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Reactions of Polynuclear Metal Carbonyl Anions with the Proton and with Carbocation Reagents. The O-Protonation and O-Alkylation of Bridging Carbonyl Ligands

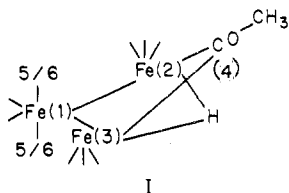
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Reactions of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ with electrophiles $\text{R} = \text{CH}_3^+$, CH_3CH_2^+ , and $\text{CH}_3\text{C}(=\text{O})^+$ lead to the O-alkyl or O-acetyl derivatives $\text{Fe}_3(\text{CO})_{10}(\text{COR})^-$. Similarly, the reaction of $\text{HFe}_3(\text{CO})_{11}^-$ with CH_3^+ , C_2H_5^+ , or H^+ gives $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$, $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_2\text{CH}_3)$, and $\text{HFe}_3(\text{CO})_{10}(\text{COH})$, respectively. Variable-temperature ^{13}C NMR spectra of $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$, $[\text{PPN}][\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)]$, $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$, and $[\text{PPN}][\text{Fe}_3(\text{CO})_{10}(\text{COC}(=\text{O})\text{CH}_3)]$ demonstrate several different CO permutation rates within each molecule. The alkyl or acyl carbon atom of $\text{Fe}_3(\text{CO})_{10}(\text{COR})^-$ is attacked by $\text{C}_6\text{H}_5\text{S}^-$ in preference to attack at the iron-coordinated carbon.

Introduction

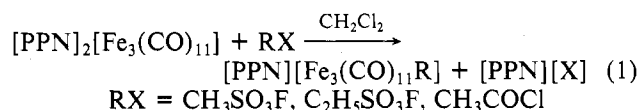
The reaction of a carbocation reagent with metal carbonyl anions provides a convenient method for the formation of metal-alkyl σ bonds.¹ Despite the importance of this reaction in synthetic organometallic chemistry, little attention has been paid to the analogous reaction involving polynuclear carbonyl anions. In a preliminary communication² of the present work it was demonstrated that the alkylation of $\text{HFe}_3(\text{CO})_{11}^-$ yields an unusual product, I, in which the methyl group is attached to the oxygen of the bridging carbonyl.



We now describe a detailed study of the reactivity of $\text{Fe}_3(\text{CO})_{11}^{2-}$ and its derivatives with some carbocation reagents. The present results, which provide new examples of the O-alkylation of bridging carbonyls, indicate that this type of reaction may be general. We also have studied the reactivity of the $\mu\text{-COCH}_3$ ligand.

Results and Discussion

General Chemistry. As summarized in eq 1, the reaction



of equimolar quantities of the dianion $\text{Fe}_3(\text{CO})_{11}^{2-}$ with a carbocation reagent yields an alkylated (or acylated) monoanionic product which is readily isolated as the bis(triphenylphosphine)iminium (PPN) salt.

The initial formation of these materials is readily followed by isolating and weighing the $[\text{PPN}][\text{X}]$ byproduct, which is precipitated from CH_2Cl_2 by addition of a fourfold excess of diethyl ether. Approximately 95% of the stoichiometric amount of $[\text{PPN}][\text{X}]$ is recovered in each case. Removal of the solvent from the filtrate, followed by crystallization from methanol, produces either the methyl or the ethyl product as deep brown, shiny crystals. Large rectangular-prismatic crystals of the acetyl derivative also are isolated from methanol. These materials were treated as air sensitive, but brief exposure to air has no deleterious effect. These compounds dissolve in a variety of air-free polar solvents with no reaction: diethyl ether, methanol, THF. As will be discussed below, all of these derivatives appear to contain an O-alkylated bridging carbonyl which may be represented by the formula $\text{Fe}_3(\text{CO})_{10}(\text{COR})^-$, $\text{R} = \text{CH}_3$, C_2H_5 , or $-\text{C}(=\text{O})\text{CH}_3$.

Protonation of $\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)^-$ or $\text{Fe}_3(\text{CO})_{10}(\text{CO-C}_2\text{H}_5)^-$ in CH_2Cl_2 with HSO_3F followed by extraction with hexane and then sublimation yields the slightly volatile deep red solid $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ or $\text{HFe}_3(\text{CO})_{10}(\text{COC}_2\text{H}_5)$. In previous work² the X-ray crystal structure of the methylhydrido derivative was shown to contain the novel feature of an O-alkylated carbonyl bridge, I, and the spectral and physical properties of the ethylhydrido derivative leave no doubt that it has an analogous structure.

Protonation of $\text{Fe}_3(\text{CO})_{10}(\text{COC}(=\text{O})\text{CH}_3)^-$ in CH_2Cl_2 with HSO_3F leads to decomposition as evidenced by the formation of $\text{Fe}_3(\text{CO})_{12}$ which was identified by color and infrared spectrum.

Structures. Infrared spectroscopy and ^{13}C NMR are excellent tools for the determination of general structural features of the products obtained from the reaction of polynuclear carbonyls with electrophilic reagents such as carbocations, protons, or neutral Lewis acids.³⁻⁸ When an electron acceptor attaches to either the metal framework or the oxygen of a CO, the stretching frequencies for the remaining carbonyl ligands increase somewhat (60–90 cm^{-1}). However, the CO stretch for the CO ligand which is O bonded to a Lewis acid decreases greatly in frequency ($\Delta\nu(\text{CO}) \sim 120\text{--}300 \text{ cm}^{-1}$). The increase for the terminal CO stretching frequencies is unmistakable for the $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, and $-\text{C}(=\text{O})\text{CH}_3$ derivatives (Table I). In addition, the bridging CO stretch shifts from ca. 1725 cm^{-1} for $\text{HFe}_3(\text{CO})_{11}^-$ to ca. 1452 cm^{-1} in $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$. This large decrease in frequency agrees with the known O-methylation of the latter compound.² However, the use of infrared as a diagnostic tool for $>\text{CO-R}$ linkages is not as straightforward as in the case of $>\text{CO-ALX}_3$ compounds because the intensity of the CO stretch in the alkyl compounds is weak and difficult to distinguish from adjacent features. Also, as may be seen in Table I, splitting of the CO stretch for $>\text{CO-R}$ may occur.

The infrared spectrum of $\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)^-$ is highly informative. In addition to the general increase of the high-frequency features, a bridging CO stretch is observed around 1746 cm^{-1} , and another weaker feature is seen at 1360 cm^{-1} . The indication is that the compound contains one C-bonded bridging CO and another CO ligand which is O-alkylated, II.

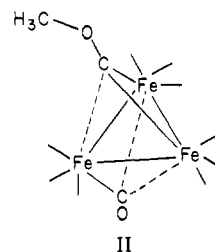


Table I. Infrared Data (cm⁻¹)

carbonyl cluster	medium ^a	$\nu(\text{CO}(\text{terminal}))^b$	$\nu(\text{CO}(\text{bridging}))$
[PPN] ₂ [Fe ₃ (CO) ₁₁]	Nujol and Fluorolube mulls	2010 vw, 1935 s, 1900 s, 1883 s, 1878 s, sh, 1865 sh	1667 m
	CH ₂ Cl ₂ ^c soln	1985 m, sh, 1943 s, 1912 s, 1994 s, 1980 s	1665 m
[PPN][HFe ₃ (CO) ₁₁]	Nujol and Fluorolube mulls	2066 w, 2008 sh, 1994 s, 1980 s, 1961 s, 1945 sh, 1937 s, 1921 m	1725 s
	CH ₂ Cl ₂ soln	2067 w, 1998 s, 1972 s, 1940 sh	1726 m
[PPN][Fe ₃ (CO) ₁₀ (COCH ₃)]	Nujol and Fluorolube mull	2052 m, 1980 s, 1952 s, 1929 sh, 1910 sh	1748 m
	CH ₂ Cl ₂ soln	2050 w, 1990 s, 1963 s, 1905 m	1746 m, 1360 m
HFe ₃ (CO) ₁₀ (COCH ₃)	Nujol mull	2098 m, 2051 s, 2038 s, 2018 s, 2003 sh, 1993 m, 1978 w	
	Fluorolube mull	2098 m, 2052 s, 2041 s, 2020 s, 1992 m, 1978 w	1452 w, 1384 vw
	CH ₂ Cl ₂ soln	2098 w, 2051 s, 2040 s, 2017 s, 1988 sh	1452
[PPN][Fe ₃ (CO) ₁₀ (COC ₂ H ₅)]	Nujol mull	2052 m, 1996 sh, 1980 s, 1966 sh, 1947 s, 1920 s, 1904 sh	1753 s
	HFe ₃ (CO) ₁₀ (COC ₂ H ₅)	2097 m, 2047 s, 2036 s, 2016 s, 1996 sh, 1988 s, 1975 m	
[PPN][Fe ₃ (CO) ₁₀ (COC(=O)CH ₃)]	Fluorolube mull	2097, 2050 s, 2038 s, 2018 s, 1986 sh, 1984 sh,	1472 vw, 1398 w, 1378 w
	Nujol and Fluorolube mull	2054 w, 1985 s, 1970 s, 1956 sh, 1945 m, 1933 m, 1922 s, 1916 sh, 1906 sh	1760 m
	CH ₂ Cl ₂ soln	2057 w, 1995 s, 1970 s, 1045 m	1760 s, 1675 vw, 1365 w

^a KBr plates are used for mulls. ^b vw = very weak; w = weak; m = medium; s = strong; sh = shoulder. ^c CH₂Cl₂ solution; 0.1-mm cell with CH₂Cl₂ in the reference beam.

This general structural pattern is even more clearly indicated by ¹³C NMR. The spectroscopic observations do not allow us to distinguish a symmetric threefold CO bridging pattern from less symmetric alternatives. Also, the low-frequency CO stretch could not be detected for Fe₃(CO)₁₀(COC₂H₅)⁻ and Fe₃(CO)₁₀(COC(=O)CH₃)⁻. Because of the general difficulty in detecting this band, no structural conclusions can be drawn from this negative evidence.

¹³C NMR spectra were obtained for the carbonyl ligands of samples enriched to about 10% ¹³CO. The distinctive low-field ¹³C NMR pattern for >CO-acid^{8,9} is seen in the low-temperature ¹³C NMR for the alkylated compound of known structure HFe₃(CO)₁₀(COCH₃) (Table II).

At -120 °C the ¹³C NMR of Fe₃(CO)₁₀(COCH₃)⁻ contains three features at δ values of 336.8, 264.0, and 215.2 relative to Me₄Si, with relative intensity 1:1:9. The position and relative intensities agree with the assignment of these bands as >CO-R, >CO, and -CO groups, respectively. (Interestingly, the terminal -CO resonance at δ 215.2 is a sharp singlet at the lowest temperature.) These data very strongly support the general features of structure II for the methyl compound.

As with the methyl derivative, the ¹³C NMR spectrum of [PPN][Fe₃(CO)₁₀(COC(=O)CH₃)] at -120 °C shows three

peaks (Table II) in a ratio of 1:1:9 (Figure 1), suggesting that the acetyl is attached to the oxygen of a bridging carbonyl group. The peak at δ 292.9 is assigned to the carbon of the acetylated carbonyl group, the one at δ 281.6 is assigned to the probably unsymmetrically face-bridging carbonyl carbon, and the rest of the terminal carbonyls, assuming that they are equivalent, are assigned to the peak at δ 214.3.

The proton NMR data for the dianion and some of its derivatives are given in Table III. The chemical shifts of the methyl group in both the methyl derivative and the methylhydrido derivative are very close suggesting similar environments which is in complete agreement with structure II, proposed earlier with the methyl attached to the oxygen of a bridging carbonyl; the same argument holds for the ethyl derivative. The chemical shift of the methyl in the acetyl derivative (δ 2.38) is not far from the methyl chemical shift in organic esters (e.g., $\delta(\text{CH}_3)$ for CH₃C(=O)-O-*n*-Bu is 2.03) which suggests that the acetyl group is similarly attached to the oxygen of a bridging carbonyl group forming an ester-type linkage. Both HFe₃(CO)₁₀(COCH₃) and HFe₃(CO)₁₀(COC₂H₅) exhibit a high-field resonance at δ -18.26 and -18.40, respectively, which is characteristic of metal hydrides.

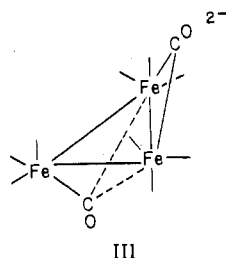
Carbonyl Ligand Dynamics. The structure of [PPN]₂[Fe₃(CO)₁₁] in the solid state is shown by X-ray analysis¹⁰

Table II. Low-Temperature ^{13}C NMR Data^a

compound	<i>t</i> , °C	δ (carbonyl carbons)	rel intens
[PPN] ₂ [Fe ₃ (CO) ₁₁]	-100	230.7	
[PPN][HFe ₃ (CO) ₁₁]	-120	284.0	1
		223.6	1
		220.9	1
		219.3	2
		215.6	2
		210.3	2
		208.8	2
[PPN][Fe ₃ (CO) ₁₀ (COCH ₃)]	-120	336.8	1
		264.0	1
		215.2	9
HFe ₃ (CO) ₁₀ (COCH ₃)	-120	356.5	1
		215.8	1
		214.1	1
		212.6	2
		210.2	2
		207.4	2
HFe ₃ (CO) ₁₀ (COH)	-100	204.2	2
		358.8	1
		217.3	1
		215.4	1
		214.0	2
		210.7	2
		208.4	2
[PPN][Fe ₃ (CO) ₁₀ (COC=OCH ₃)]	-100	204.9	2
		292.9	1
		281.6	1
		214.3	9

^a The solvent system was CHCl₃/CD₂Cl₂ for all compounds.

to have an edge-bridging carbonyl, a highly unsymmetrical face-bridging carbonyl, and nine terminal carbonyls, III. The



infrared spectra of this dianion in both the solid state and in solution are very similar, suggesting similar structures in both phases.

However, the ^{13}C NMR spectra show only one average CO resonance as a sharp singlet (δ 230.7) to the lowest temperature employed, -100°C . Similar behavior has been observed for the parent carbonyl cluster Fe₃(CO)₁₂ which also shows one peak down to -150°C , the lowest temperature reached.¹¹⁻¹³ As with Fe₃(CO)₁₂, it appears that in solution the dianion undergoes complete and rapid CO scrambling between all sites. The mechanisms by which this scrambling occurs must interchange bridging and terminal carbonyls and also permute

Table III. ^1H NMR Data

compd	solvent	δ (rel intens)		
		aromatic	aliphatic	hydride
[PPN] ₂ [Fe ₃ (CO) ₁₁]	CD ₂ Cl ₂	7.68, 7.53		
[PPN][HFe ₃ (CO) ₁₁]	CD ₃ C(=O)CD ₃	7.80, 7.73, 7.63 (30)		-14.53 (1)
[PPN][Fe ₃ (CO) ₁₀ (COCH ₃)]	CD ₂ Cl ₂	7.56, 7.43, 7.36 (10.1)	4.33 (1)	
HFe ₃ (CO) ₁₀ (COCH ₃)	C ₆ D ₆		4.23 (2.7)	-18.20 (1)
[PPN][Fe ₃ (CO) ₁₀ (COC ₂ H ₅)]	CD ₂ Cl ₂	7.51, 7.39 (5.5)	4.49 q, 1.52 t ^a (1.0)	
HFe ₃ (CO) ₁₀ (COC ₂ H ₅)	C ₆ D ₆		4.54 q, 1.24 t	-18.26
[PPN][Fe ₃ (CO) ₁₀ (COC(=O)CH ₃)]	CD ₃ CN	7.65, 7.54 (11.1)	2.38 (1.0)	

^a t = triplet; q = quartet.

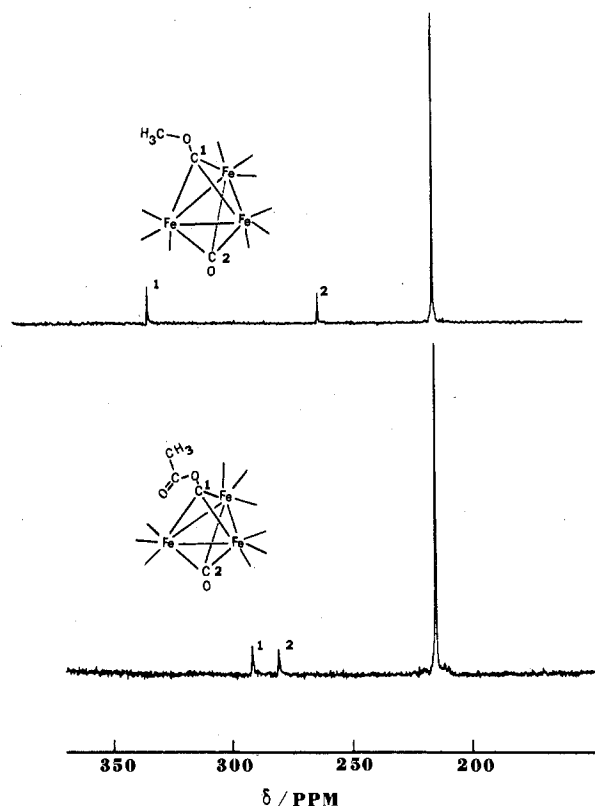


Figure 1. Carbon-13 NMR spectra for the carbonyl ligands of [PPN][Fe₃(CO)₁₀(μ_2 -COCH₃)] and [PPN][Fe₃(CO)₁₀(μ_2 -COC(=O)H₃)] at -120°C .

the terminal carbonyls perhaps by a twist mechanism.¹⁴

The variable-temperature ^{13}C NMR data obtained for [PPN][HFe₃(CO)₁₁] in the range 0 to -120°C are in good agreement with results reported by Wilkinson and Todd.⁹ At -120°C , seven peaks are observed in the carbonyl region in the ratio 1:1:1:2:2:2:2 (Table II). This is the expected pattern on the basis of the structure obtained by X-ray diffraction.¹⁵ The low-temperature scrambling mechanism proposed by Wilkinson and Todd involves a series of bridging-terminal-bridging interchanges for both CO and H ligands.⁹ At room temperature the NMR spectra indicate complete carbonyl scrambling which requires an additional exchange process.

As previously discussed, the ^{13}C NMR for Fe₃(CO)₁₀(C-OCH₃)⁻ shows three carbonyl peaks (δ 336.8, 264.0, 215.2) in the ratio of 1:1:9, Figure 2. The peak at δ 336.8 is assigned to the alkylated carbonyl carbon, the one at δ 264.0 to the face-bridging carbonyl carbon, and the third peak at δ 215.2 to the nine terminal carbonyl carbons which are unresolved because of a lack of chemical shift difference between the individual terminal carbonyls¹⁶ or because of rapid pseudorotation of the (CO)₃ groups on each Fe. Pseudorotation of this type is known to occur among pentacoordinated, monomeric iron carbonyl complexes,¹⁷ hexacoordinated mo-

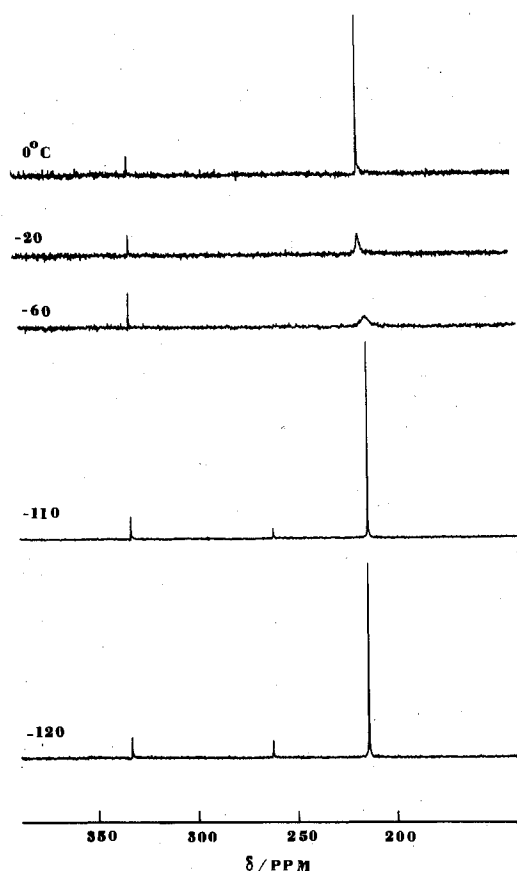


Figure 2. Variable-temperature ^{13}C NMR spectra for the carbonyl ligands of $[\text{PPN}][\text{Fe}_3(\text{CO})_{10}(\mu_2\text{-COCH}_3)]$.

lybdenum and tungsten complexes,¹⁸ and carbonyl clusters.¹⁹

When the sample is warmed to -110°C , the peak at δ 264.0 decreases in intensity and shifts slightly upfield to δ 263.8. At the same time, the peak at δ 215.2 shifts slightly downfield to δ 215.3. And at -60°C , complete exchange between the face-bridging carbonyl and the rest of the terminal carbonyls occurs with both signals coalescing into one broad signal centered at δ 216.9. When the solution was warmed further, this peak sharpens and at 0°C only two sharp peaks (δ 339.1 and 220.0) in a ratio of 1:10 are observed which are assigned respectively to the O-alkylated carbonyl carbon and the strong average signal of the face bridging and terminal carbonyl carbons.

The partial rigidity caused by the O-alkylation in $\text{Fe}_3(\text{C-O})_{10}(\text{COCH}_3)^-$ contrasts with the completely fluxional character of the dianion $\text{Fe}_3(\text{CO})_{11}^{2-}$ down to the lowest temperature studied. The chemical shift of the alkylated carbonyl carbon shows no change upon warming, demonstrating the lack of exchange between alkylated carbonyl group with others, and the bridge-terminal exchange of the remaining carbonyls is diminished by the presence of the $\mu\text{-COCH}_3$. Similarly, interaction of trialkylaluminum with the carbonyl ligands of the dimer $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ has been shown to slow down the cis-trans fluxional process.⁴ It has also been observed that the fluxional process in the anion $\text{HFe}_3(\text{CO})_{11}^-$ is slowed down by interaction with BF_3 .⁹ A pictorial representation of the CO permutational process in $\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)^-$ is given in Scheme I.

As with the methyl derivative, the ^{13}C NMR spectrum of $[\text{PPN}][\text{Fe}_3(\text{CO})_{10}(\text{COC}(=\text{O})\text{CH}_3)]$ at -120°C shows three peaks (Table II) in a ratio of 1:1:9 (Figure 1), suggesting that the acetyl is attached to the oxygen of the bridging carbonyl oxygen. The peak at δ 292.94 is assigned to the carbon of the acetylated carbonyl group, the one at δ 281.62 is assigned to

Scheme I

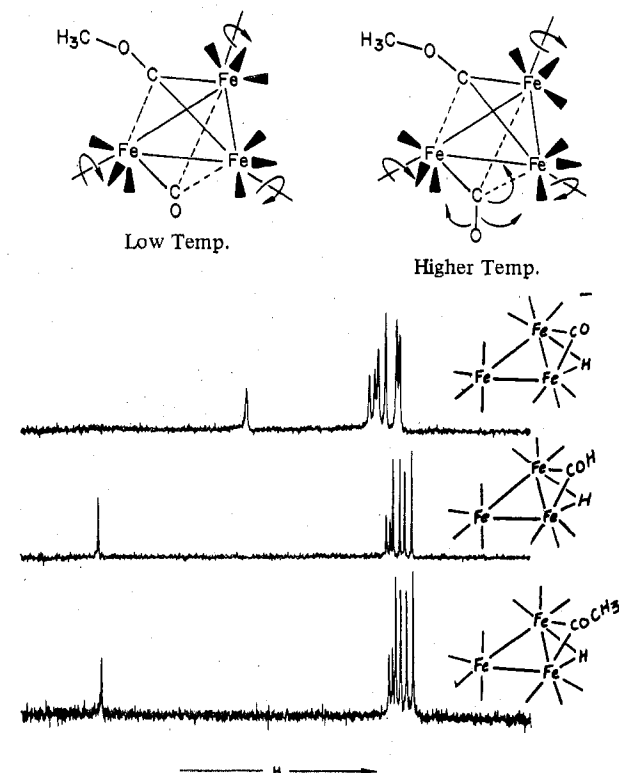


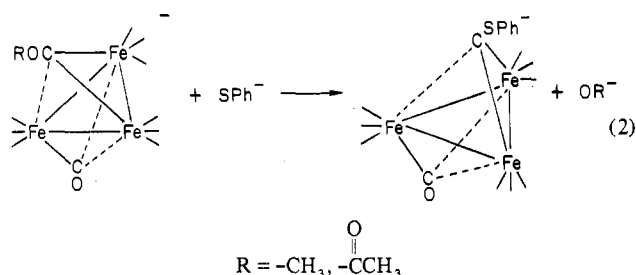
Figure 3. Carbon-13 NMR spectra for the carbonyl ligands of $\text{HFe}_3(\text{CO})_{10}(\mu_2\text{-CO})^-$ (-120°C), $\text{HFe}_3(\text{CO})_{10}(\mu_2\text{-COH})$ (-100°C), and $\text{HFe}_3(\text{CO})_{10}(\mu_2\text{-COCH}_3)$ (-120°C).

the unsymmetrically face-bridging carbonyl carbon, and the rest of the terminal carbonyls are assigned to the peak at δ 214.32.

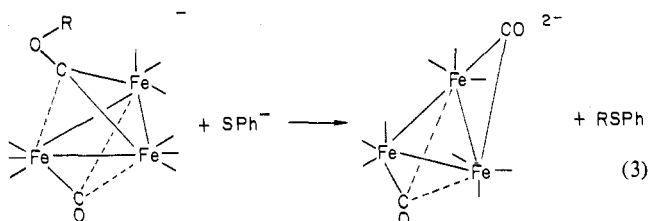
The spectrum of $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ at -120°C shows seven peaks (δ 356.48, 215.81, 214.12, 212.64, 210.19, 207.39, 204.15) in a ratio of 1:1:1:2:2:2:2, as expected for the slow exchange limit based on the molecular structure determined in the solid state.² The same general pattern has been observed for the hydrido anion $\text{HFe}_3(\text{CO})_{11}^-$ at -120°C (Figure 3). An upfield shift of about 5 ppm has been observed for the terminal carbonyl peaks of $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ relative to $\text{HFe}_3(\text{CO})_{11}^-$, and the alkylated bridging carbonyl group carbon C(4), I, is shifted downfield by more than 70 ppm to δ 356.48 (compared with δ 283.96 for $\text{HFe}_3(\text{CO})_{11}^-$). This shift is similar to the deshielding which results when a bridging carbonyl interacts with a Lewis acid.⁹ The spectrum of $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ shows six peaks in a ratio of 1:1:2:2:2:2 in the terminal carbonyl region. The first two peaks are assigned to the axial carbonyls (5 or 6) on the unique iron atom (1). The rest are assigned to the equatorial carbonyl carbons of Fe(1) and the three pairs of equivalent carbonyl carbons of Fe(2) and Fe(3), I.

The similarity of the ^{13}C NMR spectra of both $\text{HFe}_3(\text{C-O})_{10}(\text{COCH}_3)$ and $\text{HFe}_3(\text{CO})_{10}(\text{COH})$ (Figure 3) (including the number, ratio, and position of the peaks) clearly demonstrates similar structures for $\text{HFe}_3(\text{CO})_{10}(\text{COH})$ and $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$.⁸ Although both $\text{HFe}_3(\text{CO})_{11}^-$ and $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ have the same ratio and pattern of splitting at low temperature, $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ retains this pattern up to -20°C whereas the spectrum of $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ collapses into one peak at about -80°C . This difference is consistent with the decrease in CO-exchange process caused by the alkylated carbonyl bridge, which has been discussed earlier. At 0°C , $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ shows only four peaks in a ratio of 1:4:3:3; the origin of this pattern is not clear.

Nucleophilic Attack of $\text{Fe}_3(\text{CO})_{10}(\text{COR})^-$. Esters are known to undergo nucleophilic cleavage of the C–O bond by strong nucleophiles such as $\text{S}(\text{C}_6\text{H}_5)^-$.²⁰ The analogous reaction for the metal cluster is indicated in (2). Alternatively, the



thiophenoxide ion might attack the R group. The reaction of $\text{S}(\text{C}_6\text{H}_5)^-$ with $\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)^-$ and with $\text{Fe}_3(\text{C}-\text{O})_{10}(\text{COC}(=\text{O})\text{CH}_3)^-$ in dimethylformamide solution appears to occur rapidly at room temperature. In both cases the dianion $\text{Fe}_3(\text{CO})_{12}^{2-}$ was isolated in large yield, and the organic products $\text{CH}_3\text{SC}_6\text{H}_5$ and $\text{CH}_3\text{C}(=\text{O})\text{SC}_6\text{H}_5$ were identified by NMR and mass spectra for the methyl and acetyl derivatives, respectively. Thus, the course of reaction 3 is



contrary to that observed for organic esters, a fact which probably reflects a higher electron density on the metal-coordinated carbonyl than on the alkyl carbon of an organic ester. Similar results have previously been obtained in our laboratory for the reaction of NH_3 with $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$, where $[\text{CH}_3\text{NH}_3][\text{HFe}_3(\text{CO})_{11}]$ is produced.²¹ The general indication from these observations is that the electrophilic character of the $\mu\text{-CO-R}$ carbon is attenuated by interaction with the relatively electron-rich iron centers.

Experimental Section

Owing to the extremely toxic nature of methyl fluorosulfonate and ethyl fluorosulfonate,²² all operations involving these materials were carried out in an efficient fume hood with Schlenk-type apparatus. Other manipulations were carried out in Schlenk-ware, a vacuum line, or a nitrogen-filled drybox.

Spectroscopy. Infrared data were recorded on a Perkin-Elmer Model 283 instrument with KBr plates or a 0.1-mm NaCl solution cell employing a solvent blank. Proton NMR spectra were recorded on Perkin-Elmer, Hitachi R-20B, and/or Varian CFT-20 instruments. The ^{13}C NMR were obtained on a Varian CFT-20 spectrometer operating in the Fourier transform mode at a frequency of 20 MHz. Tris(acetylacetonato)chromium(III) (0.05 M) was added as a relaxation agent¹² in some cases. However, good results were obtained on $\text{HFe}_3(\text{CO})_{10}(\text{COH})$ and $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ without the relaxation agent. Dichloromethane was used as internal standard. Results were converted by using $\delta(\text{Me}_4\text{Si}) = \delta(\text{CH}_2\text{Cl}_2) + 53.80$.

Analyses. Elemental analyses were performed in the Northwestern Analytical Services Laboratory or by Galbraith Laboratories, Inc., Knoxville, TN. Mass spectra were obtained in the Northwestern Analytical Services Laboratory.

Materials. Anhydrous diethyl ether was further dried by distillation from sodium benzophenone ketyl, methanol was purified by fractional distillation, methylene chloride was distilled from phosphorus pentoxide, and methyl fluorosulfonate, ethyl fluorosulfonate, fluorosulfuric acid, and acetyl chloride were purified by fractional distillation under reduced pressure of nitrogen. Dimethylformamide was stored over KOH and then distilled under reduced pressure of nitrogen. Sodium thiophenoxide was prepared from thiophenol and sodium.²⁰

$[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]^{23}$ was prepared by a modification of the procedure of Hieber,²⁴ and $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ was prepared from $\text{Fe}(\text{CO})_5$ ²⁵ or from $\text{Fe}_3(\text{CO})_{12}$ by a modification of literature methods.^{26–28} $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ and $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ were enriched to ca. 10% ^{13}C per molecule by stirring the sample in CH_2Cl_2 solution under an atmosphere of ^{13}C at room temperature. Enriched samples of $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ and $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ were used to prepare other derivatives.

Preparation of $[\text{PPN}][\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)]$. To a solution containing 3.1 g (2.0 mmol) of $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ in 20 mL of CH_2Cl_2 was added a 0.25-mL (3.0 mmol) sample of $\text{CH}_3\text{SO}_3\text{F}$. The mixture was stirred for 30 min, and then 80 mL of diethyl ether was added. The thick precipitate of $[\text{PPN}][\text{SO}_3\text{F}]$ was filtered off and washed with 10 mL of diethyl ether. Volatiles were removed from the filtrate under vacuum. The weight of the crude product was 1.5 g (~73% yield). Crystallization from methanol gave 0.7 g (47%) of the product. Anal. Calcd for $\text{C}_{48}\text{H}_{33}\text{N}_2\text{P}_2\text{Fe}_3\text{O}_{11}$: C, 56.01; H, 3.24; N, 1.36; Fe, 16.28. Found: C, 56.37; H, 3.35; N, 1.30; Fe, 15.09.

Preparation of $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$. A 1.0-g (1.0-mmol) sample of $[\text{PPN}][\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)]$ was dissolved in 5 mL of CH_2Cl_2 and then 0.12 mL (~2 mmol) of fluorosulfuric acid was added. The color of the solution changed from dark red-brown to deep red-violet. The solution was stirred for 10 min before 30 mL of diethyl ether was added. The thick white precipitate of $[\text{PPN}][\text{SO}_3\text{F}]$ which separated was filtered off and washed with 10 mL of diethyl ether. Volatiles were removed under vacuum; the dark red crude product weighed 0.45 g (92% yield). The product was further purified by extraction with hexane. The residue was sublimed at 50 °C under hard vacuum. The mass spectrum of the sublimate showed the parent ion at m/e 492 (calcd mol wt 491.68). Anal. Calcd for $\text{C}_{12}\text{H}_4\text{Fe}_3\text{O}_{11}$: C, 29.31; H, 0.82; Fe, 34.07. Found: C, 28.95; H, 0.80; Fe, 31.97.

Preparation of $[\text{PPN}][\text{Fe}_3(\text{CO})_{10}(\text{COC}_2\text{H}_5)]$. This compound was prepared by the same procedure used for $[\text{PPN}][\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)]$ with ethyl fluorosulfonate as the carbocation reagent. The crude product was obtained in 90% yield. Crystallization from methanol gave dark red-brown crystalline product in 43% yield. Anal. Calcd for $\text{C}_{48}\text{H}_{35}\text{N}_2\text{P}_2\text{Fe}_3\text{O}_{11}$: C, 56.40; H, 3.39; N, 1.34; Fe, 16.06. Found: C, 56.48; H, 3.19; N, 1.20; Fe, 15.56.

Preparation of $\text{HFe}_3(\text{CO})_{10}(\text{COC}_2\text{H}_5)$. This compound was prepared by the procedure used for $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$. The crude product was obtained in 88% yield. Further extraction with hexane followed by sublimation at room temperature gave a dark red amorphous material. The mass spectrum showed the parent ion at m/e 506 (calcd mol wt 505.74). Anal. Calcd for $\text{C}_{13}\text{H}_6\text{Fe}_3\text{O}_{11}$: C, 30.87; H, 1.20; Fe, 33.13. Found: C, 30.18; H, 1.32; Fe, 34.04.

Preparation of $[\text{PPN}][\text{Fe}_3(\text{CO})_{10}(\text{COC}(=\text{O})\text{CH}_3)]$. To a solution of 1.6 g (1.0 mmol) of $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ in 10 mL of CH_2Cl_2 was added 0.72 mL (10.0 mmol) of acetyl chloride. The mixture was stirred for 10 min, and then 80 mL of diethyl ether was added. The thick white precipitate of $[\text{PPN}][\text{SO}_3\text{F}]$ which formed was filtered off and washed with 10 mL of diethyl ether. Volatiles were removed from the filtrate under vacuum, the dark red residue was washed with three 20-mL portions of diethyl ether to remove $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$, and the product was then dried under vacuum. Weight of the crude product was 0.90 g (~86% yield). Crystallization from methanol gave hexagonal, dark brown crystals. Anal. Calcd for $\text{C}_{49}\text{H}_{33}\text{N}_2\text{P}_2\text{Fe}_3\text{O}_{12}$: C, 55.66; H, 3.15; N, 1.33; Fe, 15.85. Found: C, 55.74; H, 3.15; N, 1.43; Fe, 16.69.

Preparation of $\text{HFe}_3(\text{CO})_{10}(\text{COH})$. Although this compound can be prepared on large scale, the procedure mentioned here describes the preparation of $\text{HFe}_3(\text{CO})_{10}(\text{COH})$ in a 5-mm NMR tube. Unlike the synthetic approach of Hieber and Brendel,²⁶ which yields a hydrated product,⁸ the preparation of $\text{HFe}_3(\text{CO})_{10}(\text{COH})$ was done here under anhydrous conditions. A solution containing 0.036 mmol of $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ in 0.6 mL of dry and air-free CD_2Cl_2 was prepared and cooled to -90 °C. To this cooled solution was added 0.036 mmol of fluorosulfuric acid under nitrogen. The resulting dark red-violet solution decomposes around -30 °C. NMR evidence discussed in a previous section demonstrates that the red-violet compound is $\text{HFe}_3(\text{CO})_{10}(\text{COH})$.

Nucleophilic Reactions. In a typical procedure 0.5 mmol of the carbonyl cluster was mixed with 1.0 mmol of sodium thiophenoxide in 10 mL of DMF. The mixture was stirred at room temperature for 1 h. Volatiles were removed and trapped (-196 °C) under reduced pressure. The gummy residue was dissolved in 20 mL of CH_2Cl_2 and filtered, and 50 mL of diethyl ether was added to filtrate. On addition

of ether, dark red-brown crystals of the $\text{Fe}_3(\text{CO})_{11}^{2-}$ salt were collected by filtration and dried under vacuum.

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Registry No. [PPN] $_2$ [$\text{Fe}_3(\text{CO})_{11}$], 66039-65-4; [PPN][$\text{HFe}_3(\text{CO})_{11}$], 23254-21-9; [PPN][$\text{Fe}_3(\text{CO})_{10}(\text{COCH}_3)$], 69421-10-9; $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$, 55992-19-3; [PPN][$\text{Fe}_3(\text{CO})_{10}(\text{COC}_2\text{H}_5)$], 69421-12-1; $\text{HFe}_3(\text{CO})_{10}(\text{COC}_2\text{H}_5)$, 69421-13-2; [PPN][$\text{Fe}_3(\text{CO})_{10}(\text{COC}(\text{=O})\text{CH}_3)$], 69421-15-4; $\text{HFe}_3(\text{CO})_{10}(\text{COH})$, 67775-42-2; $\text{CH}_3\text{SO}_3\text{F}$, 421-20-5; $\text{C}_2\text{H}_5\text{SO}_3\text{F}$, 371-69-7; acetyl chloride, 75-36-5; $\text{C}_6\text{H}_5\text{S}^-$, 13133-62-5.

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Reaction Mechanisms of Metal-Metal-Bonded Carbonyls. 22.¹ Fragmentation

Reactions of Nonacarbonyltris(tri-*n*-butylphosphine)triruthenium and Nonacarbonyltris(triphenyl phosphite)triruthenium

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The complexes $\text{Ru}_3(\text{CO})_9\text{L}_3$ ($\text{L} = \text{P-}n\text{-Bu}_3$ and P(OPh)_3) undergo thermal fragmentation reactions in decalin to form mononuclear products, and the kinetics of these reactions have been studied. A major path is shown to involve initial rate-determining dissociation of a CO ligand. When $\text{L} = \text{PPh}_3$, P(OPh)_3 , and $\text{P-}n\text{-Bu}_3$, the activation enthalpies are 33.0, 27.4, and 19.4 kcal mol⁻¹, respectively, and this can only be explained by major differences in the bonding within the intermediates $\text{Ru}_3(\text{CO})_8\text{L}_3$. Some possibilities are discussed. The detailed nature of the kinetics requires that these intermediates are not susceptible to direct attack by L but that they undergo reversible isomerization to a form that is. Fragmentation follows this attack. Assessment of results of these and other kinetic studies of triruthenium clusters suggests that initial ligand dissociation is generally much more facile than cluster fragmentation.

Introduction

Metal carbonyl clusters have been the subject of much intensive study in recent years.² Most of the effort has been concentrated on preparative and structural aspects but the growing availability of ¹³C NMR spectrometers has more recently led to a plethora of investigations into the fluxional behavior of metal carbonyl clusters and their organometallic derivatives. A recent upsurge of interest in the relationship between heterogeneous and homogeneous catalysis^{3,4} has resulted in a special effort to determine the general usefulness of clusters as catalysts and to produce especially reactive clusters.⁵ In spite of this interest very much less effort has been devoted to basic mechanistic studies of their reactions even though it is not at all clear in many cases that it is the clusters themselves that are the catalysts rather than active mononuclear fragments produced from them.⁵ If the latter were the case, then the analogies drawn between surface-active heterogeneous catalysts and metal-cluster catalysts would be misleading.

As part of a quite general interest in the mechanisms of reactions of metal-metal-bonded carbonyls and in the energetics of metal-metal bonds, kinetic studies have been carried

out of reactions of $\text{Ru}_3(\text{CO})_{12}$ and its P-donor-substituted derivatives.⁶⁻¹⁰ It has been established that even the apparently simple formation of $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ from $\text{Ru}_3(\text{CO})_{12}$ occurs via the formation of mononuclear fragments.⁷ $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ has been shown to undergo a wide variety of reactions including readily reversible fission at 50 °C into two fragments which are probably $\text{Ru}_2(\text{CO})_6(\text{PPh}_3)_2$ and paramagnetic $\text{Ru}(\text{CO})_3\text{PPh}_3$.⁹ This fragmentation and its reverse must occur ca. 10⁴ times for every fragmentation leading to $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ in the perfectly clean formation of the latter in 100% yield from $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ and PPh_3 under an atmosphere of CO. Activation parameters for fragmentation of $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n = 1-3$) have been shown¹⁰ to depend greatly on the value of n and $\text{Ru}_3(\text{CO})_{11}(\text{PBu}_3)$ must undergo relatively rapid fragmentation, even at 30 °C,⁷ whereas $\text{Ru}_3(\text{CO})_{12}$ ¹¹ and $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ ⁷ undergo fragmentation quite slowly at temperatures over 100 °C. The great dependence of the energetics on the number and nature of substituents and the wide range of mechanistic paths followed even by such relatively small clusters have prompted us to extend our studies of substituted triruthenium carbonyl clusters. We report here results of some kinetic studies of