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PREVIEW

KINETIC STUDIES OF REACTIONS BETWEEN METHYL IODIDE AND

$M^+ [Fe(CO)_3(NO)]^-$ SALTS (M = K, PPN or 18-crown-6 K)

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by

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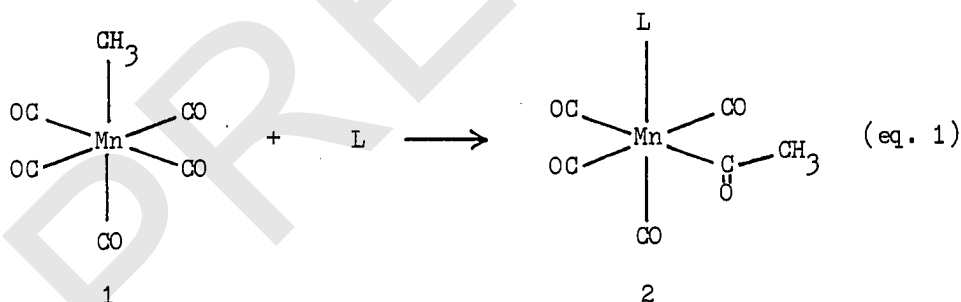
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I. Introduction

Nucleophilic attack upon a carbon atom coordinated to a transition metal is an important process in the preparation of new organometallic complexes and in the generation of reactive intermediates useful for organic synthesis. The alkyl migration is one of the most ubiquitous and well-studied reactions in organotransition metal chemistry. In addition to its fundamental importance, alkyl migration is a critical step in many important carbon-carbon bond-forming processes involved in homogeneous transition metal catalysis. For example, methyl manganese pentacarbonyl complex, 1, rearranges in the presence of ligands(L) such as CO, a tertiary phosphine, an amine, or a halide ion, affording the acyl complex, 2. (eq.1)^{1,2,3}



Acyl derivatives of tetracarbonylcobalt are recognized as important intermediates in hydroformylation and related carbonylation reactions.⁴ Their formation and reactions have been studied extensively and have shed much light on the mechanisms of such cobalt carbonyl catalysed processes. The solution structure of sodium tetracarbonylcobaltate has been extensively studied by Edgell and co-workers.⁵

Tricarbonylnitrosyliron anion, $[\text{Fe}(\text{CO})_3(\text{NO})]^-$, is isoelectronic with $[\text{Co}(\text{CO})_4]^-$. In this thesis the solution structures of this iron

complex in different systems are introduced and kinetic studies on the reactions of $M^+[\text{Fe}(\text{CO})_3(\text{NO})]^-$ with methyl iodide are reported. From these kinetic results, a mechanism for these reactions is suggested.

PREVIEW

II. The relationship between bonding and infrared spectrum

The simplest metal carbonyls are of the type $M(CO)_n$, such as $[V(CO)_6]^-$, $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, etc., . In all cases the M-C-O groups are linear. Thus the octahedral, trigonal-bipyramidal and tetrahedral structures have, respectively, strict O_h , D_{3h} and T_d symmetries.

From the molecular-orbital point of view, Cotton suggested that there are two types of bonding between the transition metal and the carbonyl group.⁶ First, there is a dative overlap of the filled carbon σ orbital with the metal orbital, as shown in Figure (1).⁷ Second, there is a retro-dative overlap of a filled $d\pi$ or hybrid $dp\pi$ metal orbital with an empty antibonding $p\pi$ orbital of carbon monoxide.

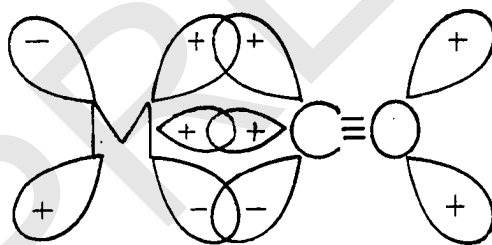


Figure (1). Bonding between transition metal and carbonyl group

This bonding mechanism is synergic, since the drift of metal electrons into CO orbitals will tend to make the CO as a whole negative and hence to increase its basicity via the σ orbital of carbon; at the same time the drift of electrons to the metal in the σ bond tends to make the CO positive, thus enhancing the acceptor strength of the π orbital. Thus, up to a point, the effects of σ bond formation strengthen the π bonding

and vice versa.

The stretching frequency for terminal CO group in neutral metal carbonyl molecule is found in the range from 2125 cm^{-1} to 1850 cm^{-1} . When changes are made that should increase the extent of M-C back-bonding, the CO stretching frequency is shifted to even lower value.

The ligands $(\text{C}_6\text{H}_5)_3\text{M}$ (M = P, As, Sb) are considered to be poor electron acceptors compared to the carbonyl group.⁸ Therefore, when one of the carbonyl groups of dicarbonyldinitrosyliron(0), $\text{Fe}(\text{CO})_2(\text{NO})_2$, is replaced by a $(\text{C}_6\text{H}_5)_3\text{M}$ group we should anticipate an increase in metal-carbon π -bonding with a consequential lowering of the CO stretching frequency of the remaining carbonyl groups. The data presented in Table(1) are in agreement with the prediction.⁹

Table (1). Carbonyl and nitrosyl infrared stretching frequencies for $\text{Fe}(\text{CO})(\text{NO})_2\text{L}$

Compound	CO(cm^{-1})	NO(cm^{-1})
$\text{Fe}(\text{CO})_2(\text{NO})_2$	2087, 2034	1810, 1756
$(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})(\text{NO})_2$	2009	1764, 1722
$(\text{C}_6\text{H}_5)_3\text{AsFe}(\text{CO})(\text{NO})_2$	2010	1767, 1726
$(\text{C}_6\text{H}_5)_3\text{SbFe}(\text{CO})(\text{NO})_2$	2010	1771, 1728

The NO molecule is closely akin to CO except that it contains one more electron, which occupies a π^* orbital. The bonding between the NO group and transition metal is almost the same as the M-CO bonding that illustrated in Fig.(1). In most nitrosyl complexes the terminal NO

stretching frequency is observed as an intense and characteristic band in the range from 1550 cm^{-1} to 1950 cm^{-1} . If there are some changes to the extent of M-N bonding, the nitrosyl stretching frequency will also be shifted by the same manner as M-CO does.

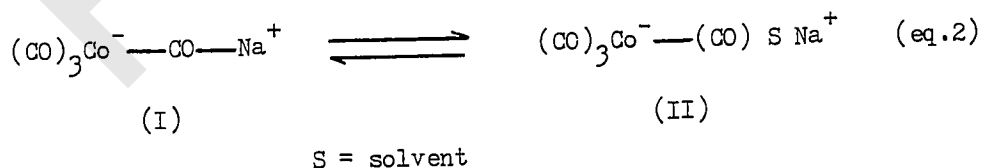
Structural data, such as bond length, suggest that under comparable circumstances M-CO and M-NO bonds are about equally strong.⁶ In a chemical sense the M-N bonds appear to be stronger, since substitution reactions on mixed carbonyl nitrosyl compounds typically result in displacement of CO in preference to NO. For example, $\text{Co}(\text{CO})_3(\text{NO})$ reacts with a variety of R_3P , X_3P and amine, to invariably yield the $\text{Co}(\text{CO})_2(\text{NO})\text{L}$ product and $\text{Fe}(\text{CO})_2(\text{NO})_2$ reacts with $(\text{C}_6\text{H}_5)_3\text{M}$ ($\text{M} = \text{P, As, Sb}$) to yield $\text{Fe}(\text{CO})(\text{NO})_2\text{L}$.^{9,10}

III. Solution structures of transition metal carbonylate salts

Solvents most commonly used for reactivity studies of transition metal carbonylate salts and their dielectric constants are : Et₂O, 4.3; CH₂Cl₂, 6.7; THF, 7.4; pyridine, 12.3; hexamethylphosphorictriamide(HMPA), 30; N,N-dimethylformamide(DMF), 35; dimethylsulfoxide(DMSO), 45. The more polar solvent is the more effective in separating ion pairs.

Since an isolated $[\text{Co}(\text{CO})_4]^-$ ion has a T_d symmetry, it would be expected to have a triply degenerate, infrared-active CO stretching frequency around 1900 cm⁻¹. When Na⁺ $[\text{Co}(\text{CO})_4]^-$ is dissolved in DMF, a single infrared absorbance is observed at 1887 cm⁻¹. However, if this alkali metallate is dissolved in THF, this single infrared band will be split into several components. An extensive studies on solution structure of tetracarbonyl alkali metallate, M⁺ $[\text{Co}(\text{CO})_4]^-$ (M⁺ = Na⁺, Li⁺, K⁺) by Edgell and co-workers have explained these results.^{5,11}

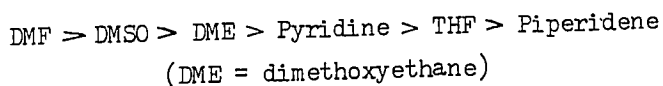
Edgell suggested that an equilibrium exists between two kind of anion environments, sodium-carbonyl oxygen interacted tight ion pair(I) and solvent-separated ion pair(II), in the Na⁺ $[\text{Co}(\text{CO})_4]^-$ / THF solution.



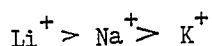
The ratio of the population of these two kind of anion environments depends on solvent, metal cation and temperature.

The solvents in the order of their ability to produce the solvent

separated anion environments were ranked as :



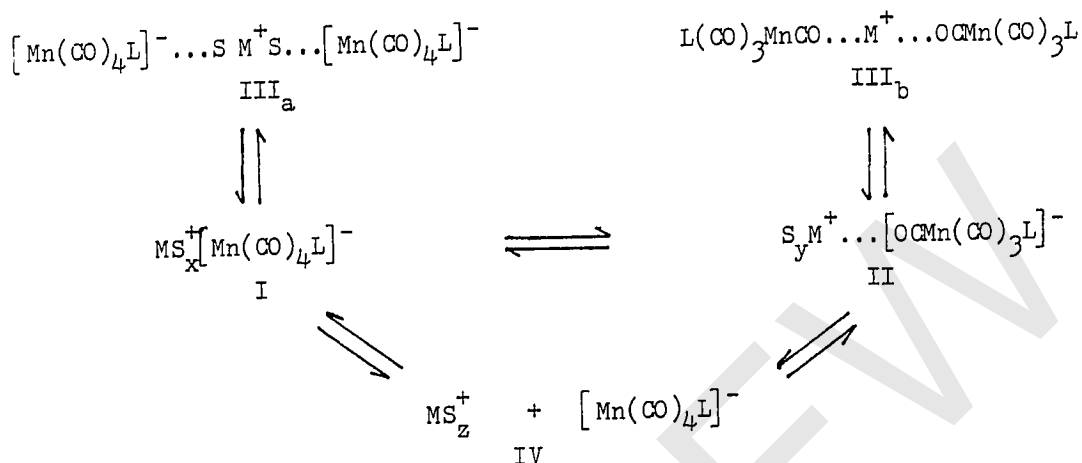
This order is paralleled with the decreasing order of their basicity. The alkali metal ions in order of their ability to produce the solvent-separated anion environment were ranked as :



This order is in agreement with the order of relative charge density which is the basis of interaction between these cations and the basic centers of solvents.

The infrared absorbances at 1893 cm^{-1} and 1860 cm^{-1} , obtained from THF solution spectra of $\text{Li}^+[\text{Mn}(\text{CO})_5]^-$, indicates that this manganese carbonylate is in a D_{3h} symmetrical environment. The same results can be found by dissolving $\text{Na}^+[\text{Mn}(\text{CO})_5]^-$ in THF which contained one-fold equivalent of cyclic polyether, 15-crown-5, or ten-fold equivalent of HMPA. However, the pure THF solution of $\text{Na}^+[\text{Mn}(\text{CO})_5]^-$ leads to a more complex spectrum. The explanation for these observations was given by Darensbourg.^{12,13}

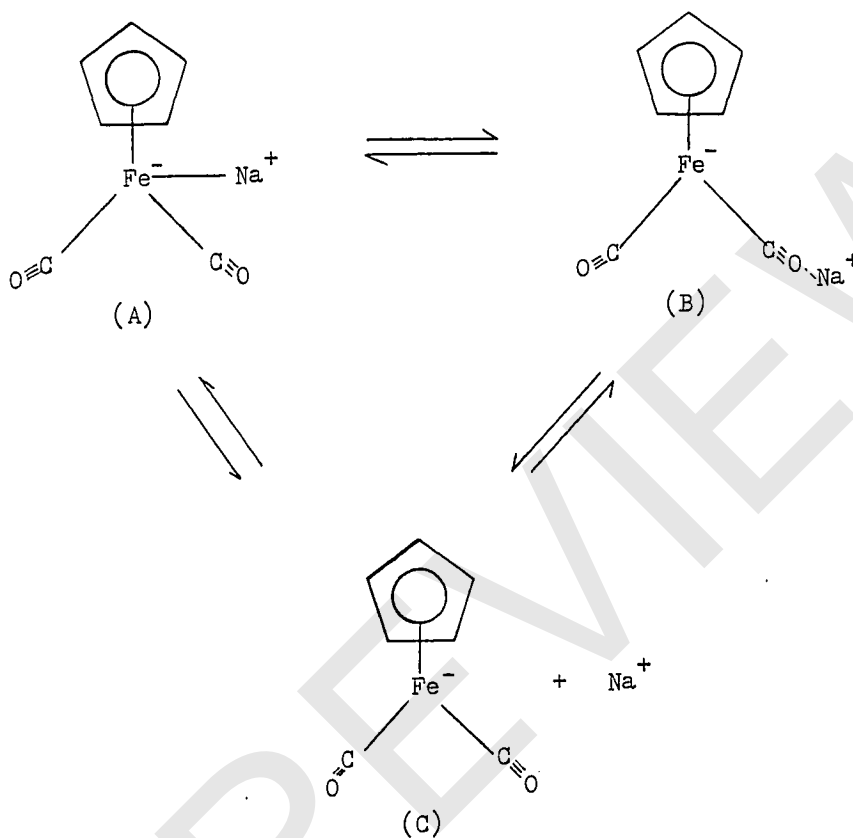
A combination of infrared, kinetic and conductivity studies of $\text{M}^+[\text{Mn}(\text{CO})_4\text{L}]^-$ ($\text{M}^+ = \text{Li}^+, \text{Na}^+$; $\text{L} = \text{PMe}_2\text{P}, \text{PPh}_3, \text{P(OPh)}_3$ and CO) by Darensbourg and co-workers indicated that species I, III_a , and IV of the following equilibria are expected to predominate for $\text{Li}^+[\text{Mn}(\text{CO})_5]^-$, $[\text{Na}^+ \cdot 15\text{-crown-5}][\text{Mn}(\text{CO})_5^-]$ and $[\text{Na}^+ \cdot \text{X} \cdot \text{HMPA}][\text{Mn}(\text{CO})_5^-]$ but a mixture of all five species for $\text{Na}^+[\text{Mn}(\text{CO})_5]^-$ and $\text{Na}^+[\text{Mn}(\text{CO})_4\text{L}]^-$.



Scheme (1). Equilibrium of $[\text{Mn}(\text{CO})_4\text{L}]^-$ in solution

In the same paper Darensbourg indicated that the equatorial carbonyl oxygen atoms are more electron rich in a trigonal-bipyramidal structure. By infrared analysis she suggested the contact ion interactions observed for $\text{Na}^+[\text{Mn}(\text{CO})_4\text{L}]^-$ to be that of Na^+ interacting with the oxygen of an equatorial CO group. It was also found that contact ion interactions for the phosphine substituted species are more extensive.

In addition to the tight ion pair involving a sodium-carbonyl oxygen interaction, other forms have been shown to exist. Extensive studies by Pannell and Jackson on the solution structure of dicarbonyl(η^5 -cyclopentadienyl)ferrate indicated that $\text{Na}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ exist in solution as a dynamic equilibrium of three species A, B and C, as outlined in Scheme (2).¹⁴ Species A contains a direct interaction between alkali and transition metal.



Scheme (2). Equilibrium of $\text{Na}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ in solution

IV. The mechanisms for reactions between alkyl halides and transition metalate anions

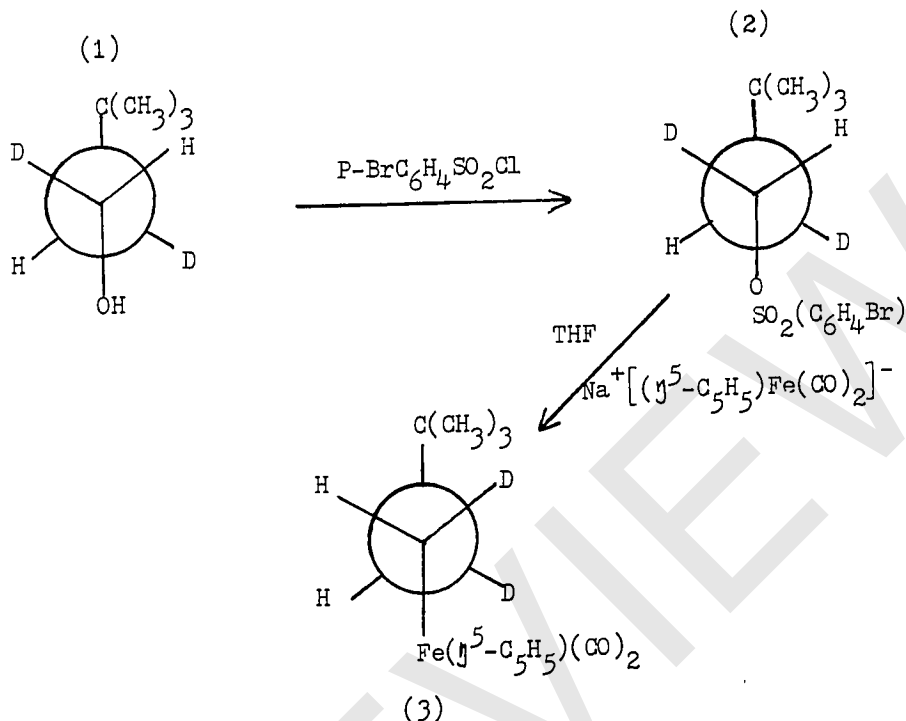
The displacement of halides and other groups from alkyl substrates by transition metalate anions represents one of the most important routes for the formation of metal-carbon σ bonds. A most valuable information to have in characterizing the mechanisms of these reactions is the stereochemistry of the transformation at the tetrahedral carbon atom which is a chiral center. With this information it is possible to judge whether a reaction involves intermediate free carbon radicals or ions or occurs by S_N2 or S_E2 transition states.

Here we introduce two kind of mechanisms for reactions between alkyl halides (or tosylates) and transition metalate anions.

1. S_N2 displacement :

The ability to differentiate spectroscopically between the erythro and threo diastereomers of $(CH_3)_3CCHD-CHDX$ provides the basis for a convenient and concincing method of determing the stereochemistry of a reaction involving a carbon-metal σ bond. Whitesides and co-workers have developed an NMR technique to do this job.^{15,16}

Erythro-3,3-dimethylbutan-1-ol-1,2- d_2 (1) was converted to erythro-3,3-dimethylbutyl-1,2- d_2 p-bromobenzenesulfonate(2) and thence to π -cyclopentadienyldicarbonyliron threo-3,3-dimethylbutyl-1,2- d_2 (3) by reaction with $Na^+[(\eta^5-C_5H_5)Fe(CO)_2]^-$, as shown in Scheme(3).



Scheme (3). Synthesis of the Deuterated organoiron compound

The NMR spectrum of the CHDCHD region of compound(3) consisted of a single AB quartet centered at $\delta = 1.38$ with $J = 4.4$ Hz. From this coupling constant, Whitesides confirmed that compound(3) has the threo configuration.

The nucleophilic displacement by $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ on the brosylate derived from erythro yields threo, established the fact that this displacement has the stereochemical characteristics expected of an unexceptional $\text{S}_{\text{N}}2$ displacement.

Besides these reactions mentioned above, there are some other reactions which formed a carbon-transition metal σ bond by $\text{S}_{\text{N}}2$ attack on the alkyl halides. For example, $\text{Na}_2\text{Fe}(\text{CO})_4$ is an inexpensive, versatile reagent for converting alkyl bromides, iodides and tosylates into aldehydes,