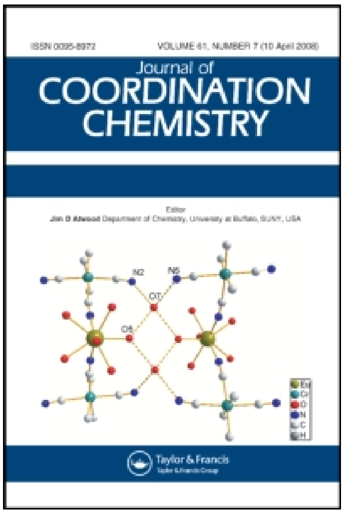

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ACETYL TRANSFER BETWEEN MANGANESE AND IRON COMPLEXES: REACTION OF ACETYLPENTACARBONYLMANGANESE WITH DICARBONYLCYCLOPENTADIENYLIRON(0)

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Reaction of $Mn(CO)_5(C(O)Me)$ with $CpFe(CO)_2^-$ results in $CpFe(CO)_2Me$, $Cp_2Fe_2(CO)_4$ and $Mn(CO)_5^-$ in less than five minutes at room temperature. Labeling the carbonyl of the acetyl puts the label only on a carbonyl of the $CpFe(CO)_2Me$. Thus the acetyl is transferred from the manganese to the iron as a group, before CO dissociation leads to the methyl product. CO dissociation from $CpFe(CO)_2(C(O)Me)$ does not occur under the experimental conditions. A scheme is suggested to accommodate these observations.

KEYWORDS: Acetyl, manganese carbonyl, electron transfer

INTRODUCTION

Acyl complexes are important in homogeneously catalyzed reactions such as hydroformylation and methanol homologation and many organic syntheses.[1] Studies of acyl complexes have focused on formation and decarbonylation reactions.[1] Acyl transfer between organic nucleophiles has remained a contentious mechanistic problem.[2] Recent studies have demonstrated H^+, R^+, CO^{2+} and X^+ transfer reactions between metal carbonyl anions.[3-5] In this manuscript acyl transfer from reaction of $Mn(C(O)CH_3)(CO)_5$ with $CpFe(CO)_2^-$ is examined.

EXPERIMENTAL AND RESULTS

Reaction of $Mn(C(O)CH_3)(CO)_5$[6] with $PPNCpFe(CO)_2$[3] in THF[7] resulted in $Mn(CO)_5^-$ (75%), $Cp_2Fe_2(CO)_4$ (25%) and $CpFe(CO)_2Me$ (~50%) in less than five minutes (sampling time by infrared) at room temperature.

$$\begin{aligned} Mn(C(O)CH_3)(CO)_5 + CpFe(CO)_2^- \rightarrow\ & \underset{75\%}{Mn(CO)_5^-} + \underset{25\%}{Cp_2Fe_2(CO)_4} \\ & + \underset{50\%}{CpFe(CO)_2Me} \end{aligned} \qquad (1)$$

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No other products in significant (>5%) yield were observed.[8] The reaction was monitored by IR and by ^{1}H and ^{13}C NMR spectroscopies. The IR, NMR and microanalytical data for the acetyl compounds are given in Table 1. In order to determine the fate of the acetyl group, $Mn(^{13}C(O)CH_3)(CO)_5$ — 90% enriched — was prepared.[9] Upon reaction with $CpFe(CO)_2^-$, $CpFe(^{13}CO)(CO)Me$ was formed. The methyl complex was highly enriched (>80% as shown by infrared spectra and ^{13}C NMR compared to authentic samples); ^{13}CO above natural abundance was not observed in any other product. To ascertain that $CpFe(^{13}CO)(CO)Me$ was formed, this complex was prepared independently by photolysis of $CpFe(^{13}C(O)CH_3)(CO)_2$.[10]

The rapidity of reaction (*1*) precludes involvement of decarbonylation of $CH_3C(O)Mn(CO)_5$ or $CH_3C(O)FeCp(CO)_2$ in formation of products. Reaction (*1*) occurs before the first infrared spectrum can be recorded ($\sim$5 min); this is the same time scale as the alkyl transfer reactions.[3d] Decarbonylation reactions for the iron and manganese acyls occur in hours,[1] usually at somewhat elevated temperatures. Decarbonylation of the iron complex, $CH_3C(O)FeCp(CO)_2$, is not catalyzed by any of the species present ($Mn(CO)_5^-$, $CpFe(CO)_2^-$ or $Cp_2Fe_2(CO)_4$). Thus we conclude that $CH_3C(O)FeCp(CO)_2$ is not an intermediate enroute to $CH_3FeCp(CO)_2$. The reaction utilizing $CH_3{}^{13}C(O)Mn(CO)_5$ producing highly enriched $CH_3FeCp(^{13}CO)(CO)$ indicates that the acyl group is transferred intact from a manganese to an iron center.

DISCUSSION

The results eliminate many of the simple approaches to the observed products of reaction (*1*). For example direct acyl transfer from the manganese complex to the

Table 1 Analytical and spectroscopic data.

Elemental analyses				
cmpds		%C	%H	% metal
$Mn(CO)_5(C(O)CH_3)$	found:	34.9	1.32	22.5
	cal:	35.3	1.27	23.1
$CpFe(CO)_2(C(O)CH_3)$	found:	48.6	3.81	24.2
	calc:	49.2	3.67	25.4
^{1}H NMR data (ppm) - d^{8}THF				
$Mn(CO)_5(C(O)CH_3)$	2.6(s)			
$CpFe(CO)_2(C(O)CH_3)$	2.48(s), 4.96(s)			
^{13}C NMR data (CD_3CN)				
$Mn(CO)_5(^{13}C(O)CH_3)$	258.9(s)			
$CpFe(CO)_2(C(O)CH_3)$	255.7(s, acetyl), 218(s, CO), 87.8(s, Cp)			
$CpFe(CO)_2CH_3$	220(s, CO), 86.9(s, Cp)			
$Cp_2Fe_2(CO)_4$	197.5(s, CO), 89.9(s, Cp)			
Infrared data (cm^{-1} in hexanes)				
$Mn(CO)_5(C(O)CH_3)$	2114(w), 2052(w), 2011(vs), 2003(s), 1663(m)			
$Mn(CO)_5(^{13}C(O)CH_3)$	2113(w), 2050(w), 2009(vs), 2003(s), 1625(m)			
$CpFe(CO)_2(C(O)CH_3)$	2021(s), 1964(s), 1670(m)			
$CpFe(CO)_2(^{13}C(O)CH_3)$	2021(s), 1964(s), 1633(m)			
$CpFe(CO)(^{13}CO)CH_3$	1999(s), 1929(s)			

iron anion or radical coupling of an acyl radical with an iron radical would produce the acyl iron complex which does not decarbonylate. Similarly, methyl transfer from manganese to iron would not produce labeled $CH_3FeCp(CO)_2$. While a full mechanistic discussion is premature, a scheme such as follows can account for the observations:

$$CpFe(CO)_2^- + CH_3C(O)Mn(CO)_5 \rightarrow CpFe(CO)_2\cdot + CH_3C(O)Mn(CO)_5^{\dot{-}} \qquad (2)$$

$$2\,CpFe(CO)_2\cdot \rightarrow Cp_2Fe_2(CO)_4 \qquad (3)$$

$$CH_3C(O)Mn(CO)_5^{\dot{-}} \rightarrow Mn(CO)_5^- + CH_3C(O)\cdot \qquad (4)$$

$$CpFe(CO)_2^- + CH_3C(O)\cdot \rightarrow CH_3C(O)FeCp(CO)_2^{\dot{-}} \qquad (5)$$

$$CH_3C(O)FeCp(CO)_2^{\dot{-}} \rightarrow CH_3FeCp(CO)_2 + CO + e^- \qquad (6)$$

Reactions (*2*) and (*3*) provide a single electron transfer route to unenriched $Cp_2Fe_2(CO)_4$; dimerization of $CpFe(CO)_2\cdot$ occurs very rapidly.[11] Since very little $CH_3Mn(CO)_5$ is observed reaction (*4*) must also occur very rapidly, before significant CO dissociation can occur. Reaction (*5*) allows the acetyl to be transferred to the iron in a molecule that is activated for CO dissociation and that would produce highly enriched $CH_3FeCp(CO)_2$ from enriched acyl. The scheme outlined in reaction (*2–6*) provides a rational approach to the formation of the observed products ($Cp_2Fe_2(CO)_4$, $Mn(CO)_5^-$ and $CH_3FeCp(CO)_2$) and is also consistent with the observed isotopic labeling.

Electrochemical results on reduction of a metal acyl complex could be useful, but, apparently have not been reported.[12] Two electron reductions of $Mn(CO)_5X$ produce $Mn(CO)_5^-$ for a number of X groups, including phenyl.[12]

It is interesting that we find no evidence for bimetallic acyl compounds. Such complexes are formed by reaction of metal carbonyl anions with indenyl complexes.[13] Reaction of $CpFe(CO)_2^-$ with $CH_3C(O)FeCp(CO)_2$ did not produce the bimetallic acetyl, but very slowly (several hours) produced $Cp_2Fe_2(CO)_4$ and $CpFe(CO)_2Me$. Labeled acyl produced a label in a CO of $CpFe(CO)_2Me$.

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7. The reactants were mixed in a 1:1 ratio (2.5×10^{-3} M) in 25 ml of THF and reacted at room temperature in an inert atmosphere glove box. Infrared spectra were recorded on a Mattson Polaris Fourier transform infrared spectrometer in 0.5 mm cells. NMR spectra were obtained using a Varian VXR-400 NMR spectrometer.
8. After recording the infrared spectrum of the product mixture in THF, the THF was removed. The neutral compounds were extracted into hexane where absorbance values were converted to yields from Beer's law plots. The anion was then determined by redissolving in THF and comparison to Beer's law plots.
9. $Mn(^{13}C(O)CH_3)(CO)_5$ was prepared from 99.5% $CH_3{}^{13}C(O)Cl$ (Cambridge Isotope Laboratories).
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