Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

STUDIES ON SUBSTITUTION, INSERTION AND DECARBONYLATION REACTIONS OF SOME CYCLOPENTADIENYLIRON COMPLEXES WITH PHOSPHORUS DONOR LIGANDS

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(Received September 22nd, 1970)

SUMMARY

The phosphite complexes $C_5H_5Fe(CO)[P(OR)_3]CH_3$ ($R = CH_3$, n-C_4H_9 or C_6H_5) have been synthesized by the interaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ with $P(OR)_3$ in tetrahydrofuran at reflux. They react readily with liquid SO_2 to afford the corresponding *S*-sulfinates, $C_5H_5Fe(CO)[P(OR)_3](SO_2CH_3)$. The reaction between $C_5H_5Fe(CO)_2CH_3$ and $P(C_6H_5)_3$ in hydrocarbon solvents at reflux yields initially $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$, which then undergoes decarbonylation to $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$. However, in refluxing dioxane, $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$ has been obtained as the only major carbonyl product. The corresponding dicarbonyl ethyl complex, $C_5H_5Fe(CO)_2C_2H_5$, reacts with $P(C_6H_5)_3$ in heptane at reflux to give $C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$ and $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$. The chloride has been shown to arise from the reaction of $CHCl_3$ with $C_5H_5Fe(CO)[P(C_6H_5)_3]H$, which results from loss of ethylene by $C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$. Photochemical reactions between $C_5H_5Fe(CO)_2C_2H_5$ and $P(C_6H_5)_3$ in petroleum ether yield $C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$ directly, without the intermediacy of $C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$. Contrary to a previous report, ultraviolet irradiation of $C_5H_5Fe(CO)[P(C_6H_5)_3](COR)$ ($R = CH_3$ or C_2H_5) in hydrocarbon solvents under several different conditions affords the corresponding $C_5H_5Fe(CO)[P(C_6H_5)_3]R$ in moderate to good yields.

INTRODUCTION

Studies on sulfur dioxide and tetracyanoethylene insertion reactions into transition metal–carbon bonds, conducted in our laboratory[1,2], necessitated synthesis of a number of complexes of the type $C_5H_5Fe(CO)(L)R$, where L is a phosphorus donor ligand. Although such compounds with tertiary phosphines as L are readily accessible by the literature methods[3,4], the corresponding phosphite carbonyls have been investigated only when R is an aryl group[4]. We have therefore examined two general reactions expected to lead to the formation of $C_5H_5Fe(CO)[P(OR')_3]R$; they are (*a*) decarbonylation of $C_5H_5Fe(CO)[P(OR')_3](COCH_3)$ and (*b*) ligand exchange in $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ using $P(OR')_3$. The results of our experiments are described herein. Also as part of this study, reaction of triphenylphosphine with $C_5H_5Fe(CO)_2CH_3$ and $C_5H_5Fe(CO)_2C_2H_5$ as well as decarbonylation of $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$ and $C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$ under several different experimental conditions have been examined. The results are presented and compared with those from related studies reported in the literature.

EXPERIMENTAL

The complexes $C_5H_5Fe(CO)_2CH_3$[5], $C_5H_5Fe(CO)_2C_2H_5$[5], $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$[3], $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$[6], and $C_5H_5Fe(CO)[P(OC_6H_5)_3](COCH_3)$[6] were prepared according to the literature methods. Triphenylphosphine was purchased from Matheson, Coleman and Bell whereas triphenyl phosphite was obtained from Aldrich Chemical Co. Trimethyl phosphite and tri-n-butyl phosphite were supplied by Eastman Organic Chemicals. All were used as received. Anhydrous grade sulfur dioxide, from Matheson, was passed through concentrated H_2SO_4 and a $P_4O_{10}/CaCl_2$ column before condensation. Tetrahydrofuran (THF) and dioxane were distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. All other chemicals and solvents, with the exception of petroleum ether (b.p. 60–110°), were of reagent grade or equivalent. Ventron alumina (neutral, grade III, except as noted) was employed in chromatographic separations and purifications.

Ultraviolet irradiations were carried out either with a 450-w Hanovia high-pressure quartz mercury-vapor lamp in a reaction vessel described earlier[6], or in pyrex test tubes using a Rayonet Model MGR-100 photochemical reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) with 3500 Å or 2537 Å lamps. All thermal and photochemical reactions were conducted under the atmosphere of dry nitrogen. A varying degree of decomposition into dark, insoluble, noncarbonyl materials invariably accompanied all of the reactions; some losses were also sustained in the course of chromatographic separations and/or purifications.

IR spectra were recorded on a Perkin–Elmer Model 337 spectrophotometer. A pair of matched 0.05-mm KBr cells was employed for solution measurements. ^1H NMR spectra were obtained using a Varian Associates A-60 spectrometer with tetramethylsilane as an internal reference. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Reaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ with $P(OR)_3$ ($R = CH_3$, n-C_4H_9 or C_6H_5)

A tetrahydrofuran solution (25 ml) of 0.50 g (1.2 mmoles) $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ and ca. 1.5 mmoles phosphite was heated at reflux until disappearance of the IR CO stretching band of the starting monocarbonyl (ca. 12 h). The mixture was cooled to 25° and filtered to remove an insoluble, noncarbonyl brown solid. Solvent was removed from the filtrate under reduced pressure (ca. 20 mm), the residue was dissolved in 10 ml of chloroform, and the resulting solution was chromatographed. In all cases, only one yellow band was eluted with $CHCl_3$. Removal of the solvent and addition of pentane with scratching afforded bright yellow crystals of $C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$. The other two phosphite complexes, $C_5H_5Fe(CO)[P(OCH_3)_3]CH_3$ and $C_5H_5Fe(CO)[P(OC_4H_9)_3]CH_3$, isolated as yellow oils, could not be induced to crystallize. They were freed of the contaminating $P(C_6H_5)_3$

TABLE 1

MELTING POINTS AND ANALYTICAL DATA FOR NEW CYCLOPENTADIENYLIRON CARBONYL COMPLEXES

Compound	M.p. (°C)[a]	C (%)		H (%)	
		Found	Calcd.	Found	Calcd.
$C_5H_5Fe(CO)[P(OCH_3)_3](SO_2CH_3)$	138	35.41	34.09	5.09	4.83
$C_5H_5Fe(CO)[P(OC_4H_9)_3](SO_2CH_3)$	oil	47.97	47.70	7.24	7.32
$C_5H_5Fe(CO)[P(OC_6H_5)_3](SO_2CH_3)$	[c]	55.61	55.76	4.16	4.28
$C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$	106				
$C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$	159–160	69.02	69.23	5.33	5.34
$C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$	155	71.02	70.91	5.78	5.68
$C_5H_5Fe(CO)[P(C_6H_5)_3]H$[b]	130 dec.	70.17	69.90	5.24	5.10

[a] Uncorrected. [b] Mol. wt. found (osmometry, *ca.* 0.01 *M* C_6H_6 solution, with a Mechrolab Model 301-A instrument): 396; calcd.: 412. [c] Not measured.

TABLE 2

IR AND ^{1}H NMR SPECTRA OF NEW CYCLOPENTADIENYLIRON CARBONYL COMPLEXES

Compound	IR spectrum (cm^{-1})[a]		^{1}H NMR spectrum[d]		
	CO stretch[b]	SO stretch[c]	Chem. shift (τ)	Rel. int.	Assignment
$C_5H_5Fe(CO)[P(OCH_3)_3]CH_3$	1930		10.13d (*J* 5Hz)	3	CH_3
			6.43d (*J* 11Hz)	9	OCH_3
			5.48s	5	C_5H_5
$C_5H_5Fe(CO)[P(OCH_3)_3](SO_2CH_3)$	1984	1165	7.0s	3	SO_2CH_3
		1030	6.15d (*J* 11Hz)	9	OCH_3
			5.10s	5	C_5H_5
$C_5H_5Fe(CO)[P(OC_4H_9)_3]CH_3$	1923		10.17d (*J* 5Hz)	3	CH_3
			9.11–8.35cp	21	$CH_2CH_2CH_3$
			6.11m	6	OCH_2
			5.46s	5	C_5H_5
$C_5H_5Fe(CO)[P(OC_4H_9)_3](SO_2CH_3)$	1990	1176	9.0–8.4cp	21	$CH_2CH_2CH_3$
		1030	7.0s	3	SO_2CH_3
			5.85bq[h]	6	OCH_2
			5.15s	5	C_5H_5
$C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$	1940		9.90d (*J* 6Hz)	3	CH_3
			5.98s	5	C_5H_5
			2.7m	15	C_6H_5
$C_5H_5Fe(CO)[P(OC_6H_5)_3](SO_2CH_3)$	1990	1190			
		1038			
$C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$	1918[e]		9.40t (*J* 7Hz)	3	CH_3
	1600(m)[f]		7.30m	2	CH_2
			5.60s	5	C_5H_5
			2.7m	15	C_6H_5
$C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$	1901				
$C_5H_5Fe(CO)[P(C_6H_5)_3]H$	1923[g]				

[a] All bands are strong. [b] CH_2Cl_2 solution. [c] Nujol mull. [d] $CDCl_3$ solution; s, singlet; d, doublet; t, triplet; bq, apparent broad quartet; m, multiplet; cp, complex pattern [e] Terminal CO. [f] Acyl CO. [g] C_6H_6 solution [h] Separation ~6Hz.

by dissolution in 20 ml of pentane, addition of *ca.* 5 ml of CH_3I, and concentration in a stream of nitrogen to precipitate $[P(C_6H_5)_3CH_3]I$, which was removed by filtration.

All three complexes were converted to the corresponding $C_5H_5Fe(CO)[P(OR)_3](SO_2CH_3)$ derivatives by the reaction with SO_2 at reflux for *ca.* 1 h. Purification of the yellow sulfinates was effected by chromatography on alumina using $CHCl_3$ eluent. The yields, based on $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$, ranged from 60 to 65%. The analytical results for the sulfinates are given in Table 1, whereas the pertinent IR and ^1H NMR data for all new phosphite complexes (both the alkyls and the sulfinates) are presented in Table 2.

Decarbonylation of $C_5H_5Fe(CO)[P(OC_6H_5)_3](COCH_3)$

(*a*). *In refluxing heptane.* A solution of 0.5 g (1 mmole) of $C_5H_5Fe(CO)[P(OC_6H_5)_3](COCH_3)$ in 25 ml of heptane was heated at reflux for 60 h. Removal of the solvent and chromatography on alumina afforded trace quantities of the unreacted material and $C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$. Considerable decomposition was noted.

When this same reaction was run for 24 h, only the starting material and a trace of $C_5H_5Fe(CO)_2CH_3$ could be detected in the product mixture.

(*b*). *In petroleum ether under ultraviolet irradiation.* Ultraviolet irradiation with the 450-w Hanovia lamp of a solution of $C_5H_5Fe(CO)[P(OC_6H_5)_3](COCH_3)$ (0.5 g, 1 mmole) in petroleum ether for 7 h at 30–35° yielded only noncarbonyl decomposition products. Shorter reaction periods led to a recovery of the starting material; no $C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$ could be detected.

Reaction of $C_5H_5Fe(CO)_2CH_3$ *with* $P(C_6H_5)_3$

A solution of equimolar amounts of $C_5H_5Fe(CO)_2CH_3$ (1–6 g) and $P(C_6H_5)_3$ in hexane, heptane, or dioxane was heated at reflux for 48 h or until completion of the reaction was indicated by disappearance of the IR CO stretching frequencies of the parent dicarbonyl. The mixture was then allowed to cool to room temperature, solvent was removed under reduced pressure, and the residue was treated with 10 ml of chloroform. The extract was filtered and the filtrate chromatographed on an alumina column eluting first with pentane/chloroform and then with chloroform. The order of elution was as follows: (1) $C_5H_5Fe(CO)_2CH_3$, (2) $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$, (3) $[C_5H_5Fe(CO)_2]_2$, and (4) $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$. Concentration of

TABLE 3

YIELDS OF VARIOUS CYCLOPENTADIENYLIRON CARBONYLS ISOLATED FROM THE REACTION BETWEEN $C_5H_5Fe(CO)_2CH_3$ AND $P(C_6H_5)_3$ IN DIFFERENT SOLVENTS HEATED AT REFLUX

Solvent	Approx. (°C)	Time (h)	Yields of compounds[a] isolated (%)			
			(I)	(II)	(III)	(VII)
Hexane	69	48	26	60	2	
Heptane	99	42		13	45	4
Dioxane	102	41		30	3	2

[a] (I) = $C_5H_5Fe(CO)_2CH_3$; (II) = $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$; (III) = $C_5H_5(CO)[P(C_6H_5)_3]CH_3$; (VII) = $[C_5H_5Fe(CO)_2]_2$.

the eluate from each band and addition of pentane yielded the respective compound, identified by its melting point an/or its IR spectrum. The yields of all products from these reactions are given in Table 3.

Decarbonylation of $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$

(*a*). *Thermal.* A solution of $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$ (0.5–0.6 g) in hexane, cyclohexane, heptane, or dioxane was heated at reflux for 12–45 h. Removal of the solvent and work-up of the residue in the manner described above afforded the compounds whose yields are listed in Table 4.

TABLE 4

YIELDS OF VARIOUS CYCLOPENTADIENYLIRON CARBONYLS ISOLATED FROM ATTEMPTED DECARBONYLATIONS OF $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$ UNDER DIFFERENT CONDITIONS

Solvent	Approx. temp. (°C)	Time (h)	Yields of compounds[a] (%)			
			(I)	(II)	(III)	(VII)
Hexane[b]	69	42		84	1	
Cyclohexane[b]	82	45	Trace	50	10	
Heptane[b]	99	20	Trace	25	27	10
Dioxane[b,c]	102	12	Trace	40	[i]	
Petroleum-ether[d]	30–35	1		20	64	Trace
Petroleum ether[d]	30–35	5			40	
Petroleum ether[e,f]	40–45	5		10[h]	24	Trace
Benzene[e,g]	40–45	4		25[h]	40	

[a] See footnote [a] in Table 3. [b] Heated at reflux. [c] White noncarbonyl precipitate forms after ca. 5 h. [d] Irradiated with Hanovia 450-w lamp. [e] Irradiated in Rayonet MGR-100 reactor. [f] At 3500 Å. [g] At 2537 Å. [h] UV spectrum of (II) shows a shoulder at ca. 3500 Å and a maximum at 2270 Å (ε 9840 l·mole^{-1}·cm^{-1}) in an 8.8×10^{-5} *M* hexane solution using a Cary Model 14 spectrometer. [i] None detected during longer (up to 60 h) or shorter reaction times.

(*b*). *Photochemical.* Ultraviolet irradiation of a solution of $C_5H_5Fe(CO)$-$[P(C_6H_5)_3](COCH_3)$ (*ca.* 0.5 g) in petroleum ether or benzene, followed by the usual work-up, gave the products whose yields are included in Table 4.

Thermal treatment of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$

Heating a solution of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ (0.3 g) in hexane (50 ml) at reflux for 27 h, followed by the usual work-up, resulted in the recovery of 70% of the starting material.

A similar treatment of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ in heptane at reflux for 17 h led to an extensive decomposition and gave only 23% of the reactant. In dioxane at reflux for 20 h, 20% of the starting material was recovered and trace amounts of $C_5H_5Fe(CO)_2CH_3$ and $[C_5H_5Fe(CO)_2]_2$ were isolated.

Reaction of $C_5H_5Fe(CO)_2C_2H_5$ with $P(C_6H_5)_3$

A solution of equimolar amounts of $C_5H_5Fe(CO)_2C_2H_5$ (4.5 g, 22 mmoles) and $P(C_6H_5)_3$ (5.7 g, 22 mmoles) in 100 ml of heptane was heated at reflux, progress of the reaction being monitored by IR spectroscopy. After *ca.* 12 h, orange crystals were observed at the bottom of the flask. When no further changes could be detected in the IR spectrum of the solution (*ca.* 48 h), the mixture was allowed to cool to room temperature. Concentration to 15 ml afforded additional orange crystals, which were collected on a filter and washed with heptane. The compound, shown to be $C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$, was purified by chromatography on alumina using chloroform eluent; yield, 6.3 g (62%). All analytical and spectral data are given in Tables 1 and 2, respectively.

Chromatography of the filtrate using 1/1 pentane/chloroform eluent afforded trace quantities of $C_5H_5Fe(CO)_2C_2H_5$ and $[C_5H_5Fe(CO)_2]_2$ as well as olive green crystals (1.0 g), ν(CO) 1956 cm^{-1} (CH_2Cl_2 soln.), m.p. 143°, identified as $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$[3]. This compound was shown to result from the interaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]H$, formed in the reaction between $C_5H_5Fe(CO)_2C_2H_5$ and $P(C_6H_5)_3$, with the solvent $CHCl_3$ (*vide infra*).

Ultraviolet irradiation with the 450-w Hanovia lamp of a solution of equimolar amounts of $C_5H_5Fe(CO)_2C_2H_5$ (3.0 g, 15 mmoles) and $P(C_6H_5)_3$ (3.9 g, 15 mmoles) in petroleum ether at 30–35° for 3 h, followed by the usual work-up and chromatography on alumina eluting with pentane/chloroform, gave, in the order of elution: (1) the orange-red $C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$ (40%), (2) $[C_5H_5Fe(CO)_2]_2$ (2%), and (3) $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$ (0.45 g). The analytical and spectral data for $C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$ are given in Tables 1 and 2, respectively.

When a similar reaction, using 2.4 g of $C_5H_5Fe(CO)_2C_2H_5$, was stopped after 1 h, 15% $C_5H_5Fe(CO)_2C_2H_5$, 30% $C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$, and 0.3 g of $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$ were isolated; also, a trace amount of $[C_5H_5Fe(CO)_2]_2$ was detected.

Decarbonylation of $C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$

Partly dissolved $C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$ (0.90 g, 1.9 mmoles) in 100 ml of petroleum ether was irradiated with the 450-w Hanovia lamp for 1 h at 30–35°. The mixture was then treated as described earlier; 0.01 g (1%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$ and 0.5 g of $C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$ were isolated.

Thermal treatment of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$

A solution of $C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$ (0.5 g) in heptane (20 ml) was heated at reflux for 20 min. The mixture was allowed to cool to room temperature, the insoluble, noncarbonyl brown solid (0.15 g) was filtered off, and the yellow solution was evaporated to dryness in a stream of nitrogen. The residue was dissolved in 10/1 pentane/ether and chromatographed on a grade IV alumina column. Two bands were developed: yellow and purple. Removal of the solvent from the yellow band afforded 0.10 g of a solid which analyzed for $C_5H_5Fe(CO)[P(C_6H_5)_3]H$ (see Table 1). Its spectral data are presented in Table 2. The compound reacts readily with $CHCl_3$ or CCl_4 to give the olive green $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$.

The second, purple band yielded 0.01 g of $[C_5H_5Fe(CO)_2]_2$.

RESULTS AND DISCUSSION

Of the preparative methods for $C_5H_5Fe(CO)[P(OR)_3]CH_3$ examined in this ly the best proved to be replacement of $P(C_6H_5)_3$ in $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ ı $P(OR)_3$ ($R=CH_3$, $n\text{-}C_4H_9$ or C_6H_5):

$$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3+P(OR)_3 \xrightarrow[\text{reflux}]{\text{THF}} \to C_5H_5Fe(CO)[P(OR)_3]CH_3+P(C_6H_5)_3 \qquad (1)$$

: substitution of $P(OR)_3$ for $P(C_6H_5)_3$ rather than for the CO group in these ıpounds is uncommon but not unprecedented in metal carbonyl chemistry; example, $Mn_2(CO)_8[P(C_6H_5)_3]_2$ reacts with $P(n\text{-}C_4H_9)_3$ to give $Mn_2(CO)_8$-$C_6H_5)_3][P(n\text{-}C_4H_9)_3]$[7]. The different behavior undoubtedly stems from the :tively strong M=CO bond as compared with the $M-P(C_6H_5)_3$ bond.

The cyclopentadienyliron phosphite complexes were isolated as yellow solids $=C_6H_5$) or oils ($R=CH_3$ or $n\text{-}C_4H_9$) which are stable to air when pure. They :t readily with liquid SO_2 at reflux to yield the corresponding *S*-sulfinates, charac-zed through the elemental analyses (Table 1) and their IR and ^1H NMR spectra ble 2):

$$C_5H_5Fe(CO)[P(OR)_3]CH_3+SO_2 \to C_5H_5Fe(CO)[P(OR)_3](SO_2CH_3) \qquad (2)$$

Thermal decarbonylation of $C_5H_5Fe(CO)[P(OC_6H_5)_3](COCH_3)$ in heptane :flux (*ca.* 99°) resulted in an appreciable decomposition of the carbonyl and yielded / a trace amount of $C_5H_5Fe(CO)[P(OC_6H_5)_3]CH_3$. Photolysis of petroleum :r solutions of $C_5H_5Fe(CO)[P(OC_6H_5)_3](COCH_3)$ with a 450-w lamp also led xtensive decomposition and a failure to isolate any decarbonylation product. This avior contrasts with that of $C_5H_5Fe(CO)_2(COCH_3)$, which is reported[8] to ergo photolytic decarbonylation in hexane affording $C_5H_5Fe(CO)_2CH_3$ in % yield.

Tor foregoing results prompted a systematic study of the carbon monoxide :rtion and decarbonylation reactions of the system $C_5H_5Fe(CO)(L)R-C_5H_5Fe$-))(L)(COR). For reasons of stability and availability of some literature data[3,6,9] selected the complexes with $R=CH_3$ and C_2H_5 and $L=P(C_6H_5)_3$. The results the methyl-acetyl compounds are presented in Tables 3 and 4.

Previous work by Bibler and Wojcicki[6] has shown that $C_5H_5Fe(CO)_2CH_3$ (I) $P(C_6H_5)_3$ react in diethyl ether or THF at reflux temperatures (34° and 65°, ›ectively) to afford the acetyl $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$ (II). There was :vidence of formation of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ (III). The above investi-on has been now extended to other, especially nonpolar, solvents and over a wider ge of temperatures.

It is readily seen upon inspection of Table 3 that the lowest-boiling nonpolar 'ent used, hexane (69°), favors the formation of (II) (60%); only a small amount ;) of (III) is obtained. This finding disagrees with the earlier report[6] that there is no :tion between (I) and $P(C_6H_5)_3$ in hexane at reflux for 48 h. We can suggest no ıon for the discrepancy. When the reaction is carried out in heptane at reflux (99°),) becomes the major product, and only 13% (II) is obtained. In addition, some (4%) $H_5Fe(CO)_2]_2$ may be isolated. The data in Table 4 show that decarbonylation of to (III) in hydrocarbon solvents proceeds more readily, albeit also with more ɔmposition, as the temperature increases by going from hexane to cyclohexane then to heptane at reflux.

These results indicate that the initial product of reaction between (I) and $P(C_6H_5)_3$ in a nonpolar solvent is (II):

$$\underset{\text{(I)}}{C_5H_5Fe(CO)_2CH_3} + P(C_6H_5)_3 \rightarrow \underset{\text{(II)}}{C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)} \quad (3)$$

which then undergoes decarbonylation to give (III):

$$\underset{\text{(II)}}{C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)} \rightarrow \underset{\text{(III)}}{C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3} + CO \quad (4)$$

That a more extensive decomposition in these reactions at higher temperatures is almost certainly due to a decreased stability of (III) receives support from thermal treatment of this complex in hexane and heptane at reflux. After 17 h, only 23% of (III) was recovered from the latter solvent, whereas after 27 h, 70% of (III) was isolated from the former solvent. The formation of trace quantities of (I) during the decarbonylation of (II) may result from a side reaction involving methyl migration[10] with displacement of $P(C_6H_5)_3$ rather than CO:

$$\underset{\text{(II)}}{C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)} \rightarrow \underset{\text{(I)}}{C_5H_5Fe(CO)_2CH_3} + P(C_6H_5)_3 \quad (5)$$

A similar behavior was noted recently[11] in a decarbonylation reaction of *fac*-$Mn(CO)_3[P(OCH_2)_3CC_2H_5]_2(COC_6H_5)$.

By contrast, the reaction between (I) and $P(C_6H_5)_3$ in an ether solvent (diethyl ether[6], THF[6] or dioxane) at reflux yields exclusively, or almost exclusively, the acetyl (II). Thus, in dioxane at 102°, the principal product is (II) (30%), with (III) (3%) and $[C_5H_5Fe(CO)_2]_2$ (2%) present in small quantities. That the isolated (III) probably does not arise from decarbonylation of (II), but rather directly from replacement of CO in (I) with $P(C_6H_5)_3$, receives some support from an attempted decarbonylation of (II) in dioxane at reflux. After 12 h, only unreacted (II) (40%) and a trace of (I) could be isolated. [Recall that in heptane at a slightly lower temperature (II) decarbonylates readily to (III)]. Since the alkyl (III) can be recovered in 20% yield after a thermal treatment in dioxane at reflux for 20 h, some of it would have survived and been detected had it indeed formed in the decarbonylation of (II). Hence it appears that (II) does not readily yield (III) under these conditions; therefore presence of a small amount of (III) in the reaction products from (I) and $P(C_6H_5)_3$ may have resulted from a direct substitution (a very minor reaction path) rather than substitution with CO insertion (the major reaction path) followed by decarbonylation. One may also generalize from these and other pertinent data found in the literature[9] that ether solvents promote the reaction represented by eqn. (3) but retard the process represented by (4), presumably by stabilizing the more polar acyl (II).

The reaction between $C_5H_5Fe(CO)_2C_2H_5$ (IV) and $P(C_6H_5)_3$ in heptane at reflux, followed by a work-up using $CHCl_3$ solvent, afforded $C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$ (V) (62%) as the main product and, unexpectedly, some $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$. No $C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5$ (VI) could be detected in the crude product mixture.

The origin of $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$ was ascertained by subjecting (VI) [obtained from photolysis of (V), *vide infra*] to thermal treatment in heptane at reflux for 20 min. Work-up of the reaction mixture yielded a yellow solid which is best mulated as the hydride $C_5H_5Fe(CO)[P(C_6H_5)_3]H$[*] on the basis of analyses, its lecular weight, determined by osmometry, and reactions with $CHCl_3$ or CCl_4 give $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$. The foregoing results support the following uence of reactions for the formation of $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$ from (IV) d $P(C_6H_5)_3$:

$$\underset{\text{(IV)}}{H_5Fe(CO)_2C_2H_5} + P(C_6H_5)_3 \rightarrow \underset{\text{(V)}}{C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)} \quad (6)$$

$$\underset{\text{(V)}}{H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)} \rightarrow \underset{\text{(VI)}}{C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5} + CO \quad (7)$$

$$\underset{\text{(VI)}}{H_5Fe(CO)[P(C_6H_5)_3]C_2H_5} \rightarrow C_5H_5Fe(CO)[P(C_6H_5)_3]H + C_2H_4 \quad (8)$$

$$H_5Fe(CO)[P(C_6H_5)_3]H + CHCl_3 \rightarrow C_5H_5Fe(CO)[P(C_6H_5)_3]Cl + CH_2Cl_2 \quad (9)$$

reaction of the type represented by eqn. (8) has been already reported for other nsition metal ethyl complexes[12]. In this study, its occurrence receives further pport from detection of gaseous ethylene upon heating of (VI) in heptane.

It is noteworthy that the amount of the propionyl (V) isolated from the reaction (IV) with $P(C_6H_5)_3$ in heptane at reflux significantly exceeds the quantity of the etyl (II) from (I) and $P(C_6H_5)_3$ under similar conditions. This difference may be e in part to a lower solubility of (V) than of (II) in hydrocarbon solvents which ould likely inhibit its decarbonylation. However, it is also possible that the propionyl mplex exhibits higher thermal stability than its acetyl counterpart; such a difrence in the relative stabilities toward loss of CO of other propionyl and the rresponding acetyl compounds has been already noted[13].

Photolysis with a 450-w lamp of (IV) and $P(C_6H_5)_3$ in petroleum ether yielded I), a small amount of $[C_5H_5Fe(CO)_2]_2$, and $C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$, which, gain, must have resulted from the interaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]H$ with e solvent chloroform. It is of interest that the propionyl complex (V) could not be tected among the products. Since ultraviolet irradiation of (V) under the same nditions as the foregoing reaction resulted in the isolation of *ca.* 55% unreacted opionyl and only 1% ethyl complex (VI), we conclude that photolysis of (IV) and $(C_6H_5)_3$ affords (VI) directly, without the intermediacy of (V):

$$\underset{\text{(IV)}}{{}_5H_5Fe(CO)_2C_2H_5} + P(C_6H_5)_3 \xrightarrow{h\nu} \underset{\text{(VI)}}{C_5H_5Fe(CO)[P(C_6H_5)_3]C_2H_5} + CO \quad (10)$$

ad the propionyl complex (V) been an intermediate in the above reaction, its presence the product mixture would not have eluded detection.

Treichel and coworkers[3] have reported that the acetyl (II) does not undergo ecarbonylation to (III) upon ultraviolet irradiation with a 150-w lamp in petroleum her (b.p. 90–100°) at reflux for 20 h. However, (III) reacts with carbon monoxide in fluxing petroleum ether at 90–100° to give (II). Since our initial studies had shown at (II) can be decarbonylated thermally to (III) (*vide supra*), the results reported by

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We have not yet been able to obtain a satisfactory ^1H NMR spectrum owing to decomposition of this mplex in solution. Its spectroscopic and chemical properties will be the subject of a later publication.

Treichel seemed rather unexpected. Therefore, a systematic examination of photolytic decarbonylation of (II) under several different conditions was undertaken. The results are summarized in Table 4.

It is readily seen that photochemical decarbonylation of (II) affords the corresponding methyl compound, (III), in moderate to good yields in every case. Since decomposition to insoluble, noncarbonyl brown solids invariably accompanies the elimination of carbon monoxide from (II), nothing definitive can be said about the effect of the intensity or the wavelength of the light used on the yield of the decarbonylated product.

These results cannot be readily reconciled with those of Treichel unless one assumes that carbon monoxide was prevented from escaping the reaction mixture in the latter case and that at the temperatures employed (90–100°) the equilibrium:

$$\underset{\text{(III)}}{C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3} + CO \rightleftharpoons \underset{\text{(II)}}{C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)} \quad (11)$$

favors strongly the acetyl (II). Such a tentative explanation would also account for an increasing ratio of (II) to (III) as a function of time in a photolytic reaction between (I) and $P(C_6H_5)_3$ in petroleum ether at 90–100° [3]*.

In summary, the results of this study show that thermal reactions between $C_5H_5Fe(CO)_2R$ ($R=CH_3$ or C_2H_5) and $P(C_6H_5)_3$ proceed via the initial formation of $C_5H_5Fe(CO)[P(C_6H_5)_3](COR)$, which at higher temperatures in hydrocarbon solvents undergo decarbonylation to $C_5H_5Fe(CO)[P(C_6H_5)_3]R$. By contrast, the corresponding photochemical processes yield $C_5H_5Fe(CO)[P(C_6H_5)_3]R$ directly. This dual mechanistic behavior is therefore analogous to that for the reactions of the corresponding aryl complexes, $C_5H_5Fe(CO)_2Ar$, with various tertiary phosphines, investigated recently by Nesmeyanov and coworkers[4].

ACKNOWLEDGEMENTS

The support of this research by the National Science Foundation (Grant GP-8135) and by the Petroleum Research Fund (Grant 2117-A3), administered by the American Chemical Society, is gratefully acknowledged.

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* *Note added in proof.* We have now successfully decarbonylated $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$ in petroleum ether at 90–100° using a 450-w Hanovia lamp.