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Chemical Decarbonylation of Organometallic Compounds

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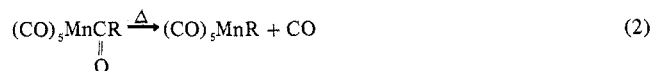
Transition metal carbonyl acyl complexes of the type $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_n\text{COR}$ ($\text{M} = \text{Fe}$, $n = 2$; $\text{M} = \text{Mo}$, $n = 3$) can be chemically decarbonylated under mild conditions using $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$. The products are a mixture of the corresponding alkyl and triphenylphosphine-substituted acyl complexes. The scope and mechanism of this reaction are discussed.

Introduction

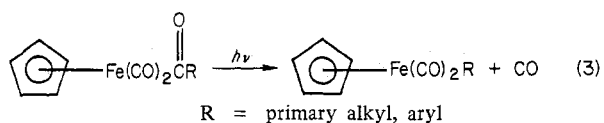
Transition metal carbonyls containing an acyl group can often be decarbonylated to yield the corresponding alkyl³



Prior to a preliminary communication⁴ concerning this work, only thermal or photochemical conditions⁵ were known to effect decarbonylation of such compounds. Unfortunately both of these methods present difficulties which often prevent their wide synthetic application. For example, although acylmanganese pentacarbonyls can readily be thermally decarbonylated



the cyclopentadienyliron dicarbonyl acyls do not undergo a similar reaction under thermal conditions. Abstraction of carbon monoxide from these complexes can be achieved photochemically



However, such vigorous reaction conditions result in low yields and, moreover, are only applicable when R is a primary alkyl or an aryl group. If R is a secondary alkyl, only decomposition is observed in attempts at photolytic decarbonylation.

Recent success⁶ in the conversion of organic acyl halides and aldehydes to alkyl halides, olefins, or alkanes with chlorotris(triphenylphosphine)rhodium(I) prompted us to employ this reagent to effect chemical decarbonylation of some transition metal organometallics under mild conditions. We report here our findings concerning the scope and mechanism of carbon monoxide abstraction by $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$.

This same compound has been recently used for decarbonylation of related molybdenum complexes.^{7,8}

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- (3) A comprehensive review of carbonylation and decarbonylation reactions of transition metal complexes is to be found in A. Wojcicki, *Advan. Organometal. Chem.*, in press.

- (4) J. J. Alexander and A. Wojcicki, *J. Organometal. Chem.*, **15**, P23 (1968).

- (5) See, for example: (a) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962); (b) B. L. Booth, R. N. Haszeldine, and N. P. Woffenden, *J. Chem. Soc. A*, 1979 (1970); (c) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964); (d) K. W. Barnett, *Inorg. Chem.*, **8**, 2009 (1969); (e) M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, **93**, 1368 (1971).

- (6) (a) K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, **90**, 99 (1968); (b) J. Blum, E. Oppenheimer, and E. D. Bergmann, *ibid.*, **89**, 2338 (1967).

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Experimental Section

All reactions were carried out under nitrogen. Reagent grade solvents were used. Tetrahydrofuran was distilled over CaH_2 immediately before use.

$\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$,⁹ $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COR}$ ($\text{R} = \text{CH}_3$,¹⁰ CF_3 ,^{5c} C_6H_5 ,^{5c} $\text{CH}=\text{CHC}_6\text{H}_5$,^{5c} $\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$,¹¹), $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{S}(\text{O})_2\text{CH}_2\text{C}_6\text{H}_5$,¹² $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{R}$ ¹³ ($\text{R} = \text{CH}_3$, $\text{CH}_2\text{C}_6\text{H}_5$), $\text{Mn}(\text{CO})_5\text{COCH}_3$,¹⁴ and $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{COCF}_3$ ^{5c} were prepared by literature methods. $\text{C}(\text{C}_6\text{H}_5)_3\text{COCl}$ and $\text{C}(\text{CH}_3)_3(\text{C}_6\text{H}_5)_2\text{COCl}$ were prepared by refluxing the acids in SOCl_2 . The crude products were recrystallized from pentane-benzene and identified by their infrared spectra.

Infrared spectra were measured on a Perkin-Elmer Model 337 instrument using NaCl solution cells of 0.1-mm thickness. Mass spectra were obtained on an AEI Model MS-9 spectrometer. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Mr. P. J. Kovi of The Ohio State University using a Coleman Model 29 analyzer. Molecular weights were determined by Dr. M. A. Steffel using a Mechrolab Model 301-A vapor pressure osmometer.

Preparation of $\text{CH}_3^{13}\text{COCl}$. A 1.0-g sample of $\text{CH}_3^{13}\text{COONa}$ (60% enriched; Merck Sharp and Dohme) and 1.4 g of CH_3COONa were heated in an excess of freshly distilled benzoyl chloride. Distillation yielded 1.6 g (69%) of ^{13}C -enriched CH_3COCl (bp 51–53°).

Preparation of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^{13}\text{COCH}_3$. A 3.54-g sample (10.0 mmol) of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ in tetrahydrofuran was reduced with excess 2% sodium amalgam. After removal of mercury, 1.6 g (20 mmol) of the $\text{CH}_3^{13}\text{COCl}$ was added and the solution was stirred for 4 hr. The solvent was removed under reduced pressure and the residue was extracted with 100 ml of pentane. The volume was reduced under a stream of N_2 and the solution was cooled to –78° to precipitate the crude product which was then sublimed to yield 2.87 g (65%) of the yellow $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^{13}\text{COCH}_3$ identified by its infrared and mass spectra.

Decarbonylation of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^{13}\text{COCH}_3$. A 1.00-g sample (4.53 mmol) of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^{13}\text{COCH}_3$ and 4.50 g (4.86 mmol) of $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$ were stirred in 30 ml of benzene for 3 hr at room temperature; 25 ml of CH_2Cl_2 was added and the solution was filtered to yield 2.24 g (58%) of yellow $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$. The solvent was then removed from the filtrate at reduced pressure and the resulting oil was chromatographed on Grade III alumina. A yellow band of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})^{13}\text{COCH}_3$ (0.35 g, 40%) was eluted with pentane and an orange band of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]^{13}\text{COCH}_3$ (0.08 g, 4%) was eluted with chloroform. Both products were identified by their infrared spectra.

This same procedure was employed for all the decarbonylations discussed here except that in some cases CH_2Cl_2 alone was used as the solvent and reaction times varied up to 15 hr. The progress of reactions was followed by infrared spectroscopy.

Preparation of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COR}$ ($\text{R} = \text{C}(\text{C}_6\text{H}_5)_3$, $\text{C}(\text{CH}_3)_3$, C_6H_5). These compounds were prepared by the same procedure as for the acetyl and identified by their infrared spectra (see Table I).

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- (10) R. B. King, *J. Amer. Chem. Soc.*, **85**, 1918 (1963).

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Table I. Infrared Spectra of Acyls (Sulfonates) and Yields of Isolated Complexes

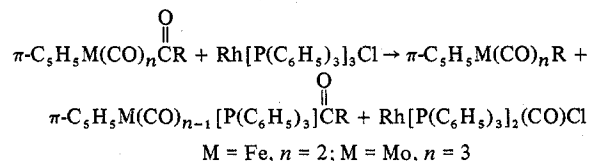
Compd	$\nu_{\text{C=O}},^a \text{ cm}^{-1}$	% Rh[P(C ₆ H ₅) ₃] ₂ (CO)Cl			
		Alkyl	Substituted acyl (sulfonate)	Starting acyl (sulfonate)	
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCH}_3$	2016, 1973	88	40	4	0
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COC}_6\text{H}_5$	2036, 1981	75	17	16 ^c	Trace
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCH}(\text{CH}_3)\text{C}_6\text{H}_5$	2015, 1960	72	54	0	0
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COC}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$	2040, 1960	85	0	0	Trace
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COC}(\text{C}_6\text{H}_5)_3$	2038, 1958	75	0	0	0
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCH=CHC}_6\text{H}_5$	2020, 1960 ^b	86	0	0	15
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$	2066, 2024	90	0	0	0
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_2\text{C}_6\text{H}_5$	2067, 2018	55	0	0	5
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{S}(\text{O})_2\text{CH}_2\text{C}_6\text{H}_5$	1957 ^b	No reaction			
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCF}_3$	2045, 1994	No reaction			
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{COCF}_3$		100		70	0
$\text{Mn}(\text{CO})_5\text{COCH}_3$		95	12	0	0

^a In CH₂Cl₂. ^b In CHCl₃. ^c $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{COC}_6\text{H}_5$ was reported earlier by A. N. Nesmeyanov, Yu. A. Chapovsky, I. V. Polovnyanyuk, and L. G. Makarova, *J. Organometal. Chem.*, **7**, 329 (1967).

Preparation of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{COCF}_3$. A 1.00-g sample (2.90 mmol) of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{COCF}_3$ and 3.30 g (3.58 mmol) of $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$ in 80 ml of CH₂Cl₂ were stirred for 1 hr at room temperature. The reaction mixture was filtered to yield 2.45 g (3.56 mmol) of $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$. The solvent was removed under reduced pressure and the residue chromatographed on Grade III alumina with chloroform as the eluent. Two bands developed. The yellow first band contained a trace of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{COCF}_3$ identified by infrared spectroscopy. Addition of hexane to the eluate of the orange second band gave 1.26 g (70%) of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{COCF}_3$. This compound is an orange solid, mp 149–151° dec, and has carbonyl stretching bands at 1965, 1893 (C=O), and 1609 cm⁻¹ (C=O) in CH₂Cl₂ solution. *Anal.* Calcd for C₂₇H₂₀O₃PF₃Mo: C, 56.31; H, 3.48. Found: C, 55.85; H, 3.62. Mol wt: Calcd, 575; found, 556 (osmometrically in CH₂Cl₂).

Results and Discussion

Scope of Chemical Decarbonylation Reaction. Treatment of several iron or molybdenum cyclopentadienyl acyls with chlorotris(triphenylphosphine)rhodium(I) was observed to give the corresponding alkyl, the triphenylphosphine-substituted acyl, or a mixture of the two in cases where products could be isolated



Varying amounts of the decarbonylated (alkyl) and substituted products were obtained depending on the nature of R and M as summarized in Table I.

Considering first the iron compounds, it may be noted that the reaction under discussion affords a synthetically useful means of preparing iron dicarbonyl alkyls containing either a primary or a secondary carbon. Although no attempt to maximize the yield was made when R = CH₃, the amount of alkyl isolated was greater than that reported^{5c} for photochemical decarbonylation. Especially significant is the fact that a secondary alkyl can be produced in this way in relatively high yield (54%). Attempts at photochemical decarbonylation of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCH}(\text{CH}_3)\text{C}_6\text{H}_5$ led only to decomposition. The yield of the phenyl compound was comparable to that under photochemical conditions.^{5c}

As we shall demonstrate in the following section, the mechanism of this reaction involves a coordinatively unsaturated intermediate produced by abstraction of a terminal CO from the starting material. The vacant position may be filled by migration of the alkyl (or aryl) group, thus

converting the bridging CO to a terminal one. Alternatively, a free $\text{P}(\text{C}_6\text{H}_5)_3$ molecule present in solution as a result of the dissociation of $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$ ¹⁵ may attack the intermediate. The relative amounts of decarbonylated and substituted products reflect the relative rates of migration and substitution, respectively. The methyl group migrates rather readily and only 4% substitution product is observed. With the compound $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCH}(\text{CH}_3)\text{C}_6\text{H}_5$ the bulkiness of both triphenylphosphine and the α -phenethyl group presumably slows down the substitution to the extent that it is no longer competitive with alkyl migration, and thus no substituted product is isolated. Both substitution and migration apparently occur at comparable rates in $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COC}_6\text{H}_5$.

We endeavored to synthesize iron-tertiary carbon bonds by this procedure but, as is apparent from Table I, only the CO abstraction occurred to give $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$. The coordinatively unsaturated intermediate containing the bulky tertiary alkyl group apparently decomposed during substitution or migration of the R group. The alkyl product, if formed, should have sufficient stability for detection and isolation under these conditions.¹⁶

In an effort to prepare iron cyclopentadienyl carbonyls containing a terminal SO₂ ligand (analogous to, e.g., $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{SO}_2$ ¹⁷), we treated $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{R}$ (R = CH₃, CH₂C₆H₅) with the rhodium complex. Again we observed that the CO abstraction step occurred; however, apparently either the coordinatively unsaturated intermediate or the product containing the terminal SO₂ was unstable and decomposed under the very mild conditions employed.

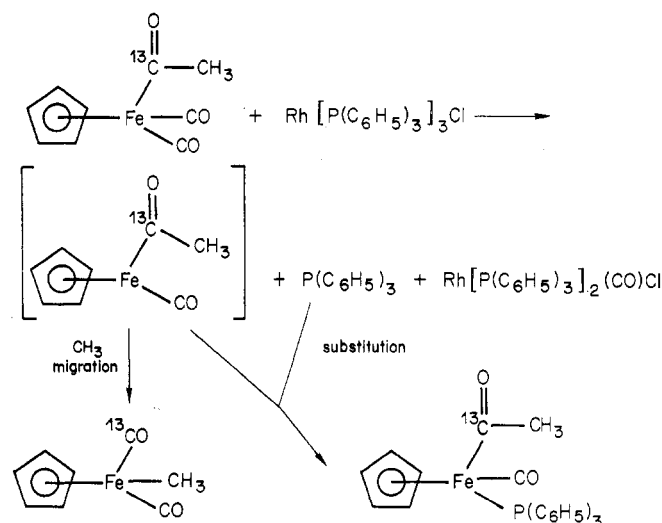
No CO abstraction by $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$ was observed with $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{S}(\text{O})_2\text{CH}_2\text{C}_6\text{H}_5$. This may be attributed to the enhanced strength of the Fe-CO π bond resulting from replacement of a carbonyl group with the more basic triphenylphosphine. The carbonyl stretching frequencies, listed in Table I, support such an explanation. Carbon monoxide abstraction also does not occur with $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCF}_3$. This unexpected inertness is difficult to rationalize in view of the rather high CO stretching frequencies (2045, 1994 cm⁻¹) for the compound. Quite possibly the rather electronegative C(O)CF₃ group withdraws charge from the iron resulting in increased strength for the metal-CO (terminal) σ bond. This effect

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Scheme I



would account for the relatively high $\nu_{\text{C}\equiv\text{O}}$ values and the apparently rather strong Fe-CO(terminal) bond in $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCF}_3$.

One molybdenum compound was tested for its reaction with $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$. Upon abstraction of a terminal CO from $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{COCF}_3$, substitution by $\text{P}(\text{C}_6\text{H}_5)_3$ occurs more rapidly than migration of the CF_3 group to produce a 70% yield of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{COCF}_3$ on work-up. The starting material can be thermally decarbonylated in 50% yield to give $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CF}_3$.^{5c} Recently, $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{COR}$ complexes ($\text{R} = \text{C}_6\text{H}_5$, $p\text{-C}_6\text{H}_4\text{F}$) have been decarbonylated to give $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{R}$ with $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$.^{7,8} Steric hindrance to further substitution by the bulky $\text{P}(\text{C}_6\text{H}_5)_3$ very likely prevented formation of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{COR}$.

Although acetylmanganese pentacarbonyl can readily be decarbonylated thermally,^{5a,14} we examined its reaction with the rhodium complex. Only a low (12%) yield of $\text{Mn}(\text{CO})_5\text{CH}_3$ was obtained, making this an impractical method of synthesis of such alkyls. Treatment of $\text{Mn}(\text{CO})_5\text{-COR}$ and $\text{Re}(\text{CO})_5\text{COR}$ ($\text{R} = \text{cyclopropyl}$) with $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$ has been reported¹⁸ to give CO abstraction, but no alkyl compounds could be isolated.

Reaction Mechanism. As mentioned previously, an analysis of products isolated suggests that the reaction of chlorotris(triphenylphosphine)rhodium(I) with cyclopentadienyliron dicarbonyl acyls proceeds in two steps: abstraction of a terminal CO to form a coordinatively unsaturated intermediate and $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$, followed by either alkyl migration or triphenylphosphine attack at the vacant coordination position. The solvated form of this proposed intermediate has been invoked¹⁹ to explain kinetic results for the carbonylation of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ with various ligands L leading to the products $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{L}(\text{COR})$. Our hypothesis was confirmed by examining the products from the reaction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^{13}\text{COCH}_3$ with $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$. The starting acyl was labeled only in the acetyl position with ^{13}C as shown by its infrared spectrum ($\text{C}\equiv\text{O}$ stretches at

Table II. Infrared Spectra of Labeled Compounds

Compd	CO str, cm^{-1}	
	Terminal	Bridging
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^{13}\text{COCH}_3$	2016, 1973 ^a	1668, 1629 ^a
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(^{13}\text{CO})\text{CH}_3$	2015, 2002, 1960, 1931 ^a	
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]^{13}\text{COCH}_3$	1923 ^b	1602, 1556 ^b

^a In hexane. ^b In CH_2Cl_2 .

2016 and 1973 cm^{-1} , $^{12}\text{C}\equiv\text{O}$ stretch at 1668 cm^{-1} , $^{13}\text{C}=\text{O}$ stretch at 1629 cm^{-1} in hexane). The course of the reaction is shown in Scheme I.

Only the natural abundance of ^{13}C is incorporated in the rhodium carbonyl (strong $^{12}\text{C}\equiv\text{O}$ stretch at 1968 cm^{-1} in CH_2Cl_2) showing that the abstracted CO must have been a terminal one.²⁰ Moreover, the $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(^{13}\text{CO})\text{CH}_3$ isolated contains substantial ^{13}C as shown by the presence of four terminal CO stretching bands at 2015, 2002, 1960, and 1931 cm^{-1} in hexane. Mass spectral measurements indicate the same abundance of ^{13}C in the parent peaks of both the starting acetyl and the product methyl compounds. Finally, the $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]^{13}\text{COCH}_3$ isolated contains labeled ^{13}C only in the bridging position as shown by the presence of only one terminal CO frequency (1923 cm^{-1}) and two bridging CO frequencies (1602 and 1556 cm^{-1}) in CH_2Cl_2 . Table II summarizes the infrared results.

We have also investigated the stereospecificity of this reaction. Treatment of $(-)\text{-}_{546}\text{-}\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CO*CH}(\text{CH}_3)\text{C}_6\text{H}_5$ ($[\alpha]_{546}^{27} -64.3^\circ$ in CHCl_3) with the rhodium complex gave in 54% yield $(+)\text{-}_{546}\text{-}\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{*CH}(\text{CH}_3)\text{C}_6\text{H}_5$ ($[\alpha]_{546}^{27} +78.4^\circ$ in CHCl_3).¹¹ Recently, Whitesides and Boschetto²¹ have shown that the carbonylation reaction of *threo*- $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CHDCHDC}(\text{CH}_3)_3$ with $\text{P}(\text{C}_6\text{H}_5)_3$ leads to the *threo* acyl with >95% configuration retention. Thus we conclude that our acyl having the *R* configuration retains the same absolute configuration at the α carbon on decarbonylation. Several optically active aldehydes are known to give optically active alkanes with configuration retention at the asymmetric carbon²² on treatment with $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$.

Registry No. $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCH}_3$, 12108-22-4; $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COC}_6\text{H}_5$, 12154-94-8; $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{COCH}(\text{CH}_3)\text{C}_6\text{H}_5$, 36118-93-1; $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$, 12080-06-7; $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$, 12126-73-7; $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{*CH}(\text{CH}_3)\text{C}_6\text{H}_5$, 36182-37-3; $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{COCF}_3$, 33134-62-2; $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$, 14694-95-2.

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(20) J. J. A. has decarbonylated $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^{13}\text{COCH}_3$ photochemically and finds that the product is $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(^{13}\text{CO})\text{CH}_3$ having relative intensities of the ^{12}CO and ^{13}CO terminal stretches the same as in the product from chemical decarbonylation. This result is taken to mean that ultraviolet irradiation of these complexes also removes a terminal rather than a bridging CO as would be expected.

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