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On the Mechanism of Photochemical Decarbonylation of Acetyldicarbonyl-η^5-cyclopentadienyliron

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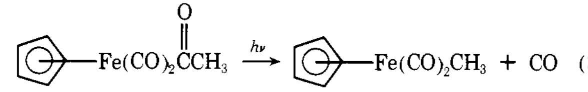
Abstract: It is demonstrated that decarbonylation of η^5-$(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$ either photochemically or in the mass spectrometer occurs with loss of a terminal carbonyl group. The intermediate resulting from the photochemical process undergoes nucleophilic attack by triphenylphosphine faster than methyl migration. Mass spectra of η^5-$(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$ show differences in the fragmentation patterns which depend on the ionization energy. At 20 eV considerably more scrambling and loss of ^{13}CO is observed than at 70 eV.

Insertion and abstraction reactions involving metal-carbon bonds are well known in organometallic chemistry.[1] Carbon monoxide was one of the first small molecules found to give insertion products with metal alkyl complexes.[2]

$$\mathrm{CH_3Mn(CO)_5 + CO \underset{\Delta}{\rightleftharpoons} CH_3C(O)Mn(CO)_5} \tag{1}$$

Two points are worthy of note in regard to reaction 1: first, that the reaction is thermally reversible to give the product resulting from CO abstraction out of the Mn-C bond; second, that the terms insertion and abstraction merely describe the structure of the product compared to that of the reactant. Indeed, it has been shown[3] that the "inserted" CO in reaction 1 is one of the CO's originally bonded to Mn.

Cyclopentadienyliron dicarbonyl alkyls and acyls will undergo reactions analogous to eq 1; however, much more vigorous conditions are required to effect these.[4,5]



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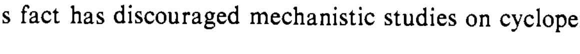


(3)

This fact has discouraged mechanistic studies on cyclopentadienyliron carbonylation reactions where the entering nucleophile is CO.

Our recent work on the chemical decarbonylation of organometallic acyl complexes[6] using chlorotris(triphenylphosphine)rhodium(I) led us to investigate the mechanism of decarbonylation of η^5-$(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$ under photolytic conditions. The results of this investigation are reported here along with some information on fragmentation pathways of η^5-$(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$ and η^5-$(C_5H_5)Fe({}^{13}CO)(CO)CH_3$ in the mass spectrometer.

Experimental Section

Materials. Solvents and chemicals were reagent grade and were used without further purification except for tetrahydrofuran which was distilled from calcium hydride. Chromatography was carried out on columns of acid-washed Grade I Woelm alumina. η^5-$(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$ was prepared by a previously published procedure.[6] Purification was accomplished by repeated vacuum sublimation at 40° onto a Dry Ice-cooled probe. The compound exhibited terminal CO stretches at 2021 (s) and 1968 (s) cm^{-1} in hexane. The acyl stretches occurred at 1671 (m) for $^{12}C{=}O$ and 1636 (m) cm^{-1} for $^{13}C{=}O$.

Decarbonylation of η^5-$(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$. The acetyl complex (0.50 g, 2.3 mmol) in 100 ml of hexane was irradiated under N_2 in a quartz vessel for 30 min with a Hanovia 450-W mercury vapor lamp. The solution was reduced in volume under a ni-

Table I. Mass Spectra of $\eta^5(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$

		70 eV, 260°		20 eV, 330°	
Fragment	m/e	Rel intensity[a]	% labeling	Rel intensity[a]	% labeling
$C_5H_5Fe({}^{12}CO)_2{}^{13}C(O)CH_3{}^+$	221	2.7	28	0.39	27
$C_5H_5Fe({}^{12}CO)_2{}^{12}C(O)CH_3{}^+$	220	7.1		1.1	
$C_5H_5Fe({}^{12}CO)_2({}^{13}CO)^+$	206	0.93	26	0.77	27
$C_5H_5Fe({}^{12}CO)_3{}^+$	205	2.7		2.1	
$C_5H_5Fe({}^{12}CO){}^{13}C(O)CH_3{}^+$	193	24	29	22	28
$C_5H_5Fe({}^{12}CO){}^{12}C(O)CH_3{}^+$	192	60		54	
$C_5H_5Fe({}^{12}CO)({}^{13}CO)^+$	178	2.1	30	1.5	16
$C_5H_5Fe({}^{12}CO)_2{}^+$	177	5.8		8.1	
$C_5H_5Fe{}^{13}C(O)CH_3{}^+$	165	16	21	17	25
$C_5H_5Fe{}^{12}C(O)CH_3{}^+$	164	61		52	
$C_5H_5Fe({}^{13}CO)^+$	150	8.8	26	2.3	16
$C_5H_5Fe({}^{12}CO)^+$	149	25		12	
$C_5H_5Fe(CH_3)^+$	136	46		25	

[a] Relative to m/e 121 = 100.

Table II. Mass Spectra of η^5-$(C_5H_5)Fe(CO)({}^{13}CO)CH_3$

		70 eV, 260°		20 eV, 330°	
Fragment	m/e	Rel intensity[a]	% labeling	Rel intensity[a]	% labeling
$C_5H_5Fe({}^{12}CO)({}^{13}CO)CH_3{}^+$	193	3.7	32	5.9	24
$C_5H_5Fe({}^{12}CO)_2CH_3{}^+$	192	9.7		19	
$C_5H_5Fe({}^{12}CO)({}^{13}CO)^+$	178	1.6	34	1.7	26
$C_5H_5Fe({}^{12}CO)_2{}^+$	177	3.1		4.7	
$C_5H_5Fe({}^{13}CO)CH_3{}^+$	165	4.4	18	7.2	12
$C_5H_5Fe({}^{12}CO)CH_3{}^+$	164	19		53	
$C_5H_5Fe({}^{13}CO)^+$	150	2.0	20	2.4	15
$C_5H_5Fe({}^{12}CO)^+$	149	7.8		13	
$C_5H_5Fe(CH_3)^+$	136	40		11	

[a] Relative to m/e 121 = 100.

trogen stream and chromatographed eluting with hexane. After evaporation of the solvent in a stream of nitrogen, the compound was purified by sublimation onto a Dry Ice-cooled probe. The product (obtained in 30% yield) had terminal CO stretches at 2015 (s), 2003 (m), 1964 (s), and 1933 (m) cm^{-1} in hexane.

Decarbonylation of η^5-$(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$ in the Presence of $P(C_6H_5)_3$. The procedure was that outlined above except that an equimolar quantity of triphenylphosphine was added to the hexane solution. Chromatography of the resulting mixture afforded four bands. Band I gave 0.24 g (23%) of η^5-$(C_5H_5)Fe({}^{13}CO)[P(C_6H_5)_3]CH_3$. From maroon band II was isolated $[\eta^5$-$(C_5H_5)Fe(CO)_2]_2$ (<0.1 g). Colorless band III contained triphenylphosphine while band IV provided a trace amount of η^5-$(C_5H_5)Fe(CO)[P(C_6H_5)_3]{}^{13}C(O)CH_3$.

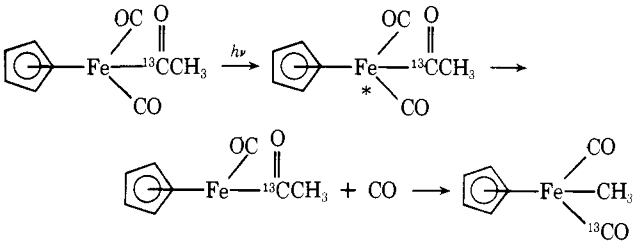
Products were identified by their infrared spectra. η^5-$(C_5H_5)Fe({}^{13}CO)[P(C_6H_5)_3]CH_3$ has a terminal CO stretch centered at 1897 cm^{-1} in $CHCl_3$ (lit. 1905 cm^{-1} in Nujol[7]) corresponding presumably to an overlap of ^{12}CO and ^{13}CO bands. The parent peaks in the mass spectrum at m/e 455, 454 indicate that the compound is 24% labeled with ^{13}C. η^5-$(C_5H_5)Fe(CO)[P(C_6H_5)_3]C(O)CH_3$ displays in $CHCl_3$ a terminal CO stretch at 1923 cm^{-1} and bridging CO stretches at 1590 ($^{12}C{=}O$) and 1551 ($^{13}C{=}O$) cm^{-1} (lit. 1920 and 1598 cm^{-1}, respectively[8]).

Physical Measurements. Infrared spectra were measured on a Beckman IR 12 instrument calibrated vs. polystyrene using 0.1-mm NaCl cells. Mass spectra were obtained on a CEC MS-9 instrument at The Ohio State University with an inlet temperature of 260° and an ionization energy of 70 eV and also on a LKB 9000 combination gas chromatograph and mass spectrometer at the University of Cincinnati College of Medicine with an inlet temperature of 330° and an ionization energy of 20 eV. Relative intensities were found by measuring peak heights with a millimeter rule. Peaks assigned as ^{13}C-labeled fragments are corrected for natural abundance of this isotope.

Results and Discussion

η^5-Cyclopentadienyliron dicarbonyl acetyl labeled to the extent of about 28% at the acetyl carbon with ^{13}C was prepared and photochemically decarbonylated to the corresponding methyl complex (reaction 3). The extent of labeling in several fragment ions in the mass spectra of the reactant and product compounds is reported in Tables I and II, respectively. The important conclusion to be drawn from the data in the tables is that substantially all the ^{13}C originally incorporated into the acetyl position in the starting compound remains in the methyl product from the photochemical decarbonylation. The apparent slight increase in extent of labeling in going from the acetyl to the methyl product in one set of spectra is probably due to the fairly large uncertainty in intensity measurement of the very weak parent peaks. The relative intensities of the labeled and unlabeled parent peaks in both the carbonylated and decarbonylated compounds are less than 10% of the most intense peak at m/e 121. The mechanism of photochemical decarbonylation must (as depicted in Scheme I) involve production of an excited species with an appreciably weakened bond between iron and a terminal CO. The terminal CO then dissociates[9] leaving an unsaturated moiety which rearranges with methyl migration to convert the bridging $^{13}C{=}O$ into a terminal $^{13}C{\equiv}O$.

Scheme I



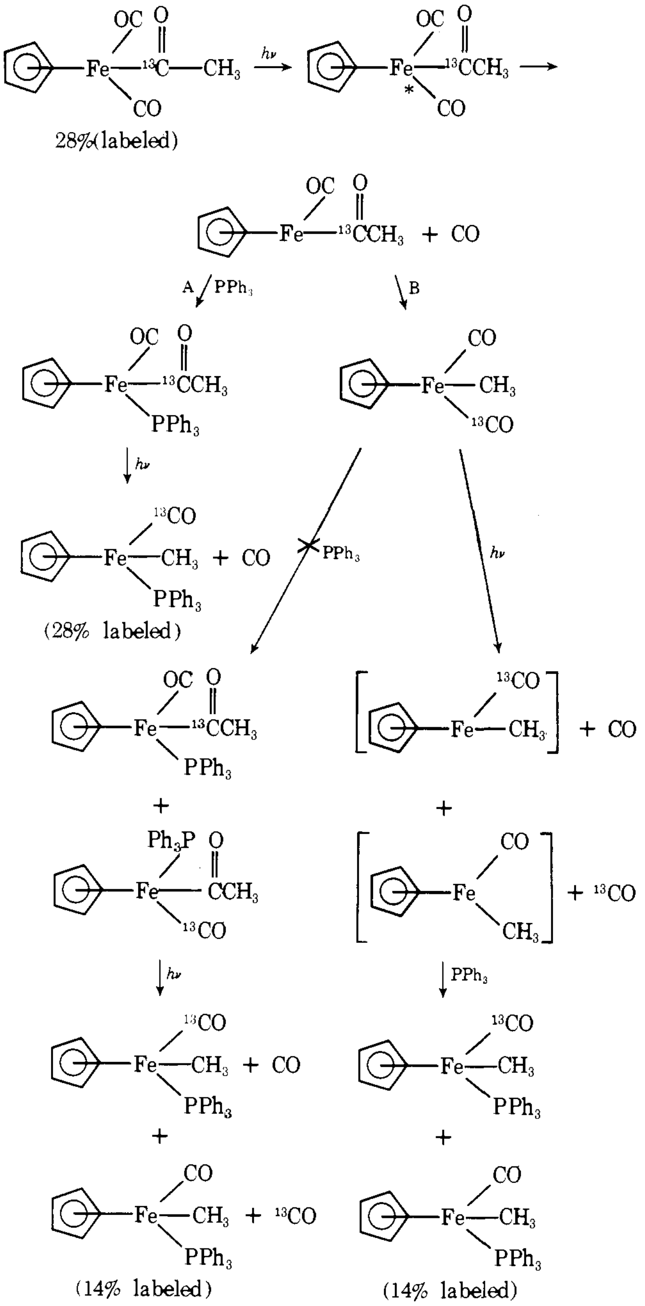
The mechanism depicted in Scheme I is very like the mechanism of decarbonylation effected by $Rh[P(C_6H_5)_3]_3Cl$,[6] the difference being that the terminal carbonyl is not abstracted by the rhodium complex.

Whether the unsaturated intermediate persists for any appreciable length of time under uv irradiation or whether loss of terminal CO is essentially coincident with methyl migration was investigated[10] by carrying out the reaction in the presence of an equimolar quantity of triphenylphosphine to compete for a vacant coordination position on the iron.

Scheme II details possible pathways for the reaction of η^5-$(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$ on irradiation in the presence of triphenylphosphine. Pathway A corresponds to the case where attack on the unsaturated intermediate occurs faster than methyl migration while pathway B corresponds to more rapid methyl migration than triphenylphosphine attack.

The experimental results allow a clear choice of pathway A as accounting for the production of the η^5-$(C_5H_5)Fe(CO)[P(C_6H_5)_3]{}^{13}C(O)CH_3$ and η^5-$(C_5H_5)Fe({}^{13}CO)[P(C_6H_5)_3]CH_3$ isolated. First, the fact that the final product, η^5-$(C_5H_5)Fe({}^{13}CO)[P(C_6H_5)_3]CH_3$, is still 24% labeled (vs. 28% predicted) is evidence that the conversion of the bridging CO to a terminal one required by pathway B is not occurring. If pathway B were effectively competing, the extent of labeling in the parent peak of the triphenylphosphine methyl product would be lower than the 24% observed on account of loss of terminal ^{13}CO. Second, the triphenylphosphine acetyl precursor[11] to the final product contains ^{13}C only in the acetyl position. By employing a solution of unlabeled η^5-$(C_5H_5)Fe(CO)[P(C_6H_5)_3]C(O)CH_3$ in chloroform as a reference, the infrared bands at 1923 and 1590 cm^{-1} can be completely eliminated from the spectrum leav-

Scheme II[14]



ing only the $^{13}C{=}O$ band at 1550 cm^{-1}. This must mean that the triphenylphosphine-substituted acetyl results from attack on a coordinatively unsaturated (or solvated) intermediate rather than from an attack on η^5-$(C_5H_5)Fe(CO)(^{13}CO)CH_3$ which would distribute the ^{13}CO between bridging and terminal positions in the η^5-$(C_5H_5)Fe(CO)[P(C_6H_5)_3]C(O)CH_3$.[13]

That the unsaturated intermediate undergoes nucleophilic attack according to pathway A more rapidly than methyl migration seems clearly established.

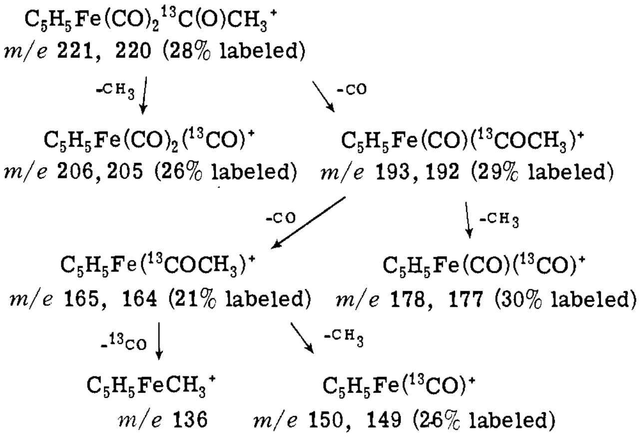
The presence of labeled fragments in the mass spectra of these iron complexes permits some heretofore inaccessible observations to be made regarding fragmentation patterns. In interpreting the extent of labeling in various fragments in terms of their origin in species of higher molecular weight, we consider it unlikely that reactions in the mass spectrometer would lead to incorporation of ^{13}CO. Also, it should be mentioned that some apparent inconsistencies in the labeling percentages are the result of experimental error which is relatively more important for peaks of low intensity.

King[12] has studied the mass spectrum of η^5-$(C_5H_5)Fe(CO)_2C(O)CH_3$ under conditions quite similar to one set in this work (source temperature 260°; 70 eV). He had observed that the main features of the fragmentation of this compound are stepwise loss of CO and competitive loss of CH$_3$. These fragmentation pathways were confirmed by location of metastable peaks.

The results of our study on the acetyl starting material presented in Table I are similar to those of King in showing the presence of fragments corresponding to the stepwise loss of CO. Moreover, the fact that the ^{13}C content in the *m/e* 193, 192 set of peaks is the same as in the parent 221, 220 peaks shows that a terminal CO is the one lost by the parent ion—a fact which earlier work could not reveal. The relative abundances of various peaks seem to indicate preferential loss of terminal carbonyls as compared to methyl groups as long as there is a choice.

Depending on the inlet temperature and ionization energy, other features of fragmentation patterns seem to differ for the acetyl complex. Scheme III depicts a proposed pathway when the temperature is 260° and ionization energy is 70 eV as employed by King.

Scheme III

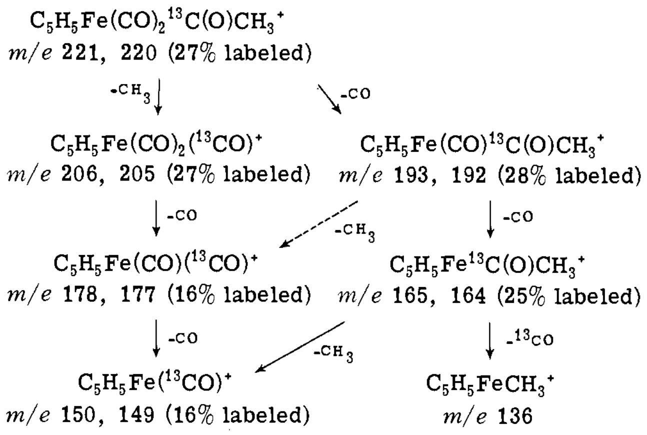


The labeling of fragments strongly implies that fragmentation along the major pathway proceeds by loss of terminal carbonyl groups more rapidly than any rearrangement can occur which would scramble the labeled CO. When both terminal CO's have been extruded to give $C_5H_5FeC(O)CH_3^+$ *m/e* 165, 164, relative intensities suggest that rearrangement and CO elimination to give $C_5H_5FeCH_3^+$ *m/e* 136 is competitive with elimination of CH$_3$ to give $C_5H_5Fe(CO)^+$ *m/e* 150, 149. Consequently, the amount of labeling in all carbonyl-containing ions is the same as that in the starting compound.

The data in Table I also reveal that under these conditions (70 eV) the principal source of $C_5H_5Fe(CO)(^{13}CO)^+$ is loss of a methyl radical from $C_5H_5Fe(CO)^{13}C(O)CH_3^+$. If CO loss from $C_5H_5Fe(CO)_2(^{13}CO)^+$ were a significant source of this fragment, one would expect the ^{13}C content to be lower than the 30% observed in *m/e* 178, 177. Likewise, the most significant source of $C_5H_5Fe(^{13}CO)^+$ appears to be $C_5H_5Fe^{13}C(O)CH_3^+$ since both are equivalently labeled. Any $C_5H_5Fe(^{13}CO)^+$ arising by carbonyl extrusion from $C_5H_5Fe(CO)(^{13}CO)^+$ would be expected to lead to a decrease the labeling observed in the *m/e* 150, 149 peaks since the loss of ^{12}CO or ^{13}CO should be equally probable statistically. These observations are consistent with the minor amounts of $C_5H_5Fe(CO)_2(^{13}CO)^+$ and $C_5H_5Fe(CO)$- $(^{13}CO)^+$ as revealed by relative intensities.

Scheme IV shows the proposed fragmentation pattern of η^5-$(C_5H_5)Fe(CO)_2{}^{13}C(O)CH_3$ when the inlet temperature is 330° and the ionization energy is 20 eV.

Scheme IV



A significant difference is evident on comparison with Scheme III: namely, that the presumably longer lifetime of ions excited by less energetic electrons permits more facile loss of methyl group from the parent ion so that now $C_5H_5Fe(CO)_2({}^{13}CO)^+$ becomes the principal source of $C_5H_5Fe(CO)({}^{13}CO)^+$ with consequent reduction in the extent of labeling. Also, the ^{13}C content of $C_5H_5Fe({}^{13}CO)^+$, *m/e* 150, 149, makes it clear that this fragment must arise from two sources: namely, loss of methyl by $C_5H_5Fe{}^{13}C(O)CH_3{}^+$ and loss of CO by $C_5H_5Fe(CO)({}^{13}CO)^+$.

Again, the major pathway appears to involve preferential loss of terminal CO more rapidly than rearrangement. Intensity measurements suggest a competition between rearrangement with loss of CO and extrusion of CH_3 for $C_5H_5Fe{}^{13}C(O)CH_3{}^+$ at *m/e* 165, 164.

The mass spectra of the alkyl reported in Table II show less satisfactory agreement with one another. The fact that the two spectra are both of the same compound yet show labeling of 32 and 24% in the parent peak gives some measure of the uncertainty in the labeling reported. Given this magnitude of uncertainty, the data reveal essentially random and preferential loss of the terminal carbonyls with less tendency to extrude the methyl group. As expected, no features attributable to a $-C(O)CH_3$ group and its rearrangements are discernible.

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(13) It is unlikely that the $[\eta^5\text{-}(C_5H_5)Fe(CO)_2]_2$ recovered results from the production of $\eta^5\text{-}(C_5H_5)Fe(CO)({}^{13}CO)CH_3$ by methyl migration competitive with triphenylphosphine attack and its subsequent decomposition. Photolysis of $\eta^5\text{-}(C_5H_5)Fe(CO)_2CH_3$ under identical conditions gives 50% recovery of the starting material and 14% of the dimer. Consequently, one would expect to isolate some $\eta^5\text{-}(C^5H^5)Fe(CO)({}^{13}CO)CH_3$ if the dimer were produced through the intermediacy of this species.
(14) Attack of $\eta^5\text{-}(C_5H_5)Fe(CO)({}^{13}CO)CH_3$ by $P(C_6H_5)_3$ would probably be negligibly slow in hexane. See ref 8.