, Pitman—Dunn Laboratory, Frankford Arsenal, Philadelphia, Pennsylvania 19137 (U.S.A.)

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Summary

Mono- (I), bis- (II), and tris-(triferrocenylphosphine)iron carbonyls (III) were obtained photochemically or thermally in high yields. The photochemical reaction of triferrocenylphosphine with iron pentacarbonyl was found to proceed only at elevated temperature, and it was discovered that I, first formed almost quantitatively, is converted to III by a disproportionation process. Complex II is not formed as an intermediate, notwithstanding the fact that II can be obtained by photochemically induced disproportionation, as well as by thermally initiated substitution, from I as starting material. Several aspects of the reaction were explored, and a mechanism is suggested to account for the observed behavior. The product of the thermally initiated reaction of triferrocenylphosphine with butadieneiron tricarbonyl was characterized as a tris(phosphine)iron dicarbonyl (IV), structurally different from III. An examination of carbonyl stretching bands indicated that I and II are very probably trigonal bipyramidal in configuration with the phosphine ligand axially disposed. Consideration is given to possible structural configurations for III and IV.

The preparation of several mono(triferrocenylphosphine)metal carbonyl complexes, including the phosphineiron tetracarbonyl, $Fc_3PFe(CO)_4$ (Fc = ferrocenyl) [1], has recently been reported [1,2]. The latter was obtained in 23% yield from the phosphine and iron pentacarbonyl thermally in diglyme. A bis-(phosphine) derivative of $Cr(CO)_6$ could not be prepared, and it was suggested that this might be due to steric effects of the bulky Fc_3P molecule [1].

We report that $Fc_3PFe(CO)_4$ (I) is obtainable from Fc_3P and $Fe(CO)_5$ photochemically in nearly quantitative yield, and that the same reaction can be made

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** Present Address, Edgewood Arsenal, Edgewood, MD, U.S.A.

TABLE 1

REACTION OF Fc₃P WITH EXCESS Fe(CO)₅ IN n-HEPTANE

Conditions	Product	Yield (%)
Reflux, 5 h, $h\nu$	I	93
Reflux, 24 h, $h\nu$	III	96
20°C, 24 h, $h\nu$	none	
Reflux, 24 h	I	9

to produce a stable tris(triferrocenylphosphine)iron dicarbonyl in equally high yield. Formation of $(Fc_3P)_3Fe(CO)_2$ (III) was wholly unexpected especially since $Fe(CO)_5$ was employed in molar excess of Fc_3P, and thus a study was conducted to provide an insight into the pathway by which that complex arises.

Results and discussion

Preparation of the triferrocenylphosphineiron carbonyls

Complex I was obtained in 93% yield when the reaction of Fc_3P with excess $Fe(CO)_5$ was conducted in n-heptane under ultraviolet light for 5 h. When the reaction time was extended to 24 h, III was isolated virtually quantitatively. In neither case was any $(Fc_3P)_2Fe(CO)_3$ (II) obtained.

In carrying out these transformations, external cooling was not applied, and the mixtures were heated to reflux temperature by the UV lamp. The same reaction, performed under reflux conditions without irradiation, produced I in less than 10% yield, while no phosphineiron complex resulted from an attempted reaction under UV light with efficient cooling. The conditions and results are summarized in Table 1. It is apparent that, while a thermal reaction occurs to a minor extent in the absence of UV light, heat is required to effect the photochemical reaction, i.e., under the conditions investigated, the photochemical reaction proceeds only at elevated temperature.
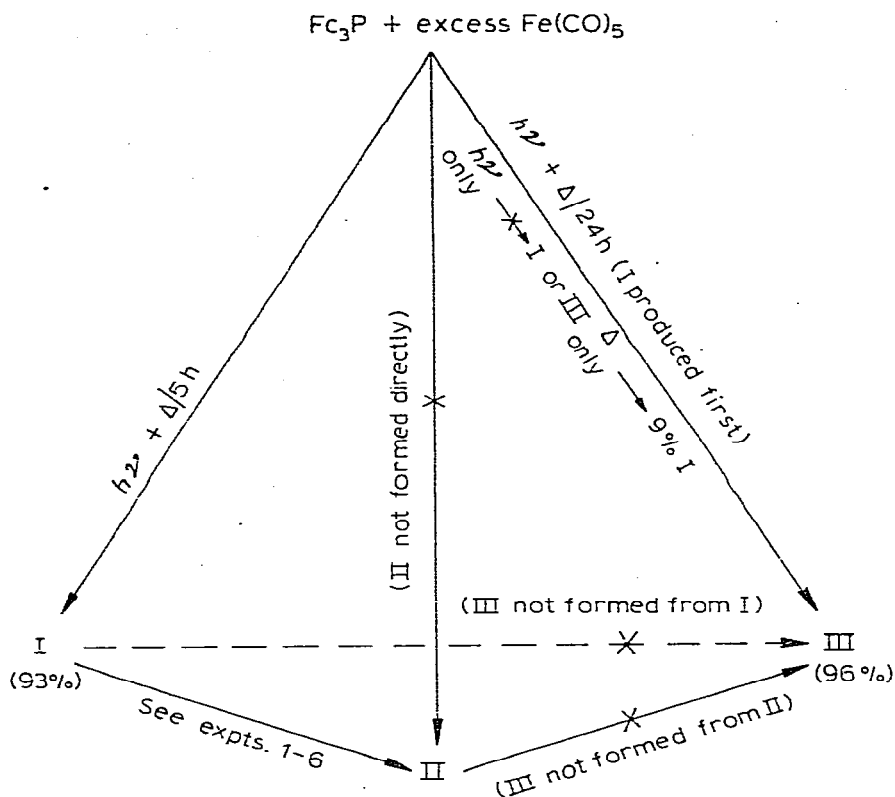
Both $Ph_3PFe(CO)_4$ and $(Ph_3P)_2Fe(CO)_3$ can be obtained thermally or photochemically from Ph_3P and $Fe(CO)_5$ [3]. It has been reported that the more highly substituted product, $(Ph_3P)_3Fe(CO)_2$, is obtained indirectly, together with $(Ph_3P)_2Fe(CO)_3$, by thermally initiated displacement of the hydrocarbon ligand from butadiene- and cycloheptatriene-iron tricarbonyls *, **. Both $[(p-FC_6H_4)_3P]_3Fe(CO)_2$ and $[(p-FC_6H_4)_3P]_2Fe(CO)_3$ have been reported to form in an analogous reaction of $C_7H_8Fe(CO)_3$ [8]. In the present work, a similar reaction of Fc_3P with $C_4H_6Fe(CO)_3$ produced a tris(phosphine)iron dicarbonyl (IV), different from complex III, in 21% yield. Structural configurations of the phosphineiron carbonyls will be considered later.

Scheme 1 indicates the pathways investigated for the formation of complexes I, II and III, and summarizes a number of experiments aimed at obtaining II and III starting with I. Complex I was converted to II in nearly quantitative yield by

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* Manuel and Stone apparently prepared and used $C_7H_8Fe(CO)_3$ rather than $C_7H_8Fe(CO)_2$ as reported by them [4,5].

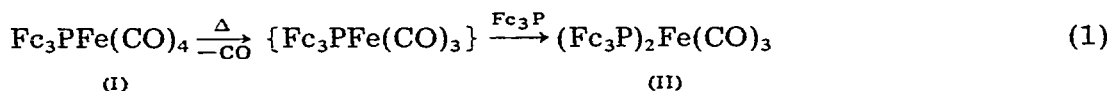** Characterization of the product as a tris(phosphine)iron dicarbonyl has been questioned [6,7].

SCHEME 1

Fc_3P + excess $Fe(CO)_5$

$h\nu$ only

$h\nu$ + Δ/24 h (I produced first)

$h\nu$ → I or III only

I only

Δ → 9% I

$h\nu$ + Δ/5 h

(II not formed directly)

I (93%) — — — — — — — — — — — ✳ — — → III (96%)

(III not formed from I)

See expts. 1-6

II

(III not formed from II)

Expt.

1. I + Fc_3P + Δ ——➤ 95 % II

2. I + Δ ——➤ 0 % II

3. I + $h\nu$ + Δ ——➤ 38 % II + small amount $Fe(CO)_5$

4. I + $h\nu$ + Δ + Fc_3P ——➤ 23 % II

5. I + $h\nu$ + Δ + $Fe(CO)_5$ ——➤ 0 % II

6. I + $h\nu$ + Δ + $Fe(CO)_5$ + Fc_3P ——➤ 0 % II (more I formed)

a thermally initiated reaction with Fc_3P in decalin near the boiling point, (expt. 1), based on a reported procedure for converting $Ph_3PFe(CO)_4$ to $(Ph_3P)_2Fe$-$(CO)_3$ [9]. A kinetic study in the latter instance suggested an S_N1 dissociative mechanism which most likely is applicable to the present case (eq. 1) *.

$$Fc_3PFe(CO)_4 \underset{-CO}{\overset{\Delta}{\rightleftharpoons}} \{Fc_3PFe(CO)_3\} \xrightarrow{Fc_3P} (Fc_3P)_2Fe(CO)_3 \qquad (1)$$

(I)   (II)

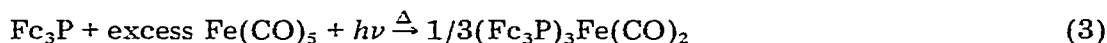Gas evolution occurs on heating I without Fc_3P present, and II is not obtained

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* Mechanistic studies of thermally initiated substitution reactions of metal carbonyl complexes have been reviewed [10].

(expt. 2). Clearly, the possibility, however remote, that II might form in the presence of Fc_3P by disproportionation (eq. 2) *, can be ruled out from the standpoint that the yield, nearly quantitative on the basis of substitution, would be doubled.

$$Fc_3PFe(CO)_4 \xrightarrow{\Delta} 1/2(Fc_3P)_2Fe(CO)_3 + 1/2Fe(CO)_5 \qquad (2)$$

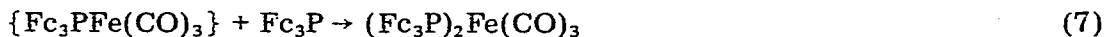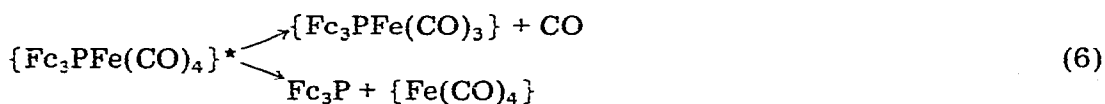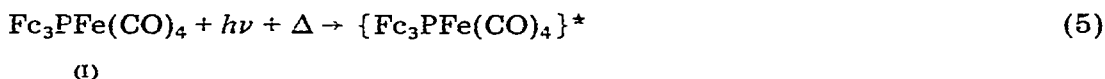$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$
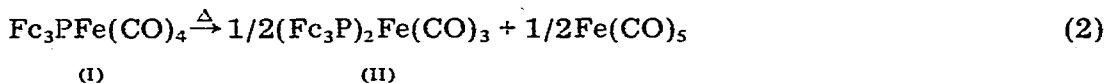
Mechanism of the formation of triferrocenylphosphineiron carbonyls by photochemical reaction

Unlike expt. 1, yield cannot be used to differentiate between stepwise substitution (eq. 3), and disproportionation (eq. 4) processes in accounting for the near-quantitative formation of III from Fc_3P and $Fe(CO)_5$ under the influence of ultraviolet light.

$$Fc_3P + \text{excess } Fe(CO)_5 + h\nu \xrightarrow{\Delta} 1/3(Fc_3P)_3Fe(CO)_2 \qquad (3)$$

$$Fc_3P + \text{excess } Fe(CO)_5 + h\nu \xrightarrow{\Delta} Fc_3PFe(CO)_4 \xrightarrow{\text{disprop.}} 1/3(Fc_3P)_3Fe(CO)_2 \qquad (4)$$

Formation of III despite the presence of $Fe(CO)_5$ in molar excess of Fc_3P suggested that the reaction pathway subsequent to the formation of I involves a process of disproportionation. The near-quantitative formation of I, hence practically complete utilization of Fc_3P prior to the formation of more highly substituted product tends to confirm that III indeed arises by a disproportionation process (eq. 4). This view found support when UV irradiation of I alone in n-heptane for 24 h (expt. 3) produced II in 38% yield together with $Fe(CO)_5$ in small quantity. CO gas evolution was observed by displacement of water.

The disproportionation of I to produce II (eq. 5—8) is viewed as proceeding by dissociation of excited molecules of I in two ways (eq. 6) and addition of the generated donors to the electron deficient metal carbonyl species (eq. 7 and 8) **. The small extent to which reaction 8 takes place is due, at least in part, to escape of CO from the reaction mixture.

$$Fc_3PFe(CO)_4 + h\nu + \Delta \rightarrow \{Fc_3PFe(CO)_4\}^* \qquad (5)$$

$$\text{(I)}$$

$$\{Fc_3PFe(CO)_4\}^* \left\langle \begin{array}{l} \{Fc_3PFe(CO)_3\} + CO \\ Fc_3P + \{Fe(CO)_4\} \end{array} \right. \qquad (6)$$

$$\{Fc_3PFe(CO)_3\} + Fc_3P \rightarrow (Fc_3P)_2Fe(CO)_3 \qquad (7)$$

$$\{Fe(CO)_4\} + CO \xrightarrow{\text{(minor)}} Fe(CO)_5 \qquad (8)$$

The photochemical transformation of I to II (expt. 3) occurred without the

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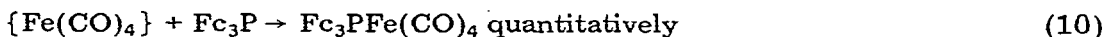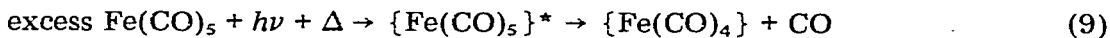* The thermally induced disproportionation of substituted chromium carbonyls has been reported [11].

** A similar type of dual dissociation is known to occur in the photo-activation of olefin—iron tetracarbonyls [12]. The overall process is reminiscent of that which characterizes the behavior of the Group VI metal carbonyls [13].

production of III, unlike the photochemical reaction of Fc_3P with $Fe(CO)_5$. The latter reaction first produced I, but did not yield II (Scheme 1). In an effort to convert I to III by circumventing the possibility that conversion to III is precluded by the insolubility of II in n-heptane *, the irradiation of I was conducted in benzene in which II shows somewhat greater solubility. However, as in the case of heptane, II was obtained, but not III.

The presence of a molar equivalent of Fc_3P during the irradiation of I (expt. 4) was found to inhibit the disproportionation process. The yield of II in this case was either 23% based on substitution, or 46% based on disproportionation. A 73% recovery of I indicated that the reaction was one of thermal substitution, with little or no disproportionation occurring. On the basis that the latter process involves the dissociation of the excited molecule $\{Fc_3PFe(CO)_4\}^*$ (eq. 6), the inhibition of that process may be due to loss of excitation energy by collision with Fc_3P.

The validity of this suggestion is enhanced from the standpoint that it provides a credible explanation for the fact that I can be isolated practically quantitatively, exclusive of more highly substituted product, from the photochemically induced reaction of Fc_3P with $Fe(CO)_5$. Until all of the Fc_3P is consumed in forming I, the disproportionation of I is effectively precluded by collision of excited molecules of I with Fc_3P. This explanation implies that collisions between Fc_3P and $\{Fe(CO)_5\}^*$, causing the latter molecules to lose their excitation energy and thereby inhibiting the formation of I, is of little consequence, while such energy loss by $\{Fc_3PFe(CO)_4\}^*$ molecules is quite significant.

Based on the inability to obtain III by irradiation of either I or II as starting material, it seems clear that II is not formed per se in proceeding from initial to final product (I to III) in the reaction of Fc_3P with $Fe(CO)_5$ (Scheme 1). The eq. 9—14 summarize the principle steps by which III might arise in that reaction.

$$\text{excess } Fe(CO)_5 + h\nu + \Delta \rightarrow \{Fe(CO)_5\}^* \rightarrow \{Fe(CO)_4\} + CO \tag{9}$$

$$\{Fe(CO)_4\} + Fc_3P \rightarrow Fc_3PFe(CO)_4 \text{ quantitatively} \tag{10}$$

$$\text{(I)}$$

Then,

$$Fc_3PFe(CO)_4 + h\nu \rightarrow \{Fc_3PFe(CO)_4\}^* \tag{11}$$

$$\text{(I)}$$

$$3\{Fc_3PFe(CO)_4\}^* \begin{cases} \rightarrow \{Fc_3PFe(CO)_3\} + CO \\ \rightarrow 2\,Fc_3P + 2\{Fe(CO)_4\} \end{cases} \tag{12}$$

$$\{Fc_3PFe(CO)_3\} + \{Fe(CO)_4\} \rightarrow \{Fc_3PFe(CO)_2\text{---}(CO)\text{---}Fe(CO)_4\} \tag{13}$$

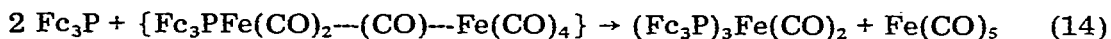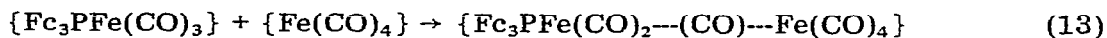$$2\,Fc_3P + \{Fc_3PFe(CO)_2\text{---}(CO)\text{---}Fe(CO)_4\} \rightarrow (Fc_3P)_3Fe(CO)_2 + Fe(CO)_5 \tag{14}$$

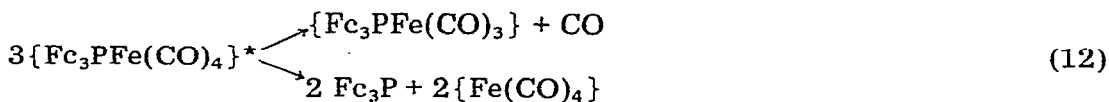$$\text{(III)}$$

It is clear that I, formed in the first phase of the overall reaction, arises by a substitution process. This phase of the photochemically induced reaction pre-

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* Both I and III show very limited solubility in boiling n-heptane, while II is practically insoluble.

sumably induced reaction presumably takes place by a dissociative mechanism (eq. 9 and 10). The disproportionation of I to III (eq. 11—14) then proceeds via two-way dissociation of excited molecules of I, as in the disproportionation producing 2 (eq. 5—8), but in this case it is necessary to show two molecules of Fc_3P formed for each CO molecule liberated (eq. 12), in view of the quantitative formation of III. To generate III from I without producing II per se, the species $\{Fe(CO)_4\}$, which should be present in greater abundance than Fc_3P (eq. 9, 10 and 12), is viewed as assisting in the removal of a second molecule of CO from I (eq. 13), while reaction with two molecules of Fc_3P takes place in a stepwise fashion (eq. 14). CO may combine with $\{Fe(CO)_4\}$ as before (eq. 8), while interaction to form II (eq. 7) does not occur.

Significantly, the disproportionation of I to II (expt. 3) was inhibited in the presence of $Fe(CO)_5$ (expt. 5). Neither was III formed in this instance, in apparent contradiction of the mechanism just outlined (eq. 11—14). It is probable that the inhibiting molecule is not the pentacarbonyl per se, since the reaction of $Fe(CO)_5$ and Fc_3P readily yields III via formation of I. More likely it is a decomposition product causing $\{Fc_3PFe(CO)_4\}^*$ molecules to lose their excitation energy. Such a product must not form in the presence of Fc_3P, and it would appear that Fc_3P precludes its formation in addition to exerting its own deactivating influence on $\{Fc_3PFe(CO)_4\}^*$ molecules (above).

In an effort to substantiate this and produce III at the same time, the irradiation of I with both $Fe(CO)_5$ and Fc_3P present (expt. 6) succeeded only in producing more I in 46% yield. The inability to produce III in this case can be attributed to the abundance of unreacted phosphine still present in the reaction mixture, and underscores the requirement that if III is to be obtained from I as reactant, the molecular environment that prevails during the reaction of Fc_3P with $Fe(CO)_5$ must be rigorously duplicated! To do so, however, presents a formidable, if not impossible task.

Configuration of the triferrocenylphosphineiron carbonyls
Tables 2 and 3 summarize the CO stretching frequencies of the triferrocenyl-

TABLE 2

CO STRETCHING FREQUENCIES OF $LFe(CO)_4$ AND $L_2Fe(CO)_3$; L = Fc_3P AND Ph_3P

Complex	Medium	$\nu(CO)$ [a] (cm^{-1})				Ref.
$Fc_3PFe(CO)_4$ (I)	$CHCl_3$	2042ms	1961m	1930s	1923s(sh)	This work [b]
	CH_2Cl_2	2041ms	1957m		1922s	This work
	CS_2	2042ms	1962m		1927s	This work
$Ph_3PFe(CO)_4$	$CHCl_3$	2059	1978		1938	14
	CH_2Cl_2	2062	1982		1940	15
	CS_2	2063	1982		1943	14
$(Fc_3P)_2Fe(CO)_3$ (II)	$CHCl_3$	1877s	1862m			This work
	CH_2Cl_2	1875s				This work
	CS_2	1874s				This work
$(Ph_3P)_2Fe(CO)_3$	$CHCl_3$	1887				14
	CH_2Cl_2	1883				15
	CS_2	1886				14

[a] s = strong; ms = moderately strong; m = medium; sh = shoulder. [b] A similar spectrum has been reported [1].

TABLE 3

CO STRETCHING FREQUENCIES OF $L_3Fe(CO)_2$; $L = Fc_3P$, Ph_3P AND $(p\text{-}FC_6H_4)_3P$

$L_3Fe(CO)_2$ {Method of preparation}	Medium	$\nu(CO)^a$ (cm^{-1})		Ref.
$(Fc_3P)_3Fe(CO)_2$ (III)	Nujol	1920 (1)	1854 (1.2)	This work
{Fc_3P + $Fe(CO)_5$ + $h\nu$}	$CHCl_3$	1921 (1)	1850 (1.2)	This work
	CH_2Cl_2	1922 (1)	1852 (1.3)	This work
	CS_2	1925 (1)	1860 (1.1)	This work
	THF	1929 (1)	1865 (1.0)	This work
$(Fc_3P)_3Fe(CO)_2$ (IV)	Nujol	1969 (1)	1910 (1.3)	This work
{Fc_3P + $C_4H_6Fe(CO)_3$ + Δ}	$CHCl_3$	1967 (1)	1901 (1.1)	This work
	CH_2Cl_2	1968 (1)	1903 (1.3)	This work
	CS_2	1973 (1)	1912 (1.0)	This work
	THF	1969 (1)	1909 (1.0)	This work
$(Ph_3P)_3Fe(CO)_2$ (V)				4
{Ph_3P + $C_4H_6Fe(CO)_3$ or				
$C_7H_8Fe(CO)_3$}	CS_2	1982	1923	4
$[(p\text{-}FC_6H_4)_3P]_3Fe(CO)_2$ (VI)				
{$(p\text{-}F(C_6H_4)_3P$ + $C_7H_8Fe(CO)_3$}	Nujol	1982	1928	8
$(Ph_3P)_3Fe(CO)_2$ (VII)				
{Ph_3P + $(Ph_3P)_2Fe(CO)_2Br_2$ + Na/Hg}	THF	1894	1841	7

^{a} All bands are intense. Relative intensities are shown in parentheses.

phosphineiron carbonyls and analogous phenylphosphine complexes. On the basis of the selection rules derived by Cotton and Parish [14], the three- and one-band spectra of I and II, respectively, in both CS_2 and CH_2Cl_2 (Table 2) indicate that the Fc_3P ligands very probably occupy the axial positions of trigonal bipyramidal configurations of C_{3v} and D_{3h} symmetry, respectively, as in the case of Ph_3P.

The extra carbonyl band shown by I and II at 1930 and 1862 cm^{-1}, respectively, in $CHCl_3$ (Table 2) is attributed to band (possibly E-mode *) splitting resulting from distortion of the complexes to lower symmetry by hydrogenbonding of solvent molecules. Similar absorptions are to be expected employing ethanol as solvent; however, the low solubility of the complexes precludes observing definitive spectra in that solvent. The possibility that the four- and two-band spectra of I and II, respectively, in $CHCl_3$ might be due to the existence of equatorially substituted trigonal bipyramidal configurations or others [14] in that solvent is discounted in view of the similarity of the spectra to those taken in CS_2 and CH_2Cl_2. A symmetry other than D_{3h} in the case of II, moreover, would imply that a third band is present in the spectrum [14], but is hidden from view.

With Fc_3P in place of Ph_3P, the CO stretching modes of the mono- and bis-

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* Cullen and co-workers have suggested that an asymmetric substituent gives rise to E-mode splitting in a C_{3v} spectrum [16].
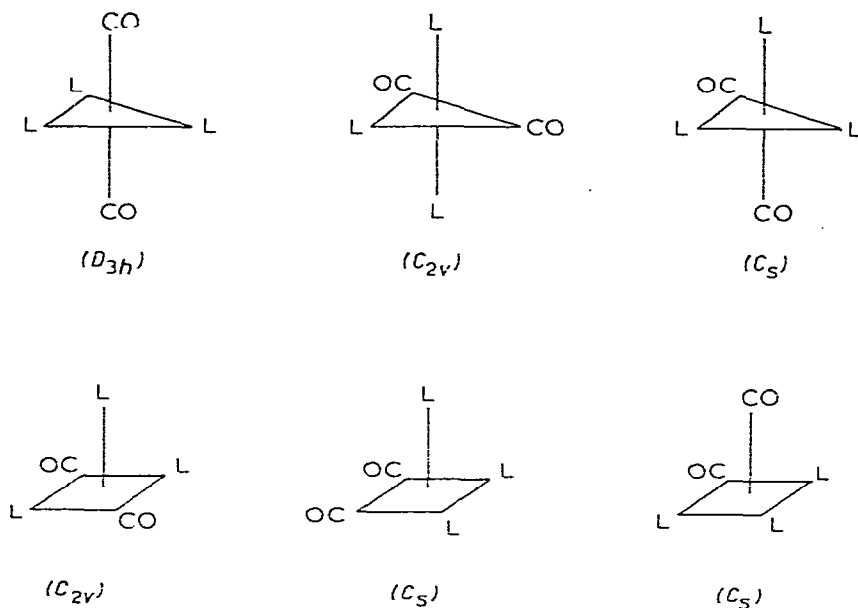
CO
L
L — L
L
CO

(D_{3h})

L
OC
L — CO
L

(C_{2v})

L
OC
L — L
CO

(C_s)

L
OC — L
L — CO

(C_{2v})

L
OC — L
OC — L

(C_s)

CO
OC — L
L — L

(C_s)

Fig. 1. Some of the discussed symmetry structures.

(phosphine)iron carbonyls are shifted approximately 10—20 cm^{-1} to lower energies (Table 2), in accordance with results of recent studies which confirmed that Fc$_3$P is a stronger σ-donor than Ph$_3$P [1,2]. A similar shift is seen in the case of the tris(phosphine)iron carbonyls (IV, V and VI) prepared from butadiene- and/or cycloheptatriene-iron tricarbonyls (Table 3), and it is thus reasonable to assume that complexes IV, V and VI have the same structural configuration. Based on the data in Table 3, such configuration must be different from that of either III or the tris(triphenylphosphine) complex (VII) obtained via reduction of triphenylphosphine-substituted iron carbonyl halides. It is apparent that structurally different tris(phosphine) iron dicarbonyls are produced depending upon the method of formation.

The two-band spectra of the tris(phosphine) complexes (Table 3) are consistent with several possible trigonal bipyramidal and tetragonal pyramidal structures of C_{2v} or C_s symmetry (Fig. 1) based on the selection rules summarized by Manuel [17]. A trigonal bipyramid of D_{3h} symmetry requires only one IR-active CO vibration, and is excluded from further consideration since band-splitting is not in evidence (Table 3). The trigonal bipyramid of C_{2v} symmetry can be discounted, and the possible configurations for complexes III and IV narrowed to the trigonal bipyramid of C_s symmetry, and any of the three tetragonal pyramids, based on the finding that the band intensity ratios for III and IV are close to unity (Table 3) *. This is in accord with assignment of the C_{2v} trigonal bipyramidal configura-

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* The small deviations from unity are probably indicative of some distortion of the molecules. The intensities of the CO vibrational modes are related to the dipole moment change during the CO stretch (μ'_{MCO}) and α (the angle between the bisecting plane of symmetry and one of the sides in the trigonal or tetragonal plane). For the C_{2v} trigonal bipyramid ($A_1 + B_2$ vibrations): $I_{A_1} = 2 G_{tt} \cos^2\alpha(\mu'_{MCO})^2$ and $I_{B_2} = 2 G_{tt} \sin^2\alpha(\mu'_{MCO})^2$ where $\alpha \cong 60°$. Assuming all μ'_{MCO}'s are approx-

tion to the tris(triphenyl)phosphine complex VII [7].

It is tempting to suggest that complex IV, hence complexes V and VI as well, are more probably tetragonal pyramidal than III in view of their formation from precursors that approximate tetragonal pyramids; that the tetragonal pyramid is more likely to show C_s than C_{2v} symmetry in view of the *cis* configuration of the precursors *. However, in the absence of supporting evidence, any suggestion that product structure is kinetically determined by reactant structure in the case of 5-coordinate complexes known for their flucionality and ease of trigonal bipyramidal-tetragonal pyramidal interconversion, must be viewed with caution **.

Experimental

General

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. GC analysis for $Fe(CO)_5$ was obtained on a Hewlett—Packard F & M 5750 gas chromatograph (8-ft column, 20% Apiezon T on 70-80 mesh WAWDMCS 5756). Spectra were obtained on a Perkin—Elmer 521 infrared spectrophotometer. Relative intensities (Table 3) were obtained from areas under the bands determined with a planimeter. Iron pentacarbonyl was obtained from Strem Chemicals, Inc. Butadieneiron tricarbonyl was obtained from Research Organic/Inorganic Chemical Corp. Triferrocenylphosphine was prepared as previously [22].

General procedure for work-up of reaction mixtures

Volatiles were removed in a rotary vacuum evaporator under reduced pressure. Residues were extracted with boiling benzene in portions until the extracts were nearly colorless. The combined extracts were chromatographed on activated alumina (chromatographic grade; 80-200 mesh). Elution with benzene afforded unchanged Fc_3P followed by $Fc_3PFe(CO)_4$ (I) or $(Fc_3P)_3Fe(CO)_2$ (III). Unchanged $C_4H_6Fe(CO)_3$ and $(Fc_3P)_3Fe(CO)_2$ (IV) preceded Fc_3P in that order, as applicable. Elution last with chloroform removed the oxide of Fc_3P [21] if present. The benzene-insoluble residue was washed with benzene, and the suspended brown solids were separated by decantation from $(Fc_3P)_2Fe(CO)_3$ (II) as applicable.

$Fc_3PFe(CO)_5$ (I) from $Fe(CO)_5$ and Fc_3P

In a Pyrex reaction flask, triferrocenylphosphine (4.1 g, 7.0 mmol) and iron

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imately the same [18]. I_{B_2}/I_{A_1} = 3.0. For the C_s trigonal bipyramid (A' + A'' vibrations): $I_{A'}$ = 2 $G_{tt}(\mu'_{MCO})^2$ and $I_{A''}$ = 2 $G_{tt}[\cos^2\alpha(\mu'_{MCO})^2 + \sin^2\alpha(\mu'_{MCO})^2]$, and consequently $I_{A'}/I_{A''}$ = 1.0. For the C_s tetragonal pyramids (2 A' vibrations): Assuming no vibrational coupling, $I_{A'}$ = 2 G_{tt}-$(\mu'_{MCO})^2$ and consequently $I_{A'}/I_{A'}$ = 1.0. For the C_{2v} tetragonal pyramid (A_1 + B_2 vibrations): I_{A_1} = 2 $G_{tt} \cos^2\alpha(\mu'_{MCO})^2$ and I_{B_2} = 2 $G_{tt} \sin^2\alpha(\mu'_{MCO})^2$ where $\alpha \cong 45°$, and consequently I_{B_2}/I_{A_1} = 1.0. The authors thank Dr. J. Lannon for assistance in formulating this rationale, and a reviewer for suggesting that relative band intensities be taken into account in considering structures for complexes III and IV.

* It is reasonable to assume that cycloheptatrieneiron tricarbonyl, like the basally *cis*-1,3-dieneiron tricarbonyl moiety [19], approximates a tetragonal pyramid since one of the three double bonds is non-coordinated; cf. [20,21].

** This point was emphasized by a reviewer.

pentacarbonyl (2.7 g, 14 mmol) in n-heptane (200 ml) were irradiated under
nitrogen or argon with a 140 W (Hanovia) ultraviolet lamp external to the flask
for 5 h with stirring. The reaction flask and lamp were wrapped with aluminum
foil to concentrate the light and maintain refluxing by means of the heat gener-
ated from the lamp. Work-up according to the general procedure above gave 4.9
g (93%) of I; reddish orange crystals from benzene, m.p. (infusible) (lit. [1]
225—230°C, dec.). Anal.: Found: C, 54.27; H, 3.48; O, 8.46; P, 4.19. $C_{34}H_{27}$-
Fe_4O_4P calcd.: C, 54.16; H, 3.61; O, 8.49; P, 4.11%. The IR spectrum taken
from a Nujol mull showed intense bands in the CO stretching region at 2050,
1978, 1960, 1949 and 1929 cm^{-1}, besides the principal absorptions contained
in the spectrum of Fc_3P [21]. CO stretching frequencies taken from solutions
are shown in Table 2.

$(Fc_3P)_3Fe(CO)_2$ (III) from $Fe(CO)_5$ and Fc_3P

In a procedure similar to the preceding, the reaction was carried out under
argon, and the reaction time was extended to 24 h. Work-up according to the
general procedure above gave 4.2 g (96%) of III; dark orange crystal, m.p. 248—
250°C (benzene) on immersion of the sample in the heating bath ~200°C. Anal.:
Found: C, 59.07; H, 4.31; O, 2.02; P, 4.46. $C_{92}H_{81}Fe_{10}O_2P_3$ calcd.: C, 59.09; H,
4.37; O, 1.71; P, 4.97%. The IR spectrum taken from a Nujol mull showed ν(CO)
cited in Table 3, besides the principal absorptions contained in the spectrum of
Fc_3P [21].

Table 1 summarizes the results of related reactions attempted under modified
conditions *.

$(Fc_3P)_2Fe(CO)_3$ (II) from $Fc_3PFe(CO)_4$ (I)

In a procedure similar to the preceding, triferrocenylphosphineiron tetracar-
bonyl (1.5 g, 2.0 mmol) in n-heptane (100 ml) was irradiated under argon for
24 h with stirring. For several hours during this period, with the argon inlet
closed and the top of the condenser connected via a cold trap (Dry Ice/acetone)
to a capture tube, gaseous (CO) evolution was observed by displacement of
water. Work-up according to the general procedure above afforded 0.3 g (20%)
of unchanged I and 0.5 g (38%) of II. The latter was identical to the product
obtained thermally (below), as determined by IR spectrum. Iron pentacarbonyl
in low concentration was detected in the heptane phase of the reaction mixture
by gas chromatography.

Complex II was obtained in nearly 40% yield when the reaction was con-
ducted in benzene. Approximately 50% of I was recovered unchanged.

The same reaction, conducted in 200 ml of n-heptane with 1.2 g (2.0 mmol)
of triferrocenylphosphine present, afforded 0.6 g of 2 (23% based on substitu-
tion), and 1.1 g (73%) of I unchanged. With iron pentacarbonyl (0.5 ml) present
instead of Fc_3P, II was not obtained, and 93% of $Fc_3PFe(CO)_4$ was recovered
unchanged. In a reaction with both iron pentacarbonyl and triferrocenylphos-
phine present, I was recovered unchanged, and in addition, more I was obtained
in 46% yield.

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* A water-cooled immersion-type UV lamp (100 W, quartz jacketed Ace—Hanovia) was employed
for the attempted photochemical reaction at 20°C (Table 1).

$(Fc_3P)_2Fe(CO)_3$ (II) from $Fc_3PFe(CO)_4$ (I) and Fc_3P

Triferrocenylphosphine (1.2 g, 2.0 mmol) and triferrocenylphosphineiron tetracarbonyl (1.5 g, 2.0 mmol) in decalin (125 ml) were heated under nitrogen at 180—190°C for 5 h with stirring. The insoluble solids were collected on a filter, and the brown portion was removed by sedimentation in benzene (cf. general procedure) from 2.25 g (86%) of II; yellow-orange powder from chlorobenzene, m.p. (infusible). They yield (2.5 g) was practically quantitative when the reaction period was extended to 24 h. Anal.: Found: C, 57.70; H, 4.27; O, 4.04; P, 4.73. $C_{63}H_{54}Fe_7O_3P_2$ calcd.: C, 57.67; H, 4.15; O, 3.66; P, 4.72%. The IR spectrum taken from a Nujol mull showed a weak band at 1980 and intense bands at 1893 and 1875 cm^{-1} in the CO stretching region, besides the principal absorptions contained in the spectrum of Fc_3P [21]. CO stretching frequencies taken from solutions are shown in Table 2.

In another run without Fc_3P present, CO gas evolution was detected as in the preceding, and work-up of the reaction mixture yielded only triferrocenylphosphine oxide.

$(Fc_3P)_3Fe(CO)_2$ (IV) from $C_4H_6Fe(CO)_3$ and Fc_3P

Triferrocenylphosphine (11.7 g, 20 mmol) and butadieneiron tricarbonyl (3.9 g, 20 mmol) in n-octane (150 ml) were refluxed under nitrogen for 24 h. Work-up according to the general procedure above gave 9.0 g (77%) of unchanged Fc_3P, and 2.7 g (21%) of IV; orange crystals, m.p. 230—232°C (dec.) (benzene/heptane) on immersion of the sample in the heating bath ~200°C. Anal.: Found: C, 58.90; H, 4.55; O, 2.08; P, 4.52. $C_{92}H_{81}Fe_{10}O_2P_3$ calcd.: C, 59.09; H, 4.37; O, 1.71; P, 4.97%. The IR spectrum taken from a Nujol mull showed $\nu(CO)$ cited in Table 3, besides the principal absorptions contained in the spectrum of Fc_3P [21].

References

1 C.U. Pittman, Jr. and G.O. Evans, J. Organometal. Chem., 43 (1972) 361.
2 J.C. Kotz and C.L. Nivert, J. Organometal. Chem., 52 (1973) 387.
3 J. Lewis, R.S. Nyholm, S.S. Sandhu and M.H.B. Stiddard, J. Chem. Soc., (1964) 2825, and references cited therein.
4 T.A. Manuel and F.G.A. Stone, J. Amer. Chem. Soc., 82 (1960) 366.
5 R. Pettit and G.F. Emerson, Adv. Organometal. Chem., 1 (1964) 21, and refs. therein.
6 A. Reckziegel and M. Bigorgne, C. R. Acad. Sci. Paris, Sér. C, 258 (1964) 4065.
7 W. Hieber and J. Muschi, Chem. Ber., 98 (1965) 3931.
8 F.T. Delbeke and G.P. Van Der Kelen, J. Organometal. Chem., 21 (1970) 155.
9 E.E. Siefert and R.J. Angelici, J. Organometal. Chem., 8 (1967) 374.
10 H. Werner, Angew. Chem. Int. Ed., 7 (1968) 930.
11 T.A. Magee, C.H. Matthews, T.S. Wang and J.H. Wotiz, J. Amer. Chem. Soc., 83 (1961) 3200; H. Behrens and N. Harder, Ber., 97 (1964) 426.
12 P. Kirsch, J. Buchkremer, O. Jaenicke, R. Knoesel, R. Rumin, J. Shields and E. Koerner van Gustorf, Abstracts of First Meeting of the Division of Photochemistry, Gesellschaft Deutscher Chemiker, Göttingen, November, 1973.
13 W. Strohmeier, Angew. Chem. Int. Ed., 3 (1964) 730 and refs. cited therein.
14 F.A. Cotton and R.V. Parish, J. Chem. Soc., (1960) 1440.
15 A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1962) 3653.
16 W.R. Cullen, D.A. Harbourne, B.V. Liengme and J.R. Sams, Inorg. Chem., 8 (1969) 1464.
17 T.A. Manuel, Adv. Organometal. Chem., 3 (1965) 190.
18 M.Y. Darensbourg and D. Burns, Inorg. Chem., 13 (1974) 2970.
19 F.A. Cotton, V.W. Day, B.A. Frenz, K.I. Hardcastle and J.M. Troup, J. Amer. Chem. Soc., 95 (1973) 4522.
20 R. Burton, L. Pratt and G. Wilkinson, J. Chem. Soc., (1961) 594.
21 L. Kruczynski and J. Takats, J. Amer. Chem. Soc., 93 (1974) 932.
22 G.P. Soliott and W.R. Peterson, Jr., J. Organometal. Chem., 19 (1969) 143.