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Studies on the Abstraction of Small Molecules from Organometallic Compounds by Rh(PPh$_3$)$_3$Cl

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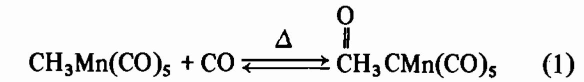
The synthetic utility of Rh(PPh$_3$)$_3$Cl for the abstraction of small molecules from some cyclopentadienyl iron carbonyl complexes is discussed with attention to mechanism. Terminal carbonyl and thiocarbonyl ligands are found to be removed preferentially. Experimental evidence suggests that the reaction proceeds by nucleophilic attack on the coordinated ligand by Rh(PPh$_3$)$_2$Cl.

Introduction

The insertion of small molecules into metal–alkyl bonds and their abstraction therefrom are well known occurances in organometallic chemistry [1]. The first directly observed insertion occurred with carbon monoxide into a methyl–manganese bond [2].



$$CH_3Mn(CO)_5 + CO \overset{\Delta}{\rightleftharpoons} CH_3\overset{O}{\overset{\|}{C}}Mn(CO)_5 \qquad (1)$$

The reverse of this reaction, the decarbonylation of transition metal complexes, has been accomplished by both thermal and photochemical methods. Acylcobalt tetracarbonyl and acylmanganese pentacarbonyl complexes easily eliminate CO upon heating to give the corresponding alkyl whereas cyclopentadienyliron dicarbonyl acyls do not [3–8]. The latter do undergo photolytic decarbonylation but only if the alkyl group [9] is primary.

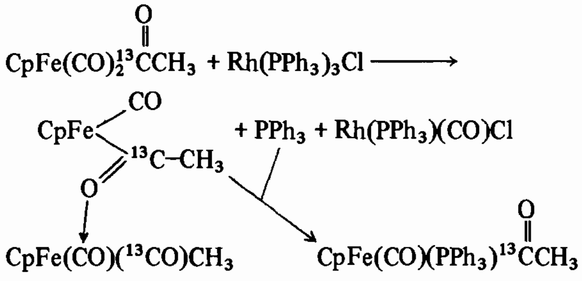
Chlorotris(triphenylphosphine)rhodium(I) has proved successful in abstracting CO from organic acyl halides and aldehydes to give alkyl halides, olefins and alkanes [10–20]. This rhodium complex has also been employed to effect decarbonylation of some iron, manganese and molybdenum organometallics under mild conditions [9, 21–23].

The synthetic utility and selectivity of Rh(PPh$_3$)$_3$Cl as an abstraction agent not only for CO but other small molecules from organometallics have been examined and mechanistic studies carried out. Also, a comparison of the decarbonylation of organic compounds by Rh(PPh$_3$)$_3$Cl with those of metal carbonyls has been made. This paper summarizes our results.

Results and Discussion

In order to distinguish between preferential removal of a terminal metal-bound carbonyl and the *p*-formyl organic carbonyl, the complex CpFe(CO)$_2$C(O)C$_6$H$_4$C(O)H was synthesized. Although the compound decomposed in the solid state too rapidly to obtain an elemental analysis, spectral parameters reported in the Experimental Section leave no doubt as to its identity.

Treatment of the Fe complex with Rh(PPh$_3$)$_3$Cl at 25 °C in benzene afforded a 50.6% yield of CpFe(CO)(PPh$_3$)C(O)C$_6$H$_4$C(O)H, 5% CpFe(CO)$_2$C(O)C$_6$H$_5$, 23.2% of the starting iron complex and 80.3% Rh(PPh$_3$)$_2$(CO)Cl. The products were separated by HPLC and identified by comparison of their chromatographic retention times with those of the photochemically prepared CpFe(CO)(PPh$_3$)C(O)C$_6$H$_4$C(O)H and the known CpFe(CO)$_2$C(O)C$_6$H$_5$. These results can be understood in the light of earlier work [9] which showed that Rh(PPh$_3$)$_3$Cl abstracts a terminal CO from CpFe(CO)$_2^{13}$C(O)CH$_3$ affording a coordinatively unsaturated intermediate which is capable of suffering either methyl migration (to give CpFe(CO)(^{13}CO)CH$_3$) or PPh$_3$ attack by phosphine released from Rh (to give CpFe(CO)(PPh$_3$)^{13}C(O)CH$_3$). See Scheme I.



Scheme I

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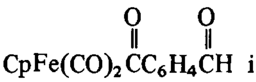
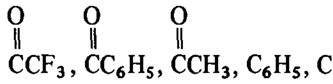
In the present case, the principal product undoubtedly results from abstraction of a terminal CO giving a coordinatively unsaturated intermediate which is attacked by PPh_3 faster than migration can occur. Indeed, there was no evidence of (*p*-formyl)-phenyl migration either in the Rh-induced or photochemical decarbonylation. The minor product $CpFe(CO)_2C(O)C_6H_5$ is the result of decarbonylation of the aldehyde group. The results of ref. 9 argue against the loss of the Fe-bound acyl group. That the total yield of $Rh(PPh_3)_2(CO)Cl$ surpasses the combined yield of decarbonylated species by only ~2% is evidence against significant decomposition of the unsaturated Fe intermediate which would release CO into the solution. Thus, the ratio of rates of metal-bound CO: aldehyde CO removed must be about the 10:1 ratio of the respective products.

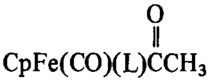
Tsuji and Ohno [13] noted that refluxing benzaldehyde with $Rh(PPh_3)_3Cl$ gave 80% CO abstraction in 5 min while a 77% yield of $Rh(PPh_3)_2(CO)Cl$ was obtained at the end of 24 hr at room temperature. The temperature dependence of the decarbonylation of organic aldehydes would suggest a significant energy of activation that may be associated with the presumed breaking of the C–H bond in the oxidative addition of the aldehyde to the rhodium complex [13, 24–27]. However, the decarbonylation of these organoiron complexes cannot be directly compared to these reactions at elevated temperatures since no iron-containing products can be isolated, due to the thermal instability of the iron compound and intermediates. Solutions of $Rh(PPh_3)_3Cl$ and  $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$ in refluxing benzene resulted in good yields of $Rh(PPh_3)_3(CO)Cl$ with only negligible amounts of organoiron products recovered.

The positive character of CO which donates a σ-pair to the metal is likely to be enhanced as compared to that of the free ligand. Sufficient positive character could activate the terminal CO to nucleophilic attack by the d_{z^2} electrons on Rh. The process of nucleophilic attack would, on the basis of our observations on $CpFe(CO)_2C(O)C_6H_4C(O)H$, seem to have a lower activation energy than the oxidative addition step [27] which initiates aldehyde abstraction.

In order to define more precisely the amount of positive character required for carbonyls to be abstracted by $Rh(PPh_3)_3Cl$ we examined three series of related iron complexes in their reactions with the rhodium compound.

Series I $CpFe(CO)_2(L)^+$
$L = CS, CO, CNCH_3, PPh_3$

Series II $CpFe(CO)_2X$
$X = NCS, SO_2CH_3, CN, F, Cl, Br, I,$

$\overset{O}{\overset{\|}{C}}CF_3, \overset{O}{\overset{\|}{C}}C_6H_5, \overset{O}{\overset{\|}{C}}CH_3, C_6H_5, CH_3$


Series III $CpFe(CO)(L)\overset{O}{\overset{\|}{C}}CH_3$
$L = CO, P(OPh)_3, P(On\text{-}C_4H_9)_3, CNCH_3,$
$PPh_3, P(n\text{-}C_4H_9)_3$

A few of these compounds had been previously examined [9].

A measure of the positive character of C in coordinated CO is provided by the value of $\nu_{C\equiv O}$. Donation from the highest filled σ-orbital increases positive charge on C and increases $\nu_{C\equiv O}$ (since it is slightly C–O antibonding [28]. Back donation into π* orbitals lowers positive charge on C as well as decreases $\nu_{C\equiv O}$. Thus the larger the stretching frequency, the more positive the carbon. ^{13}C chemical shifts have also been shown [29] to correlate with $\nu_{C\equiv O}$ and hence with the positive character of C.

In our experiments equimolar quantities of iron complex and $Rh(PPh_3)_3Cl$ were stirred in an

TABLE I. Decarbonylation of $CpFe(CO)_2(L)^+$ by $Rh(PPh_3)_3Cl$ in CH_3CN.

L	$\delta\,^{13}CO$	ν_{CO} cm^{-1}	% Yield $Rh(PPh_3)_2(CO)Cl$ after 2 hr	% Yield $CpFe(CO)(PPh_3)(L)^+$ after 2 hr	Other Products
CS	202.9	2063^a	56.5	42.8 (L = CS or CO)	29.3% $Rh(PPh_3)_2(CS)Cl$
CO	202.7	2075^a	88.0	49.6	24.8% starting iron complex
$CNCH_3$	207.2	2071, 2033^b	66.4	–	
$NCCH_3$	209.1	2070, 2029^b	14.7	–	
PPh_3	210.1	2055, 2010^b	–	–	

^{a}Nujol mull. ^{b}CH_2Cl_2 soln.

appropriate solvent (dictated by solubility properties of the Fe compounds) under N_2. Reaction progress was monitored by infrared spectra. After two hours the reaction was stopped and the products separated and isolated.

Table I shows the results obtained with the cationic complexes of Series I. If the average of the symmetric and antisymmetric $\nu_{C\equiv O}$ values is taken as a measure of positive C character, it is seen that the extent of decarbonylation (as measured by the yield of $Rh(PPh_3)_2(CO)Cl$) falls off with increasing electron density on the carbonyl. Such results are consistent with nucleophilic attack on C by a Rh species. Apparently the overall positive charge does not polarize the carbonyl ligands sufficiently to permit attack and subsequent Fe–C bond breaking when L = PPh_3. No Fe-containing products were isolated when L = $CNCH_3$, CH_3CN or PPh_3.

Thi thiocarbonyl $CpFe(CO)_2(CS)^+PF_6^-$ has been shown [30] to undergo nucleophilic attack by azide, alkoxides and amines at the thiocarbonyl in preference to the carbonyl. The reaction of $CpFe(CO)_2(CS)^+$ with $Rh(PPh_3)_3Cl$ gave a 2:1 mixture of $Rh(PPh_3)_2(CO)Cl$ to $Rh(PPh_3)_2(CS)Cl$ [31] as found by comparison of the ir spectra with those of known mixtures, suggesting no preference for attack at CS over CO when the statistical factor is taken into account.

$$\begin{aligned}&CpFe(CO)_2(CS)^+ + Rh(PPh_3)_3Cl \longrightarrow\\ &CpFe(CO)(CS)(PPh_3)^+ + CpFe(CO)_2(PPh_3)^+ +\\ &\qquad 56.5\%\ Rh(PPh_3)_2(CO)Cl +\\ &\qquad 29.3\%\ Rh(PPh_3)_2(CS)Cl \qquad (2)\end{aligned}$$

A problem arises in interpreting this result in that these cationic iron complexes can undergo substitution by free PPh_3 [32] arising from the rhodium complex so that the substitution-released CO would react with $Rh(PPh_3)_3Cl$ giving the appearance of CO abstraction. The following is the possible course of the reaction:

$$Rh(PPh_3)_3Cl + CO \longrightarrow Rh(PPh_3)_2(CO)Cl + PPh_3$$

$$PPh_3 + CpFe(CO)_3^+ \longrightarrow 85\%\ CpFe(CO)_2(PPh_3)^+ + CO \qquad (3)$$

Thus some of the $Rh(PPh_3)_2(CO)Cl$ produced may result from the release of free CO in the above reaction.

To examine the reaction without the complication of excess triphenylphosphine and its possible attack on cationic iron complexes, $[Rh(PPh_3)_2Cl]_2$ was employed as a decarbonylating agent. This complex possesses a chloride-bridged dimeric structure, is soluble in strongly coordinating solvents to give $Rh(PPh_3)_2(S)Cl$ where S is a molecule of solvent and can react with CO to form $Rh(PPh_3)_2(CO)Cl$ without the loss of PPh_3 [12, 32]. The results of decarbonylations using this rhodium dimer are listed in Table II.

Employing $Rh(PPh_3)_2(CH_3CN)Cl$ in acetonitrile, the thiocarbonyl was found to be preferentially abstracted in a 3:1 ratio by the rhodium. Without the availability of free PPh_3, there was no chance for formation of a stable iron product of the type $CpFe(CO)(CS)(PPh_3)^+$. Decomposition of the intermediate iron complex with release of CO could lead to the minor amount of $Rh(PPh_3)_2(CO)Cl$ that was still observed. Nevertheless, the results demonstrate that the rhodium complex behaves like nucleophiles previously investigated [31] in showing preferential attack at the thiocarbonyl ligand.

In an attempt to abstract other small molecules, several isocyanide complexes were studied. Treatment of $CpFe(CO)_2(CNCH_3)^+PF_6^-$ with $Rh(PPh_3)_3Cl$ or its dimer in acetonitrile results in the abstraction of a carbonyl only, although the corresponding $Rh(PP_3)_2(CNCH_3)Cl$ [33] is known to be stable. $CpFe(CO)(CNCH_3)_2^+PF_6^-$ and $CpFe(CNCH_3)_3^+PF_6^-$ afforded no abstraction with $Rh(PPh_3)_2(CH_3CN)Cl$ even in refluxing acetonitrile. Both of these iron complexes, like $CpFe(CO)_2(PPh_3)^+PF_6^-$, have presumably reduced their ability for extensive dissipation of negative charge by pi backbonding, as evidenced by carbonyl stretching frequency and C^{13} carbonyl resonance.

That CO and CS are attacked while $CNCH_3$ is not makes plausible a model in which the electron-rich Rh species is considered to attack the LUMO of a ligand polarized by coordination to the metal.

TABLE II. Decarbonylation of Fe Cationic Complexes by $Rh(PPh_3)_2(CH_3CN)Cl$.

Complex	% Yield $Rh(PPh_3)_2(CO)Cl$	Other Products
$CpFe(CO)_2CS^+$	13.1	42.4% $Rh(PPh_3)_2(CS)Cl$
$CpFe(CO)_3^+$	68.2	
$CpFe(CO)_2(CNCH_3)^+$	62.0	
$CpFe(CO)(CNCH_3)_2^+$	no rxn	
$CpFe(CNCH_3)_3^+$	no rxn	

TABLE III. Decarbonylation of $CpFe(CO)_2X$ by $Rh(PPh_3)_3Cl$.

X	σ_I	$\delta^{13}CO$	$\nu_{C\equiv O}$ (cm^{-1})	% Yield $Rh(PPh_3)_2(CO)Cl$	% Yield $CpFe(CO)(PPh_3)X$	Other Products
NCS		209.8	2072, 2035	65	–	14% $Rh(PPh_3)_2(CO)NCS$
SO_2CH_3	0.59	210.0	2063, 2053	90	–	
CN	0.58	211.4	2055, 2009	24	–	
F	0.52	212.0	2050, 2000	99	trace	
Cl	0.47	212.9	2050, 2002	82	10	
Br	0.45	213.2	2045, 1999	78	13	
I	0.39	213.8	2038, 1998	77	14	
$C(O)CF_3$		212.1	2046, 1995	–	–	
$C(O)C_6H_5$		213.7	2018, 1963	98	44	40% $CpFe(CO)_2C_6H_5$
$C(O)CH_3$	0.28	215.0	2015, 1963	88	11	44% $CpFe(CO)_2CH_3$
C_6H_5	0.10	217.1	2011, 1965	–		
CH_3	−0.05	218.3	2003, 1949	–		

Lichtenberger and Fenske in their comparison of photoelectron spectra and molecular orbital calculations [34] on $CpMn(CO)_3$ and $CpMn(CO)_2(CS)$ noted the lower energy of the CS π^* orbital as compared to the CO π^*. Molecular orbital calculations [35] on $Mn(CO)_5(CNCH_3)^+$ indicate that π^* on isocyanide is of higher energy than CO π^*. Thus the order of decreasing stability of π^* orbitals CS > CO > $CNCH_3$ parallels the ability of $Rh(PPh_3)_3Cl$ to abstract these molecules.

Table III presents our results on reactions of the second series, $CpFe(CO)_2X$ as X is varied. A rough correspondence may again be noted between $\nu_{C\equiv O}$ and the extent of CO abstraction as measured by the yield of $Rh(PPh_3)_2(CO)Cl$ isolated. No monotonic decrease in yield is seen as $\nu_{C\equiv O}$ and Taft σ_I decrease. However, compounds having values for these parameters below a certain minimum do not lose CO to the Rh species. It is undoubtedly true also that the yield of $Rh(PPh_3)_2(CO)Cl$ is not a particularly accurate measure of the ability of the Rh species to effect decarbonylation since the various unsaturated intermediates may decompose at different rates releasing CO which reacts with $Rh(PPh_3)_2Cl$ giving $Rh(PPh_3)_2(CO)Cl$.

Aside from the general features just noted, several facets of the series where X = halide or pseudohalide are of interest. Although no iron-containing products were isolated when X = NCS, $Rh(PPh_3)_2(CO)NCS$ [36] was recovered. This product may also be prepared by the reaction of SCN^- with $Rh(PPh_3)_2(CO)Cl$. Thus its presence here may result from substitution by the SCN^- arising from the decomposition of the unsaturated iron intermediate. Note that no $CpFe(CO)(PPh_3)NCS$ was isolated presumably reflecting the instability of the iron intermediate. The appearance of only one CN and CO ir stretch in the rhodium complex would imply the existence of only one isomer; the ir band at 837 cm^{-1} (lit. [36] 839 cm^{-1}) identifies it as the Rh–NCS isomer.

Rhodium-induced decarbonylation of $CpFe(CO)_2X$ where X is a halide, proceeded to give the phosphine substituted iron products along with substantial yields of $Rh(PPh_3)_2(CO)Cl$. These phosphine complexes were also obtained as one of the products (less than 50%) along with $CpFe(CO)_2(PPh_3)^+$ by the action of PPh_3 on the iron halide complex [37]. Since these decarbonylations were complete within 15 min at room temperature and did not yield any cationic products, the following mechanism involving free PPh_3 from $Rh(PPh_3)_3Cl$ seems highly unlikely. Remember that $CpFe(CO)_2(PPh_3)^+$ and $CpFe(CO)(PPh_3)X$ were not decarbonylated under these conditions.

$$CpFe(CO)_2X + PPh_3 \longrightarrow CpFe(CO)(PPh_3)X + CO + CpFe(CO)_2(PPh_3)^+X^- \quad (4)$$

$$Rh(PPh_3)_3Cl + CO \longrightarrow Rh(PPh_3)_2(CO)Cl + PPh_3$$

$$CpFe(CO)_2(PPh_3)^+X^- + Rh(PPh_3)_3Cl \not\longrightarrow$$

$$CpFe(CO)(PPh_3)X + Rh(PPh_3)_3Cl \not\longrightarrow$$

Thus the reactions of these cyclopentadienyl iron dicarbonyl halides appear to be rhodium-induced decarbonylations and not PPh_3 attack with release of CO, giving the appearance of CO abstraction.

An attempt was made to synthesize the unknown $CpFe(CO)X_2^-$ by conducting these decarbonylations in the presence of a tenfold excess of the tetrabutylammonium halide or bis(triphenylphosphine)imminium chloride in the hope that the presumed intermediates, CpFe(CO)X, would be captured by the halide. The ir showed only the existence of $Rh(PPh_3)_2(CO)Cl$ and $CpFe(CO)(PPh_3)X$. The failure to synthesize $CpFe(CO)X_2^-$ can most probably be attributed to the instability of these anions.

We were surprised by (and have no ready explanation for) the low reactivity of $CpFe(CO)_2CN$. The

TABLE IV. Decarbonylation of $CpFe(CO)_2C(O)R$.

R	% Yield $CpFe(CO)_2R$	% Yield $CpFe(CO)(PPh_3)C(O)R$	% Yield $Rh(PPh_3)_2(CO)Cl$	Solvent
Using $Rh(PPh_3)_3Cl$				
$C(CH_3)(C_6H_5)_2$	–	–	85	C_6H_6
$CH(CH_3)(C_6H_5)$	54	–	72	C_6H_6
CH_3	46	4	95	C_6H_6
CH_3	46	11	98	CH_2Cl_2
C_6H_5	40	44	98	CH_2Cl_2
p-C_6H_4Cl	32	30	76	CH_2Cl_2
p-$C_6H_4OCH_3$	7	39	76	C_6H_6
p-$C_6H_5OCH_3$	–	42	98	CH_2Cl_2
p-$C_6H_4C(O)H$	–	51	80	CH_2Cl_2
Using $Rh(PPh_3)(CH_3CN)Cl$				
C_6H_5	32	–	56	CH_3CN
p-$C_6H_5OCH_3$	49	–	92	CH_3CN

values of $\nu_{C\equiv O}$ and σ_I would imply that CO should be positively polarized. The possibility that mixing of CO and CN modes leads to a false picture of the CO bond strength is ruled out by work of Darensbourg [38] who calculated force constants taking mixing into account. He found that CO force constants decreased in the order X = CN > Cl > I. This trend parallels $\nu_{C\equiv O}$.

Table IV provides a comparison of results for decarbonylation of several acyls. If an unsaturated intermediate is produced on CO abstraction, such a species would likely be stabilized by solvent coordination. Indeed, Rosenblum [39] has detected the presence of $CpFe(CO)C(O)CH_3(DMSO)$ in a recent kinetic study. Since in our reactions a coordinated solvent molecule would have to be displaced either by a migrating R group or an attacking PPh_3, it is conceivable that product distribution could be modified by changing the solvent. Some evidence that this is the case is provided by the results for R = CH_3 and p-$C_6H_4OCH_3$.

If the assumption is made that in the same solvent the rate of PPh_3 attack does not vary substantially, then the ratio of alkyl to phosphine-substituted products can be thought of as reflecting the migratory ability of various R. The order is $CH_3 > C_6H_5 > C_6H_4Cl > p$-$C_6H_4OCH_3 > p$-$C_6H_4C(O)H$ which parallels their electron donor ability. A similar effect was seen in a kinetic study on the migration rates of various R onto unsaturated Ir [40]. By employing $[Rh(PPh_3)_2Cl]_2$ in CH_3CN as the decarbonylating agent (thereby excluding the presence of free PPh_3) the yield of $CpFe(CO)_2C_6H_4OCH_3$ could be increased from 7 to 49%.

Kinetic and Mechanistic Studies

The reaction of $CpFe(CO)_2C(O)CH_3$ with $Rh(PPh_3)_3Cl$ was investigated by observing the disappearance of the iron acyl stretch at 1668 cm^{-1}. Although monitoring the terminal CO stretching frequencies (with their greater intensity) would be more desirable, overlapping absorptions due to products and reactants as well as solvent interferences prevailed against use of this region.

The ultraviolet–visible spectral region could not be monitored for several reasons. First, $Rh(PPh_3)_3Cl$ does not obey Beer's law upon diluting benzene solutions of this complex. This observation can be attributed [32] to formation of the dimeric $[Rh(PPh_3)_2Cl]_2$ complex which is inactive as a decarbonylating agent under these conditions (*i.e.* in a noncoordinating solvent). Second, the extreme sensitivity of these rhodium complexes toward oxygen resulting in $[RhCl(O_2)(PPh_3)_2]_2$ [41] would necessitate careful purging of all oxygen from the system. Even with such precautions molecular weight measurements have been reported to be in error due to the presence of trace amounts of O_2 [42]. By using more concentrated solutions in the ir study, a smaller percentage of the rhodium complex would be lost by oxidation.

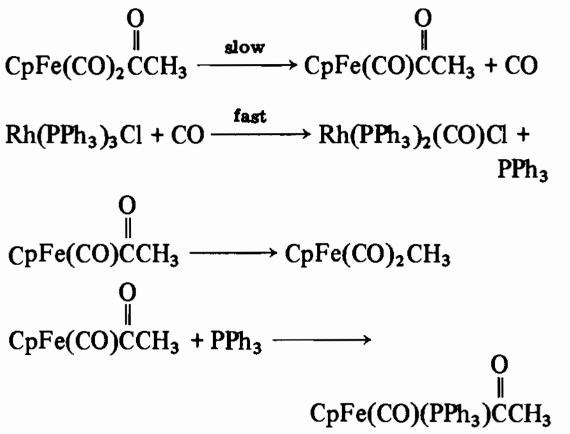
By observing the disappearance of the acyl stretch in the ir, the reaction of $Rh(PPh_3)_3Cl$ with $CpFe(CO)_2C(O)CH_3$ was found to be first order in each of the reactants for approximately one half-life of the reaction. After that time, decomposition of the unsaturated $CpFe(CO)C(O)CH_3$ intermediate with loss of CO leads to the formation of more $Rh(PPh_3)_2(CO)Cl$ beyond the one to one expected stoichiometry for this reaction and resulted in decreasing values for k_{obs}. The results showed a value of 3.20 ± 0.35 $\times$ 10^{-1} M^{-1} sec^{-1} for the rate constant, k_{obs}. Table V shows the effect of added PPh_3, resulting in a decrease in the value of k_{obs}. An increase in electron density on the rhodium center as in $Rh(PPh_3)_3Br$, resulted in an increase in k_{obs} to 4.98 ± 0.56 $\times$ 10^{-1} M^{-1} sec^{-1}.

TABLE V. Effect of Added PPh_3 on k_{obs} with 10.0×10^{-3} M in $CpFe(CO)_2\overset{\overset{O}{\|}}{C}CH_3$ and 8.00×10^{-5} M in $Rh(PPh_3)_3Cl$.

PPh_3 Added	k_{obs} (M^{-1} sec^{-1})
4.00×10^{-3} M	$6.42 \pm 0.59 \times 10^{-2}$
8.00×10^{-3}	3.97×10^{-2}
16.0×10^{-3}	1.83×10^{-2}
24.0×10^{-3}	1.12×10^{-2}
32.0×10^{-3}	0.867×10^{-2}
40.0×10^{-3}	0.803×10^{-2}

Several mechanistic possibilities present themselves as models for the $Rh(PPh_3)_3Cl$ decarbonylation of organometals. One possibility would have initial dissociation of CO from the iron as the rate determining step (Scheme II):

Scheme II



$$CpFe(CO)_2\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{slow} CpFe(CO)\overset{\overset{O}{\|}}{C}CH_3 + CO$$

$$Rh(PPh_3)_3Cl + CO \xrightarrow{fast} Rh(PPh_3)_2(CO)Cl + PPh_3$$

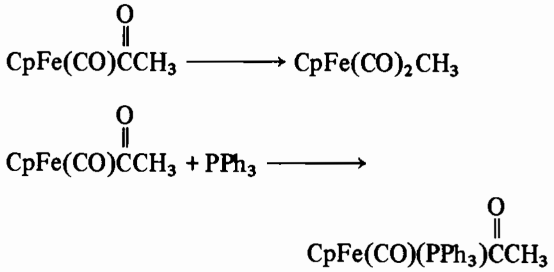
$$CpFe(CO)\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow CpFe(CO)_2CH_3$$

$$CpFe(CO)\overset{\overset{O}{\|}}{C}CH_3 + PPh_3 \longrightarrow CpFe(CO)(PPh_3)\overset{\overset{O}{\|}}{C}CH_3$$

This scheme would imply a thermal decarbonylation pathway. Heating solutions of the iron acetyl or mixtures of the iron acetyl and triphenylphosphine in benzene or THF failed to show any decarbonylated or phosphine substituted products [43]. It is also known that the reaction of CO with $Rh(PPh_3)_3Cl$ is instantaneous requiring the second step to be fast. Since the kinetics were found to be second order, this scheme can be ruled out.

The following two steps which appear in all reaction schemes cannot be rate determing:

Scheme III



$$CpFe(CO)\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow CpFe(CO)_2CH_3$$

$$CpFe(CO)\overset{\overset{O}{\|}}{C}CH_3 + PPh_3 \longrightarrow CpFe(CO)(PPh_3)\overset{\overset{O}{\|}}{C}CH_3$$

By increasing the concentration of added PPh_3, an increasing fraction of the intermediate should be (and is observed to be) diverted to the phosphine-substituted acyl (see Table VI). If these steps were rate-determining, the whole reaction should have been speeded up by increasing the concentration of PPh_3. Instead it was retarded.

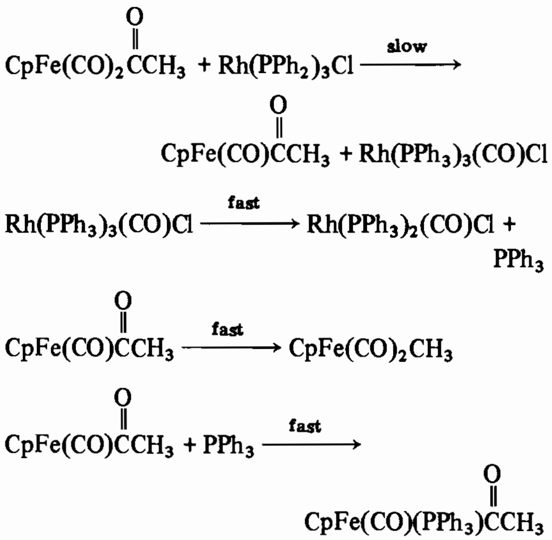
TABLE VI. Product Distributions from the Decarbonylation of $CpFe(CO)_2\overset{\overset{O}{\|}}{C}CH_3$ by $Rh(PPh_3)_3Cl$ in the Presence of Added PPh_3.

		% Reacted[a]	Ratio $\frac{\text{Methyl Migration}}{PPh_3 \text{ Substitution}}$
I	No PPh_3 Added	84	9.5 : 1.0
II	1:1 Fe:PPh_3	80	7.0 : 1.0
III	1:5 Fe:PPh_3	60	2.5 : 1.0
IV	1:10 Fe:PPh_3	55	2.0 : 1.0

[a] All reactions were carried out in benzene. Product ratios were determined at the end of three hr by NMR.

A second mechanistic possibility is attack by the four-coordinate rhodium species (Scheme IV):

Scheme IV



$$CpFe(CO)_2\overset{\overset{O}{\|}}{C}CH_3 + Rh(PPh_2)_3Cl \xrightarrow{slow} CpFe(CO)\overset{\overset{O}{\|}}{C}CH_3 + Rh(PPh_3)_3(CO)Cl$$

$$Rh(PPh_3)_3(CO)Cl \xrightarrow{fast} Rh(PPh_3)_2(CO)Cl + PPh_3$$

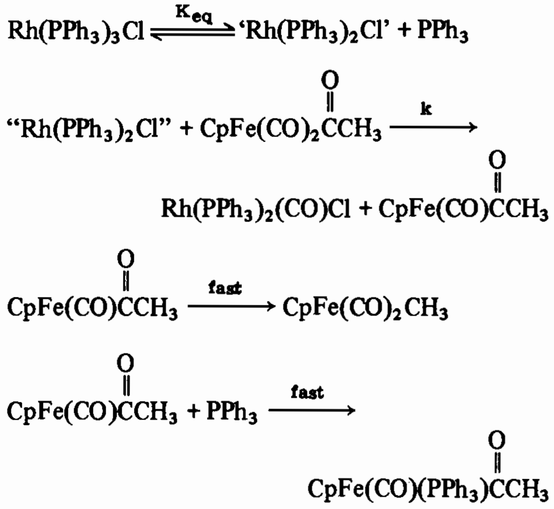
$$CpFe(CO)\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{fast} CpFe(CO)_2CH_3$$

$$CpFe(CO)\overset{\overset{O}{\|}}{C}CH_3 + PPh_3 \xrightarrow{fast} CpFe(CO)(PPh_3)\overset{\overset{O}{\|}}{C}CH_3$$

Direct attack on these iron complexes by four coordinate rhodium would seem unlikely based on the following observations: first, the repression of the reaction rate upon addition of PPh_3 to the reaction would indicate the importance of PPh_3 dissociation in the rate determining step or in a prior equilibrium. The lack of success in preparing $Rh(PPh_3)_3(CO)Cl$ implies that PPh_3 dissociation from this complex cannot be the rate determining step. Second, the failure of the chelated $Rh(PhP(CH_2CH_2CH_2CH_2PPh_2)_2)Cl$ (where phosphine dissociation would be minimized) to effect decarbonylation or give any indication of formation of an intermediate complex would suggest that four coordinate rhodium is not the actual decarbonylating species.

These observations make plausible the following reaction scheme where $Rh(PPh_3)_3Cl$ dissociates into a reactive "$Rh(PPh_3)_2Cl$" before attacking the iron complex (Scheme V):

Scheme V



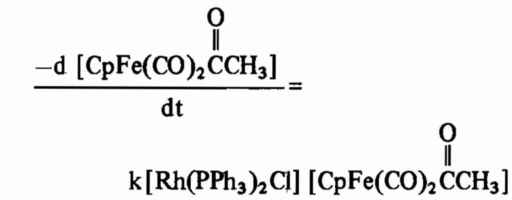
$$\mathrm{Rh(PPh_3)_3Cl} \overset{K_{eq}}{\rightleftharpoons} \text{'}\mathrm{Rh(PPh_3)_2Cl}\text{'} + \mathrm{PPh_3}$$

$$\text{"}\mathrm{Rh(PPh_3)_2Cl}\text{"} + \mathrm{CpFe(CO)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow{k} \mathrm{Rh(PPh_3)_2(CO)Cl} + \mathrm{CpFe(CO)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$$

$$\mathrm{CpFe(CO)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow{\text{fast}} \mathrm{CpFe(CO)_2CH_3}$$

$$\mathrm{CpFe(CO)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} + \mathrm{PPh_3} \xrightarrow{\text{fast}} \mathrm{CpFe(CO)(PPh_3)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$$

Assuming that the second step is rate determining, the rate expression becomes:



(5)

$$\frac{-d\,[\mathrm{CpFe(CO)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}]}{dt} = k[\mathrm{Rh(PPh_3)_2Cl}]\,[\mathrm{CpFe(CO)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}] \quad (5)$$

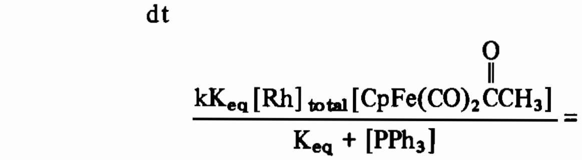
and solving for $[Rh(PPh_3)_2Cl]$ from

$$K_{eq} = \frac{[Rh(PPh_3)_2Cl]\,[PPh_3]}{[Rh(PPh_3)_3Cl]} \quad (6)$$

and

$$[Rh]_{total} = [Rh(PPh_3)_3Cl] + [Rh(PPh_3)_2Cl]$$

the rate expression becomes:



(7)

$$\frac{-d\,[\mathrm{CpFe(CO)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}]}{dt} = \frac{kK_{eq}[\mathrm{Rh}]_{total}[\mathrm{CpFe(CO)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}]}{K_{eq} + [\mathrm{PPh_3}]} = k_{obs}[\mathrm{Rh}]_{total}[\mathrm{CpFe(CO)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}] \quad (7)$$

where

$$\frac{kK_{eq}}{K_{eq} + [PPh_3]} = k_{obs} \quad (8)$$

Since the concentration of PPh_3 was continually changing due to increasing capture of triphenylphosphine by the unsaturated iron with increasing phosphine concentration, the data from Table V could not be used to determine k and thus K_{eq} accurately by a Lineweaver and Burk plots since the error was quite large. Even though associated with a large error, the value of K_{eq} (7.8×10^{-5}) is of about the expected magnitude based on other results (*vide infra*). Increasing the concentration of PPh_3 to a 100 fold excess slowed the reaction to the point that photochemical and oxygen-induced decomposition prevailed.

From this rate expression, the repression of the reaction rate upon addition of PPh_3 is easily understood. Experimental detection of the proposed intermediate resulting from PPh_3 dissociation has not been accomplished, however. Solutions of $Rh(PPh_3)_3Cl$ have shown deviations from Beer's Law which have been accounted for in terms of a monomer–dimer equilibrium with $K' = 3.3 \pm 0.4 \times 10^{-4}$ *M* in benzene at 25 °C and not the formation of "$Rh(PPh_3)_2Cl$" [34].

$$2Rh(PPh_3)_3Cl \overset{K'}{\rightleftharpoons} [Rh(PPh_3)_2Cl]_2 + 2PPh_3 \quad (9)$$

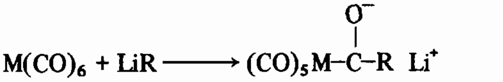
Also ^{31}P nmr showed no evidence of any "$Rh(PPh_3)_2Cl$" species. However, $[Rh(PPh_3)_2Cl]_2$ failed to show any decarbonylating activity toward these organoiron complexes in benzene, dichloromethane or chloroform. They did effect decarbonylation in acetonitrile presumably due to the breaking of the chloride bridged dimer and formation of $Rh(PPh_3)_2(CH_3CN)Cl$ [44]. Failure to observe '$Rh(PPh_3)_2Cl$' either spectrophotometrically or by ^{31}P magnetic resonance does not invalidate its use as a kinetic intermediate. On the contrary, the rapid exchange of phosphine on $Rh(PPh_3)_3Cl$ which occurs above 45 °C has been shown not to involve dimer and not to occur by an associative process, suggesting the following equilibrium [32]:

$$Rh(PPh_3)_3Cl \overset{K_{eq}}{\rightleftharpoons} Rh(PPh_3)_2Cl + PPh_3 \quad (10)$$

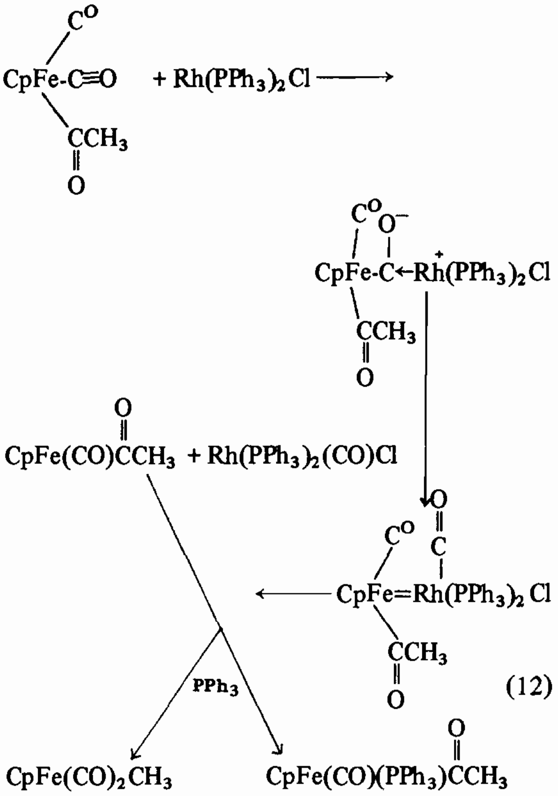
Also, Tolman *et al.* [32] in their kinetic study on the hydrogenation of cyclohexene by $Rh(PToly_3)_3Cl$ concluded that "$Rh(PToly_3)_2Cl$" was the rhodium species involved in activating H_2 and they set an upper limit of K_{eq} for this complex to be less than 5×10^{-5} *M*, in close agreement with our value for the PPh_3 complex.

The relative rates observed for the reaction involving $Rh(PPh_3)_3Br$ (4.98×10^{-1} M^{-1} sec^{-1}) as compared with $Rh(PPh_3)_3Cl$ (3.20×10^{-1} M^{-1} sec^{-1}) agree with the notion of nucleophilic attack by rhodium, since substitution of Cl^- by Br^- should make the rhodium a better nucleophile assuming that the K_{eq} for these two complexes are comparable. The effect is rather small, however.

This nucleophilic attack at a terminal carbonyl can be envisioned to parallel the attack by alkyllithium reagents with the formation of a carbene:

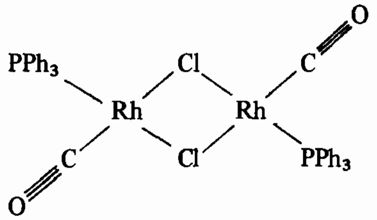


$$M(CO)_6 + LiR \longrightarrow (CO)_5M\overset{O^-}{\overset{|}{C}}{-}R\ Li^+ \qquad (11)$$



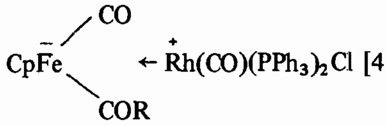
(12)

The carbene-like intermediate then rearranges to give the unsaturated iron intermediate and $Rh(PPh_3)_2(CO)Cl$. In an attempt to isolate any intermediates, these reactions were conducted at 0 °C with excess iron complex for 3 min followed by quenching with hexanes and cooling to −78 °C. This procedure yielded a yellow solid with ir stretches at 1976 and 1957 cm^{-1}, the latter band identical to the carbonyl stretch in *trans*-$Rh(PPh_3)_2(CO)Cl$. The band at 1976 cm^{-1} could be the *cis* isomer of the rhodium complex [11]. An alternate structure such as



with ν_{CO} 1980 cm^{-1} could be proposed [45, 46] However, this second structure would seem more improbable for several reasons. First, free PPh_3 would need to remain after the ether washings to give the *trans*-$Rh(PPh_3)_2(CO)Cl$ obtained upon dissolving this solid in benzene. Second, this dimeric structure would suggest that $[Rh(PPh_3)_2Cl]_2$ is the active decarbonylating species for these iron complexes in benzene and dichloromethane which does not seem to be the case. Since $Rh(PPh_3)_3Cl$ has a square planar configuration common for Rh(I) complexes and considering the *trans* effect, one would anticipate that one of the *trans*-phosphines would be labile [44]. Thus substitution by CO would result initially in the formation of the *cis* isomer that could then rearrange to give the more thermodynamically stable *trans* form.

Moreover, irradiation of benzene solutions of $CpFe(CO)_2\overset{O}{\overset{\|}{C}}R$ and $Rh(PPh_3)_2(CO)Cl$ failed to yield a stable species of composition



[47].

Thus, one may only postulate the existence of these iron–rhodium intermediates.

The unsaturated iron intermediate has also been suggested inthe photochemical decarbonylation of $CpFe(CO)_2\overset{O}{\overset{\|}{C}}CH_3$ [48, 49]. This mechanism involves the formation of an excited state with an appreciably weakened bond between the iron and the terminal CO. Dissociation of this terminal CO results in an unsaturated moiety which rearranges with methyl migration to give $CpFe(CO)_2CH_3$. The addition of PPh_3 to this photochemical reaction would approximate the conditions for the chemical decarbonylation by $Rh(PPh_3)_3Cl$ where PPh_3 has the chance to attack the unsaturated intermediate. For the photochemical reaction in hexane, PPh_3 attack on the unsaturated iron intermediate was found to be faster than methyl migration [48]. This is in contrast to the rhodium-induced decarbonylation in benzene or dichloromethane where methyl migration was the major reaction, even in the presence of excess PPh_3 (Table VI).

Duplication of the photochemical decarbonylation of the iron complex with excess PPh$_3$ in benzene gave product ratios as determined by pmr that resembled those in Table VI in that methyl migration was faster than PPh$_3$ substitution. Thus generation of the same intermediate in either photochemical or Ph(PPh$_3$)$_3$Cl induced decarbonylation is quite probable. The difference in photochemical behavior of these iron complexes in hexane and either benzene or dichloromethane solutions could possibly arise from the formation of solvated intermediates in benzene or dichloromethane. Thus in the presence of PPh$_3$, this ligand must displace the coordinated solvent molecule in competition with methyl migration. However, in hexane, where solvent coordination would be minimal, the coordinatively unsaturated iron intermediate would be more electrophilic, with PPh$_3$ substitution occurring at a faster rate.

Experimental

Materials

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran, THF, was distilled over CaH$_2$ immediately before use. All other solvents were certified A.C.S. grade and unless otherwise stated used without further purification. Thionyl chloride was purified by distillation from dipentene.

Iron pentacarbonyl was purchased from Alfa Products, Ventron Corporation. Rhodium trichloride trihydrate was obtained from Engelhard Industries; $p\text{-}CH_3OC_6H_5\overset{O}{\overset{\|}{C}}Cl$, $p\text{-}ClC_6H_4\overset{O}{\overset{\|}{C}}Cl$ and $p\text{-}H\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}OH$ were obtained from Aldrich Chemicals. All these compounds were used as received.

The following compounds were prepared by literature methods: [CpFe(CO)$_2$]$_2$ [50], Rh(PPh$_3$)$_3$Cl [51], Rh(PPh$_3$)$_3$Br [51], Rh(PPh$_3$)$_2$(CO)NCS [36], CpFe(CO)$_2$SO$_2$CH$_3$ [52], CpFe(CO)$_2$NCS [30], CpFe(CO)$_2$CN [53], CpFe(CO)$_2$Cl [53], CpFe(CO)$_2$Br [54], CpFe(CO)$_2$I [54], CpFe(CO)$_2$C(O)C$_6$H$_5$ [3], CpFe(CO)$_2$C(O)CH$_3$ [55], CpFe(CO)$_2$C$_6$H$_5$ [3], CpFe(CO)$_2$CH$_3$ [55], CpFe(CO)$_3^+$PF$_6^-$ [56], CpFe(CO)$_2$(CS)$^+$PF$_6^-$ [57], CpFe(CO)$_2$(CNCH$_3$)$^+$PF$_6^-$ [58], CpFe(CO)$_2$(NCCH$_3$)$^+$PF$_6^-$ [59], CpFe(CO)LC(O)CH$_3$ (L = P(OPh)$_3$, PPh$_3$, P(On-C$_4$H$_9$)$_3$P(n-C$_4$H$_9$)$_3$) [60], CpFe(CO)(CNCH$_3$)C(O)CH$_3$ [61].

Preparation of $H\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}Cl$

A 3.75 g sample (25.0 mmol) of $H\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}OH$ and 5 mL of purified SOCl$_2$ in 50 mL of CHCl$_3$ [62] were refluxed for 12 hr. The solvent was removed under reduced pressure and the residue extracted with pentane. The solution was filtered and evaporated to give 3.94 g (93.5% yield) of pure, white acid chloride; mp. 40 °C. Spectral data: pmr: 8.00 (m, 4H), 10.1 (s, 1H); ir(pentane): 1780, 1750, 1715 cm^{-1} (CO).

Preparation of $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4X$, X = $\overset{O}{\overset{\|}{C}}H$, OCH$_3$, Cl

A 4.25 g sample (12.0 mmol) of [CpFe(CO)$_2$]$_2$ in THF was reduced with excess 2% sodium amalgam. After removal of the amalgam, the NaFe(CO)$_2$Cp in the THF was slowly added to a solution of 3.94 g (23.4 mmol) of $H\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}Cl$ at 0 °C in THF and stirred for 8 hr. The solvent was removed under reduced pressure and the residue extracted with CHCl$_3$ and filtered through alumina. The volume was reduced under a stream of N$_2$ and hexanes slowly added to precipitate the crude $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$. The product was purified by column chromatography to give 1.78 g (24.6% yield) of pure, yellow $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$; mp. 129 °C. Spectral data: pmr: 4.90 (s, 5H), 7.73 (m, 4H), 10.0 (s, 1H); ir: 2015, 1965, 1700, 1610 cm^{-1} (CO).

$CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4OCH_3$ and $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4Cl$ were prepared in a similar manner from NaFe(CO)$_2$Cp and $CH_3OC_6H_4\overset{O}{\overset{\|}{C}}Cl$ or $ClC_6H_4\overset{O}{\overset{\|}{C}}Cl$. $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4OCH_3$ is a yellow solid, mp. 112 °C. Spectral data: pmr: 3.81 (s, 3H), 4.87 (s, 5H), 7.18 (m, 4H); ir: 2017, 1958, 1608 cm^{-1} (CO). *Anal.* for C$_{15}$H$_{12}$FeO$_4$: Calcd. C 57.7%, H 3.87%. Found C 57.6%, H 4.00%. $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4Cl$ is a yellow solid, mp. 89–90 °C. Spectral data: pmr: 4.86 (s, 5H), 7.33 (m, 4H); ir: 2021, 1964, 1610 cm^{-1} (CO). *Anal.* for C$_{14}$H$_9$ClFeO$_3$: Calcd. C 53.1%, H 2.87%. Found C 52.9%, H 2.84%.

Decarbonylation of $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_5\overset{O}{\overset{\|}{C}}H$ by Rh(PPh$_3$)$_3$Cl

A 1.12 g sample (3.62 mmol) of $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$ and 3.57 g (3.86 mmol) of Rh(PPh$_3$)$_3$Cl were stirred in 25 mL of CH_2Cl_2 for 4 hr at room temperature. The solution was then cooled and filtered to yield 2.14 g (80.3% yield) or $Rh(PPh_3)_2(CO)Cl$. The solvent was removed under a stream of N_2 and the residue was chromatographed on Grade III alumina to give 0.654 g of a mixture of iron acyls. These products were separated by HPLC to give 23.2% $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$, 5.0% $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_5$ and 50.6% $CpFe(CO)(PPh_3)\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$ identified by comparison to retention times of the known compounds. $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_5$ is a yellow solid, mp. 57 °C, lit. [3] 59–62 °C. Spectral data: pmr: 4.80 (s, 5H), 7.31 (s, 5H), lit. [3] 4.79 and 7.31 ppm; ir: 2022, 1964, 1611 cm^{-1} (CO), lit. [3] 2029, 1972 and 1603 cm^{-1}. $CpFe(CO)(PPh_3)\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$ is a yellow-orange solid. Spectral data: pmr: 4.53 (d, 5H), 7.30 (m, 4H), 9.90 (s, 1H); ir: 1922, 1700, 1585 cm^{-1} (CO).

Preparation of $CpFe(CO)(PPh_3)\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$

A solution of 0.477 g (1.82 mmol, 10% excess) of triphenylphosphine and 0.513 g (1.65 mmol) of $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_5\overset{O}{\overset{\|}{C}}H$ in benzene was irradiated with a Hanovia mercury-vapor lamp for 20 min. Progress of the reaction was monitored by infrared spectroscopy. The solvent was removed at reduced pressure and the residue was chromatographed on alumina to give a mixture of the starting iron dicarbonyl and the yellow-orange $CpFe(CO)(PPh_3)\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$ identical to the phosphine product obtained from the rhodium-induced decarbonylation of $CpFe(CO)_2\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}H$. Attempts to separate these products by fractional recrystalization or chromatography on alumina, silica gel or fluorisil failed. However, the complexes were separated and identified by HPLC.

Preparation of $CpFe(CO)_2(PPh_3)^+PF_6^-$

To 0.350 g (1.00 mmol) of $CpFe(CO)_3^+PF_6^-$ in dry acetone was added 1.05 g (4.00 mmol) of PPh_3 and the mixture stirred for 24 hr. The solvent was reduced under a stream of nitrogen and the product precipitated by the dropwise addition of diethylether and recrystalized from acetone–ether to give 0.496 g (0.849 mmol, 84.9% yield) of $CpFe(CO)_2(PPh_3)^+PF_6^-$ as a pale yellow solid, mp. 200 °C. Spectral data: pmr: (d_6-acetone) 5.62 (d, 5H), 7.63 (m, 15H), lit. [65] 5.62 and 7.68; ir: (nujol) 2035, 1998 cm^{-1} (CO), lit. [38] (CH_2Cl_2) 2055 and 2010 cm^{-1}.

Decarbonylation of $CpFe(CO)_2(L)^+PF_6^-$ *by* $Rh(PPh_3)_3Cl$ *(L = CS, CO,* $CNCH_3$, $NCCH_3$, PPh_3*)*

0.350 g (1.00 mmol) of $CpFe(CO)_3^+PF_6^-$ and 0.925 g (1.00 mmol) of $Rh(PPh_3)_3Cl$ were stirred in 15 mL of CH_3CN for 2 hr. The solvent was removed under reduced pressure and the residue chromatographed on Grade III alumina to give 0.607 g (0.880 mmol, 88.0% yield) of $Rh(PPh_3)_2(CO)Cl$, 0.0867 g (0.248 mmol, 24.8% yield) of starting $CpFe(CO)_3^+PF_6^-$ and 0.290 g (0.496 mmol, 49.6% yield) of $CpFe(CO)_2(PPh_3)^+PF_6^-$.

This same procedure was employed for all decarbonylations listed above. Yields are listed in Table I. $CpFe(CO)(CS)(PPh_3)^+PF_6^-$ is a yellow solid. Spectral data for products when L = CS: pmr: (d_6-acetone) 5.60 (d, 5H), 7.88 (m, 15H) lit. [63] 5.69 and 7.83 ppm; ir: (nujol) 2030 cm^{-1} (CO) 1320 cm^{-1} (CS), lit. [65] 2035 and 1320 cm^{-1}. $Rh(PPh_3)_2(CS)Cl$ is an orange solid, mp. 248 °C, lit. [66] 250–252 °C. Ir: (nujol) 1301 (CS), lit. [64] 1299 cm^{-1} in benzene.

Decarbonylation of $CpFe(CO)_2(L)^+PF_6^-$ *by* $[Rh(PPh_3)_2Cl]_2$ *(L = CS, CO,* $CNCH_3$*)*

0.350 g (1.00 mmol) of $CpFe(CO)_3^+PF_6^-$ and 0.662 g (0.500 mmol) of $[Rh(PPh_3)_2Cl]_2$ were stirred in 15 mL of CH_3CN for 20 hr. The solvent was removed under reduced pressure and the residue chromatographed on Grade III alumina to give 0.471 g (0.682 mmol, 68.2% yield) of $Rh(PPh_3)_2(CO)Cl$. There was no evidence of any stable iron complex.

This same procedure was employed for all decarbonylations listed above including those of $CpFe(CO)(CNCH_3)_2^+PF_6^-$ and $CpFe(CNCH_3)_3^+PF_6^-$. Yields are presented in Table II.

Decarbonylation of $CpFe(CO)_2X$ *by* $Rh(PPh_3)_3Cl$ *(X = NCS,* SO_2CH_3*, CN, F, Cl, Br, I,* $\overset{O}{\overset{\|}{C}}CF_3$, $\overset{O}{\overset{\|}{C}}C_6H_5$, $\overset{O}{\overset{\|}{C}}CH_3$, C_6H_5, CH_3*)*

0.304 g (1.00 mmol) of $CpFe(CO)_2I$ and 0.925 g (1.00 mmol) of $Rh(PPh_3)_3Cl$ were stirred in 10 mL of CH_2Cl_2 under a N_2 atmosphere for 3 hr. The solution was cooled and filtered to yield 0.528 g (0.765 mmol, 76.5% yield) of $Rh(PPh_3)_2(CO)Cl$. The solvent was removed under reduced pressure and the residue chromatographed on Grade III alumina to give 0.0753 g (0.140 mmol, 14% yield) of green $CpFe(CO)(PPh_3)I$, mp. 186 °C. Spectral data: pmr: 4.43 (d, 5H), 7.37 (m, 15H); ir: 1962 cm^{-1} (CO), lit. [38] 1938 cm^{-1}.

This same procedure was employed for all decarbonylations listed above. Yields are given in Table III.

Spectral data for the product when X = F: CpFe(CO)(PPh$_3$)F is a green solid. pmr: 4.45 (d, 5H), 7.40 (m, 15H); ir: 1956 cm^{-1} (CO).

Spectral data for the product when X = Cl: CpFe(CO)(PPh$_3$)Cl is a green solid. pmr: 4.45 (d, 5H), 7.41 (m, 15H); ir: 1960 cm^{-1} (CO), lit. [38] 1960 cm^{-1}.

Spectral data for the product when X = Br: CpFe(CO)(PPh$_3$)Br is a green solid, mp. 168–169 °C. pmr: 4.47 (d, 5H), 7.40 (m, 15H); ir: 1970 cm^{-1} (CO), lit. [38] 1965 cm^{-1}.

Spectral data for the product when X = $\overset{\overset{O}{\|}}{C}C_6H_5$: $CpFe(CO)(PPh_3)\overset{\overset{O}{\|}}{C}C_6H_5$ is an orange solid, mp. 164 °C, lit. [65] 165 °C. pmr: 4.51 (d, 5H), 7.28 (m, 20H); ir: 1920, 1595 cm^{-1} (CO). CpFe(CO)$_2$C$_6$H$_5$ is a yellow solid, mp. 34 °C, lit. 35–36 °C. pmr: 4.75 (s, 5H), 7.25 (s, 5H), lit. [3] 4.73 and 7.26 ppm; ir: 2001, 1904 cm^{-1} (CO), lit. [3] (halocarbon mull) 2021, 1969 cm^{-1}.

Spectral data for the product when X = $\overset{\overset{O}{\|}}{C}CH_3$: $CpFe(CO)(PPh_3)\overset{\overset{O}{\|}}{C}CH_3$ is a yellow orange solid, mp 145 °C, lit. [61] 145 °C. pmr: 2.33 (s, 3H), 4.43 (d, 5H), 7.36 (m, 15), lit. [61] 2.52, 4.62, 7.59 ppm; ir: 1920, 1595 cm^{-1} (CO), lit. [62] 1920, 1598 cm^{-1}. CpFe(CO)$_2$CH$_3$ is a yellow, waxy solid. pmr: 0.17 (s, 3H), 4.70 (s, 5H); ir: 2003, 1949 cm^{-1} (CO).

Attempted Decarbonylation of $CpFe(CO)(L)\overset{\overset{O}{\|}}{C}CH_3$ by Rh(PPh$_3$)$_3$Cl (L = PPh$_3$, P(OPh)$_3$, P(n-C$_4$H$_9$)$_3$, P(On-C$_4$H$_9$)$_3$, CNCH$_3$, CNC$_6$H$_5$)

0.502 g (1.00 mmol) of $CpFe(CO)(P(OPh)_3)\overset{\overset{O}{\|}}{C}CH_3$ and 0.925 g (1.00 mmol) of Rh(PPh$_3$)$_3$Cl in 15 mL of CH$_2$Cl$_2$ were stirred for 18 hr. During this time, the reaction was monitored by ir which showed no evidence of any Rh(PPh$_3$)$_2$(CO)Cl being formed. The reaction was repeated in benzene at room temperature and also under refluxing conditions without any decarbonylation.

This same procedure was employed for all the attempted decarbonylations listed above.

Preparation of Ph$_2$PCH$_2$CH$_2$CH$_2$Cl

26.2 g (0.101 mmol) of PPh$_3$ was added to 165 ml of dry THF and 1.40 g (0.202 mol) lithium metal. The mixture was refluxed for 8 hr and unreacted lithium was removed. 9.40 g (0.100 mol) of freshly distilled t-butyl chloride was added dropwise to destroy the phenyllithium [66, 67]. The solution of LiPPh$_2$ was then added over a period of 3 hr to an excess (100 g) of 1,3 dichloropropane at 0 °C and stirred overnight. The solvent was evaporated under reduced pressure, the residue dissolved in 55 mL of CHCl$_3$ and 55 mL of a saturated, aqueous solution of NH$_4$Cl was added, the layers separated and the organic layer dried over Na$_2$CO$_3$. The removal of CHCl$_3$ *in vacuo* resulted in 22.1 g (0.0843 mol, 84.3% yield) of Ph$_2$PCH$_2$CH$_2$CH$_2$Cl as a viscous oil. Spectral data: pmr: 2.03 (br, 4H), 3.45 (br, 2H), 7.23 (m, 10H); ir: (neat) 3054, 2932, 1594, 1484, 1439, 1316, 1267, 1194, 1125, 1097, 1070, 1027, 999, 942, 920, 889, 735, 695 cm^{-1}.

Preparation of PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$

PhPLi$_2$ was prepared by refluxing 1.17 g (0.168 mol) of lithium metal and 7.54 g (0.0422 mol) of PhPCl$_2$ in 150 mL of THF. The excess lithium metal was removed and this solution was slowly added over several hours to a solution of 22.1 g (0.0843 mol) of Ph$_2$PCH$_2$CH$_2$CH$_2$Cl at 0 °C in THF. This mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue dissolved in 50 ml of CHCl$_3$. 50 mL of a saturated, aqueous solution of NH$_4$Cl was added and the layers were separated, the organic layer dried over Na$_2$CO$_3$. The CHCl$_3$ was removed *in vacuo* and the residue chromatographed on Grade III neutral alumina eluting with benzene. Evaporation of the benzene resulted in 12.9 g (0.0229 mol, 54.2% yield) of PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$ as a viscous, white oil. Spectral data: pmr: 1.38–2.38 (br, 12H), 7.23–7.42 (br, 25H); ir: (neat) 3038, 2920, 2851, 1970, 1904, 1825, 1598, 1488, 1441, 1320, 1185, 1118, 1068, 1026, 997, 943, 675–755 cm^{-1}.

Attempted Decarbonylation of $CpFe(CO)_2\overset{\overset{O}{\|}}{C}CH_3$ by Rh[PhP(CH$_2$CH$_2$CH$_2$PPh)$_2$]$_2$Cl

0.350 g (0.500 mmol) of Rh[PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$] Cl [68] and 0.110 g (0.500 mmol) of $CpFe(CO)_2\overset{\overset{O}{\|}}{C}CH_3$ were dissolved in 20 mL of CH$_2$Cl$_2$ under N$_2$. The solution was monitored for 48 hr by ir without observing the appearance of any new bands. This reaction was also attempted with a tenfold excess of the iron complex at 0 °C and −23 °C in CH$_2$Cl$_2$ without the formation of any intermediates as determined by ir.

Decarbonylation of $CpFe(CO)_2\overset{\overset{O}{\|}}{C}CH_3$ by Rh(PPh$_3$)$_3$-Cl in the Presence of Added PPh$_3$

0.100 g (0.454 mmol) of $CpFe(CO)_2\overset{\overset{O}{\|}}{C}CH_3$ and 0.420 g (0.454 mmol) of Rh(PPh$_3$)$_3$Cl were dissolved in 25.0 mL of N_2-saturated benzene. Four reactions were monitored: one with no added PPh_3, the second with an equimolar amount of PPh_3 and iron complex, the third with a five fold excess and the fourth with a 10 fold excess of PPh_3. After three hours, iron products were quantitatively analyzed by comparison of their ir spectra to those of known mixtures and by integration of their pmr spectra. The results are listed in Table VI.

Kinetic Measurements

Solutions of $Rh(PPh_3)_3Cl$ and $Rh(PPh_3)_3Br$ in benzene were prepared under a N_2 atmosphere and allowed to equilibrate at 25° ± 0.2 °C for 30 min. Freshly sublimed $CpFe(CO)_2\overset{O}{\overset{\|}{C}}CH_3$ was then added at zero time. Samples of the reaction solution were withdrawn by syringe through a serum cap and the disappearance of $CpFe(CO)_2\overset{O}{\overset{\|}{C}}CH_3$ was monitored by observing the decrease in intensity of the acyl stretch at 1668 cm^{-1} using 0.5 mm sodium chloride cells. This acyl band obeyed the Lambert–Beer Law over the range of concentrations used.

Since decomposition of the unsaturated iron intermediate results in the formation of more $Rh(PPh_3)_2(CO)Cl$, over the expected stoichiometric amount, measurements could only be taken over a period of the first half life. Linear plots were then obtained from the data by plotting

$$\frac{1}{B_0 - A_0} \ln \frac{A_0B}{B_0A}$$

versus time where A_0 and B_0 are the initial concentration and A and B are the concentration at time t. The slopes of these plots were then evaluated by a linear least-squares program to give k_{obs}.

The concentration of $Rh(PPh_3)_3Cl$ or $Rh(PPh_3)_3Br$ was only varied from 6.00×10^{-3} to 10.0×10^{-3} to 20.0×10^{-3} *M*. The effect of added PPh_3 on the rate constant was determined by varying the amount of added PPh_3 between 4.00×10^{-3} to 40.0×10^{-3} *M* with a constant initial concentration of $CpFe(CO)_2\overset{O}{\overset{\|}{C}}CH_3$ of 10.0×10^{-3} *M* and that of $Rh(PPh_3)_3Cl$ at 8.00×10^{-3} *M*.

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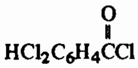
62 If the acid is refluxed in neat SOCl$_2$,  $HCl_2C_6H_4\overset{O}{\overset{\|}{C}}Cl$ is formed.
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