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# DECARBONYLATION OF ACYLIRON COMPOUNDS BY GROUP VIII METAL COMPLEXES

ERVEN J. KUHLMANN and JOHN J. ALEXANDER *

*Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221 (U.S.A.)*

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## Summary

Acylcyclopentadienyliron dicarbonyl complexes can be chemically decarbonylated by $Ir(PPh_3)_3Cl$ and $Ru(PPh_3)_3Cl_2$ whereas $Ir(PPh_3)_2(N_2)Cl$, $Pt(PPh_3)_4$ and $Pt(PPh_3)_3$ failed to show any decarbonylating activity. $[Rh(PPh_3)_2Cl]_2$ in acetonitrile has proved to be synthetically useful in the preparation of the corresponding alkyl compound, $CpFe(CO)_2R$ without the complications of triphenylphosphine substitution on the iron intermediate.

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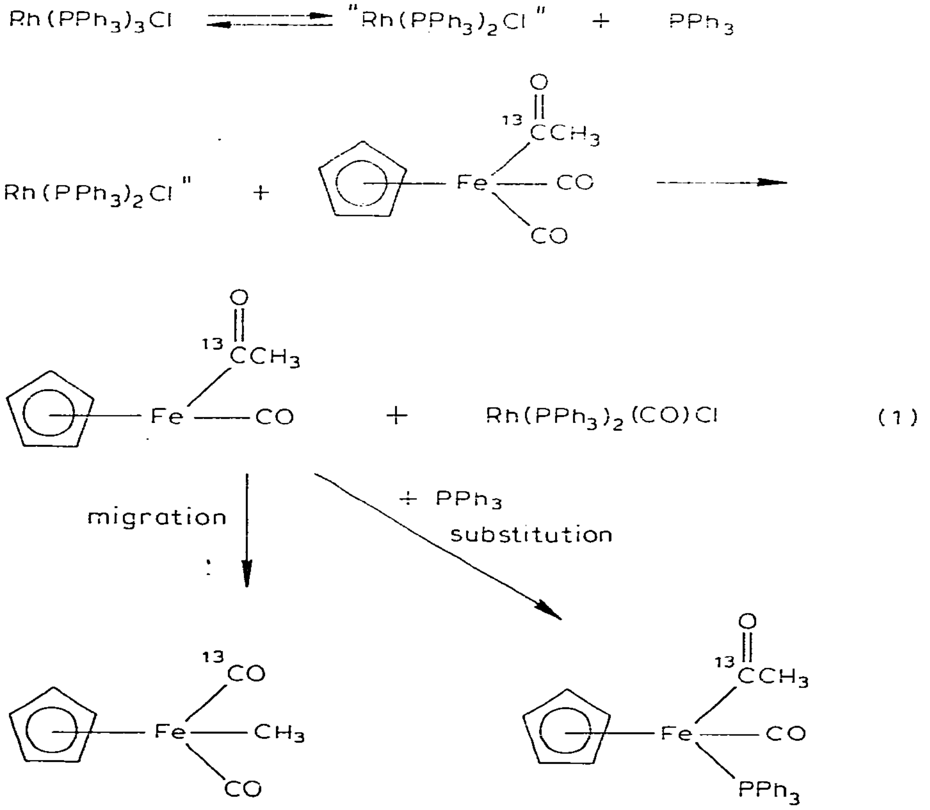
## Introduction

$Rh(PPh_3)_3Cl$ has been employed to abstract carbon monoxide from several transition metal carbonyl complexes of iron [1—3], manganese [1,2,4], rhenium [1,4] and molybdenum [1,5,6]. From kinetic data [3], and a $^{13}C$ labeling experiment [2], the mechanism shown in Scheme 1 would be suggested.

CO transfer from one metal center to a stable four-coordinate 16-electron rhodium complex has been demonstrated [7]. However, direct attack on these iron complexes by four-coordinate rhodium would seem unlikely based on the following observations [3]: first, the repression of the reaction rate upon addition of $PPh_3$ would indicate the importance of $PPh_3$ dissociation in the rate-determining step or in a prior equilibrium; second, the failure of the chelated $Rh[PhP(CH_2CH_2CH_2PPh_2)_2]Cl$ (where phosphine dissociation would be minimized) to effect decarbonylation or give any indication of the formation of an intermediate complex would suggest that four-coordinate rhodium is not the actual decarbonylating species. These observations suggest that $Rh(PPh_3)_3Cl$ dissociates a $PPh_3$ to give "$Rh(PPh_3)_2Cl$", the active decarbonylating agent. Tolman et al. [8] in their kinetic study on the hydrogenation of cyclohexene by $Rh[P(C_6H_4CH_3)_3]_3Cl$ concluded that a species of composition "$Rh[P(C_6H_4CH_3)_3]_2Cl$" must be postulated as being involved in activating $H_2$.

SCHEME 1



The reaction of $CpFe(CO)_2{}^{13}C(=O)CH_3$ with "$Rh(PPh_3)_2Cl$" results in the abstraction of a terminal carbonyl to give *trans*-$Rh(PPh_3)_2(CO)Cl$ and the coordinatively unsaturated intermediate $CpFe(CO){}^{13}C(=O)CH_3$. This intermediate can then undergo alkyl migration converting the bridging CO to a terminal one or attack by free $PPh_3$ (from the $Rh(PPh_3)_3Cl$) at the vacant coordination site. The results showed that this decarbonylating agent affords a synthetically useful means of preparing metal—alkyl bonds, i.e. $CpFe(Co)_2R$ from $CpFe(CO)_2C(=O)R$ [2,3] and $CpMo(CO)_2(PPh_3)R$ from $CpMo(CO)_2(PPh_3)C(=O)R$ [5,6]. For these iron and molybdenum complexes, yields were, for the most part, higher than those obtained from photochemical decarbonylations. Especially significant is the fact that a secondary alkyl can be prepared stereospecifically and in relatively high yield by the reaction of an acyliron compound with $Rh(PPh_3)_3Cl$ [2], a feat that is not observed in the photochemical reaction.

In continuing this work, the possibility of employing other Group VIII complexes as decarbonylating agents was examined. If one lists the possible requisites for these decarbonylating agents as extrapolated from our work on $Rh(PPh_3)_3Cl$ [3], the following would be included: (1) the formation of a stable complex with carbon monoxide, (2) ligand dissociation to give a coordinatively unsaturated intermediate and (3) substantial electron density in nonbonding orbitals on the metal for nucleophilic attack. Metal complexes of rhodium, iridium, ruthenium and platinum were investigated for their possible decarbonylation activity toward organometallic species.

## Results and discussion

To avoid the formation of the $PPh_3$-substituted acyliron complex and thus maximize the product of alkyl migration, $[Rh(PPh_3)_2Cl]_2$ was employed as a decarbonylating agent. This complex possesses a chloride-bridged dimeric structure, is insoluble in dichloromethane or benzene, but is soluble in strongly coordinating solvents such as acetonitrile, presumably giving rise to $Rh(PPh_3)_2(CH_3CN)Cl$. The dimer reacts with CO to form $Rh(PPh_3)_2(CO)Cl$ without the loss of $PPh_3$ [8,9]. Employing $[Rh(PPh_3)_2Cl]_2$ in acetonitrile, $CpFe(CO)_2C(=O)C_6H_4OCH_3$ was decarbonylated to give $CpFe(CO)_2C_6H_4OCH_3$ in a 49% yield. In comparison, a 39% yield of $CpFe(CO)(PPh_3)C(=O)C_6H_4OCH_3$ along with a trace amount of $CpFe(CO)_2C_6H_4OCH_3$ was observed when $Rh(PPh_3)_3Cl$ was used as the decarbonylating agent [3]. As with $Rh(PPh_3)_3Cl$, no CO abstraction by $[Rh(PPh_3)_2Cl]_2$ in acetonitrile was observed with $CpFe(CO)_2C(=O)CF_3$. Nevertheless, one can easily avoid the complications of the $PPh_3$ substitution and maximize the yield of alkyl migration product by the use of $[Rh(PPh_3)_2Cl]_2$ in acetonitrile.

In view of the ability of $Rh(PPh_3)_3Cl$ to effect decarbonylation, the possibility of employing the analogous $Ir(PPh_3)_3Cl$ was studied. $Ir(PPh_3)_3Cl$ can be prepared easily in situ by the action of $PPh_3$ on a solution of $Ir(PPh_3)_2(N_2)Cl$ (prepared from $Ir(PPh_3)_2(CO)Cl$ and $ArCON_3$). This procedure would provide a recycling pathway for this decarbonylating agent. For the rhodium complex *, reconversion to $Rh(PPh_3)_3Cl$ is not as yet quantitative.

The reaction of $Ir(PPh_3)_3Cl$ with $CpFe(CO)_2C(=O)R$ in benzene at room temperature resulted in modest yields of $Ir(PPh_3)_2(CO)Cl$ as listed in Table 1. These CO abstractions proceeded at a much slower rate than those of the rhodium complexes. After 4 h, there was little evidence of any $Ir(PPh_3)_2(CO)Cl$ formation. On heating, solutions of $Ir(PPh_3)_3Cl$ are known to undergo *ortho*-metallation to give $IrH[(o\text{-}C_6H_4)Ph_2P](PPh_3)_2Cl$ [12]. However, the infrared spectrum of the reaction mixture showed no evidence for formation of this compound at room temperature. Thus, the sluggishness in reactivity is in agreement with the postulated coordinatively unsaturated "$Rh(PPh_3)_2Cl$" acting as the active decarbonylation agent in that system since $Ir(PPh_3)_3Cl$ has been reported to undergo dissociation to a lesser extent than the corresponding rhodium complex [13]. Although this iridium complex could be recycled, long reaction times and low yields would make $Ir(PPh_3)_3Cl$ less desirable than the corresponding rhodium complex as a decarbonylating agent for organometallic compounds.

In an attempt to facilitate production of a coordinatively unsaturated iridium complex, $Ir(PPh_3)_2(N_2)Cl$ was employed as a possible decarbonylation agent

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* Stille et al. reported a method of regenerating $Rh(PPh_3)_3Cl$ from $Rh(PPh_3)_2(CO)Cl$. However, the yields are low and the product seems to be sluggish in its decarbonylating ability [10]. Also, Geoffroy has reported the photo-induced oxidation of the CO in $Rh(PPh_3)_2(CO)Cl$ to $CO_2$ and the subsequent addition of $PPh_3$ to regenerate $Rh(PPh_3)_3Cl$ in a 61% yield [11].

TABLE 1

PRODUCTS FROM THE DECARBONYLATION OF $CpFe(CO)_2C(=O)R$

| Decarbonylating agent | R | % $Rh(PPh_3)_2(CO)Cl$ | % $CpFe(CO)_2R$ | % $CpFe(CO)(PPh_3)C(=O)R$ |
|---|---|---|---|---|
| $Rh(PPh_3)_3Cl$ | $p$-$C_6H_4OCH_3$ | 76 | trace | 39 |
| $Rh(PPh_3)_3Cl$ | $C_6H_5$ | 98 | 40 | 44 |
| $Rh(PPh_3)_3Cl$ | $CH_3$ | 98 | 46 | 11 |
| | | % $Rh(PPh_3)_2(CO)Cl$ | | |
| $[Rh(PPh_3)_2Cl]_2$ [a] | $p$-$C_6H_4OCH_3$ | 92 | 49 | — |
| $[Rh(PPh_3)_2Cl]_2$ [a] | $C_6H_5$ | 56 | 32 | — |
| $[Rh(PPh_3)_3Cl]_2$ [a] | $CF_3$ | — | — | — |
| | | % $Ir(PPh_3)_2(CO)Cl$ | | |
| $Ir(PPh_3)_3Cl$ | $p$-$C_6H_4OCH_3$ | 35 | — | 23 |
| $Ir(PPh_3)_3Cl$ | $C_6H_5$ | 39 | 18 | 16 |
| $Ir(PPh_3)_3Cl$ | $CH_3$ | 39 | 17 | 6 |
| | | % $Ru(PPh_3)_2(CO)_2Cl_2$ | | |
| $Ru(PPh_3)_3Cl_2$ | $C_6H_5$ | 30 | trace | trace |
| $Ru(PPh_3)_3Cl_2$ | $CH_3$ | 30 | trace | trace |

[a] In acetonitrile.

with the hope that loss of the labile $N_2$ would generate "$Ir(PPh_3)_2Cl$." However, $Ir(PPh_3)_2(N_2)Cl$ afforded no CO abstraction with either $CpFe(CO)_2C(=O)CH_3$ or $CpFe(CO)_2C(=O)C_6H_4OCH_3$ at room temperature in benzene. Refluxing resulted only in the decomposition of the iridium dinitrogen complex. Although $Ir(PPh_3)_2(N_2)Cl$ in the presence of base is reported to undergo *ortho*-metallation, this was not observed under our reaction conditions.

Since chloroform solutions of $Ir(PPh_3)_2(N_2)Cl$ are known to decompose [14] with $N_2$ loss, these decarbonylation attempts were also carried out in chloroform with no success. Evidently, decomposition of the dinitrogen complex does not result in formation of "$Ir(PPh_3)_2Cl$" or any other active decarbonylating species.

$RuCl_2(PPh_3)_3$ would seem a suitable candidate for chemically induced decarbonylations of metal carbonyls. This complex exists as a monomer and is known to undergo some association in benzene to give the corresponding dimeric complex with $K_{ass} = 2.7 \pm 0.5 \times 10^{-3}$ [15,16] and to react with CO to give the stable *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$ [17].

Benzene solutions of $RuCl_2(PPh_3)_3$ and $CpFe(CO)_2C(=O)R$ where R was $CH_3$ and $C_6H_5$ showed no evidence in the IR of any decarbonylation after 14 h at room temperature. However, after refluxing for 8 to 12 h, *cis*-$RuCl_2(CO)_2(PPh_3)_2$ could be isolated in 25 to 30% yields by column chromatography. Approximately 70% of the unreacted starting iron complexes were recovered along with $PPh_3$ and trace amounts of $CpFe(CO)_2R$ and $CpFe(CO)(PPh_3)C(=O)R$. The thermal instability of the iron intermediates at these temperatures is undoubtedly responsible for the low yields of iron products.

The limited ability for $RuCl_2(PPh_3)_3$ to effect CO abstraction is not surprising in retrospect. The greater charge on the metal, while reducing its nucleophilicity and ability to attack at a coordinated carbonyl, would also lead to bonding with a stronger $\sigma$ donor such as the phosphines over a $\pi$ back-bonding ligand such as CO. The high temperatures necessary for decarbonylation and the resulting low yields would make this ruthenium complex impractical for these reactions.

To continue the survey of Group VIII complexes, a $d^{10}$ platinum(0) complex was investigated as a possible decarbonylation agent. A solution of either $Pt(PPh_3)_4$ or $Pt(PPh_3)_3$ in benzene or THF failed to decarbonylate $CpFe(CO)_2C(=O)C_6H_5$ even under refluxing conditions. The disappointing failure of these complexes to effect decarbonylation may be due to the fact that no great increase in thermodynamic stability would result upon substitution of a phosphine by CO. The facts are that platinum does not form a stable, simple carbonyl $Pt(CO)_4$ (although $Pt(CO)_4$ has been observed in the infrared by matrix isolation [18]), and that $Pt(PPh_3)_3$ does not add $H_2$ [19]; together these may account for the failure of $Pt(PPh_3)_4$ as a decarbonylating agent.

## Experimental

Infrared spectra were measured on a Perkin—Elmer Model 337 Grating Infrared Spectrophotometer using sodium chloride (0.1 mm) cells. Unless otherwise noted, all spectra were recorded in Nujol mulls except for the spectrum of the carbonyl region which was obtained in $CHCl_3$. The spectra were calibrated against the 1601 and 907 $cm^{-1}$ bands of a polystyrene film.

The $^1H$ NMR measurements were conducted on a Varian T-60 or A-60 instrument in $CDCl_3$ employing TMS as an internal reference.

Product separation and purification by column chromatography were carried out on Grade III Woelm acidic alumina.

All reaction 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, were used without further purification.

Iron pentacarbonyl was purchased from Alfa Products, Ventron Corporation. Rhodium trichloride trihydrate, ruthenium trichloride hydrate and iridium trichloride hydrate were obtained from Engelhard Industries; potassium tetrachloroplatinate(II) was obtained from Fischer Scientific. $p$-$CH_3OC_6H_4C(=O)Cl$ was obtained from Aldrich Chemicals. All these compounds were used as received.

The following compounds were prepared by standard literature methods: $(CpFe(CO)_2)_2$ [20], $Rh(PPh_3)_3Cl$ [21], $CpFe(CO)_2C(=O)CH_3$ [22], $CpFe(CO)_2C(=O)C_6H_5$ [23], $CpFe(CO)_2C(=O)CF_3$ [23], $CpFe(CO)_2C(=O)C_6H_4OCH_3$ [3], $Ir(PPh_3)_2(CO)Cl$ [24], $Ir(PPh_3)_2(N_2)Cl$ [14], $Ru(PPh_3)_3Cl_2$ [25], $Pt(PPh_3)_4$ [26], and $Pt(PPh_3)_3$ [26].

### *Decarbonylation of $CpFe(CO)_2C(=O)R$ by $Rh(PPh_3)_3Cl$ ($R = CH_3$, $C_6H_5$, $p$-$C_6H_4OCH_3$)*

0.220 g (1.00 mmol) of $CpFe(CO)_2C(=O)CH_3$ and 0.925 g (1.00 mmol) of $Rh(PPh_3)_3Cl$ were stirred in 10 ml of $CH_2Cl_2$ under a nitrogen atmosphere for

3 h. The solution was cooled and filtered to yield 0.679 g (0.984 mmol, 98.4% yield) of $Rh(PPh_3)_2(CO)Cl$. The solvent was removed under reduced pressure and the residue chromatographed on Grade III alumina eluting with hexanes to give 0.088 g (0.46 mmol, 46% yield) of $CpFe(CO)_2CH_3$ and with a mixture of hexane/diethyl ether to give 0.051 g (0.11 mmol, 11% yield) of $CpFe(CO)(PPh_3)C(=O)CH_3$ and 0.030 g (13% recovered) of starting iron complex. Yields for R = $CH_3$, $C_6H_5$ and $p$-$C_6H_4OCH_3$ are reported in Table 1. Compounds were identified from their IR and pmr spectra [3,23,27,28].

### *Decarbonylation of* $CpFe(CO)_2C(=O)C_6H_4OCH_3$ *by* $[Rh(PPh_3)_2Cl_2]_2$

0.312 g (1.00 mmol) of $CpFe(CO)_2C(=O)C_6H_5OCH_3$ and 0.662 g (0.500 mmol) of $[Rh(PPh_3)_2Cl]_2$ were stirred in 15 ml of acetonitrile under a nitrogen atmosphere for 20 h. The solvent was removed under reduced pressure and the residue chromatographed on Grade III alumina with a mixture of hexane/diethyl ether to give 0.140 g (0.493 mmol, 49.3% yield) of $CpFe(CO)_2C_6H_4OCH_3$ and 0.090 g (28.8% recovered) of starting iron complex and with chloroform to give 0.633 g (0.917 mmol, 91.7% yield) of $Rh(PPh_3)_2(CO)Cl$.

### *Decarbonylation of* $CpFe(CO)_2C(=O)C_6H_4OCH_3$ *by* $Ir(PPh_3)_3Cl$

$Ir(PPh_3)_3Cl$ was prepared in situ by combining 0.339 g (0.434 mmol) of $Ir(PPh_3)_2(N_2)Cl$ and 0.114 g (0.434 mmol) of triphenylphosphine in 15 ml of benzene under a $N_2$ atmosphere. The solution immediately became deep red in color with evolution of nitrogen.

0.135 g (0.434 mmol) of $CpFe(CO)_2C(=O)C_6H_4OCH_3$ was added and the solution was stirred for 24 h. The solvent was removed under reduced pressure and the residue chromatographed on Grade III acidic alumina with a mixture of hexanes and diethyl ether to give 0.0533 g (0.0976 mmol, 22.5% yield) of $CpFe(CO)(PPh_3)C(=O)C_6H_4OCH_3$ and 72.0% unreacted starting iron material and with chloroform to give 0.120 g (0.154 mmol, 35.4% yield) of *trans*-$Ir(PPh_3)_2(CO)Cl$.

### *Decarbonylation of* $CpFe(CO)C(=O)CH_3$ *by* $Ru(PPh_3)_3Cl_2$

0.480 g (0.500 mmol) of $Ru(PPh_3)_3Cl_2$ and 0.220 g (1.00 mmol) of $CpFe(CO)_2C(=O)CH_3$ were refluxed for 8 h in 10 ml of benzene under $N_2$. The solvent was removed under reduced pressure and the residue chromatographed wih hexanes to give 0.018 g (0.095 mmol, 9.6% yield) of $CpFe(CO)_2CH_3$ and with methylene chloride to give 0.120 g (0.159 mmol, 31.9% yield) of *cis*-$Ru(PPh_3)_2(CO)_2Cl_2$. *cis*-$Ru(PPh_3)_2(CO)_2Cl_2$ is a white solid, m.p. 274°C darkens, lit. [17] 230–235°C. Spectral data: IR (Nujol): 2065, 1994 $cm^{-1}$ ($\nu$(CO)); lit. [17] 2064, 2001 $cm^{-1}$.

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