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Mechanisms of Carbon Monoxide Replacement in Metal Carbonyls

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The late Professor Walter Hieber, the 'father' of metal carbonyl chemistry, at the 3rd International Conference on Coordination Chemistry (ICCC) held in Amsterdam in May, 1955, gave a plenary lecture summarizing the elegant research done in his laboratory on the reactions and syntheses of metal carbonyls. I was fortunately present at his lecture, after which I congratulated him and his students for all of the fine work they had done and I asked if they had any knowledge as to how some of these reactions take place. With the aid of an interpreter, Professor Hieber kindly responded "we have been interested in real chemistry (reactions and syntheses) not the philosophy of chemistry (bonding and mechanisms)". His talk and his comment were largely responsible for my becoming interested in doing some work on the kinetics and mechanisms of metal carbonyls. Very little research of this type had been reported, and in the late fifties there was not much interest in the chemistry of metal carbonyls. This meant that almost anything we did would generate new publishable results, and also the field was not crowded with large numbers of investigators all rushing to do the same or similar experiments.

One would think that graduate students should want to work on such problems which are almost certain to lead to publications and to acceptable doctoral theses. Yet, at first, students were reluctant to choose a thesis problem dealing with metal carbonyls because all of the other people in my research group were working on Werner complexes in aqueous solution. Students felt more comfortable working with Werner complexes than with toxic metal carbonyls. Wojcicki was the first brave student willing to work with metal carbonyls, and largely because of his excellent work it later developed that students often preferred to work with these systems.

Dissociation (S_N1) Reactions

Wojcicki and I decided that since almost nothing had been reported on the kinetics and mechanism of substitution reactions of metal carbonyls we should stick to the simple binary metal carbonyls and to their 'uncomplicated' carbon monoxide exchange. We decided to work with only the first row transition metals and to ask and seek answers to questions such as (1) the effect of coordination number on the rates and mechanism of reaction, and (2) whether bridging carbonyls and terminal carbonyls react at different rates.

We were in for several surprises, because little had been done on the mechanisms of substitution reactions of metal carbonyls and we had little to base any 'educated' guesses on. We and others had, however, done considerable work of this type on the substitution reactions of the classical metal complexes [1]. Most of that work was on the six-coordinate cobalt(III) complexes and on the four-coordinate platinum(II) complexes. The general picture that had emerged from those studies was that octahedral substitutions take place by dissociative S_N1 (or I_d) [2] processes, whereas square planar substitutions are associative S_N2 or (I_a) reactions.

Because of this, we were surprised to find that the four-coordinate $Ni(CO)_4$ reacts by means of a dissociative process [3]. Our initial experiments on the rates of carbon monoxide exchange were done by circulating ^{14}CO through a solution of $Ni(CO)_4$ and monitoring the change or radioactivity of the CO in the gas phase. Because of experimental difficulties the experiments had to be repeated later by Day [4] using $C^{18}O$ and an infrared technique. He also carried out substitution reactions using triphenyl phosphine. The data collected fit the rate law (1)

$$\text{Rate} = k[Ni(CO)_4] \qquad (1)$$

which is in accord with the dissociative mechanism represented by (2) and (3).

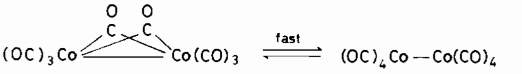
$$Ni(CO)_4 \overset{k}{\rightarrow} Ni(CO)_3 + CO\ (\text{slow}) \qquad (2)$$

$$Ni(CO)_3 + L \rightarrow Ni(CO)_3L\ (\text{fast}) \qquad (3)$$

This mechanism is also in accord with the enthalpy (24 kcal/mole) and entropy (+14 e.u.) of activation.

The surprise to us was that a four-coordinate metal complex does not expand its coordination number and react by an associative process. Why should this be different than the four-coordinate platinum(II) complexes? My pedestrian understanding at the time (and now) was that the platinum(II) has a vacant *p* orbital which could accommodate a pair of electrons from the entering nucleophile and provide a low energy path for ligand displacement. In contrast when a nucleophile takes a look at $Ni(CO)_4$ it sees the four carbonyls and between these are five *d* orbitals, each containing a pair of electrons for this d^{10} system. The entering nucleophile finds no easy place to put its pair of electrons unless one of the carbonyl groups leaves by a dissociation process. This same concept also helped me understand the dissociative substitution reactions of $Fe(CO)_5$ and $Cr(CO)_6$.

Yet another surprise came when we found [3] that all eight carbonyls of $Co_2(CO)_8$ exchange at the same rate with ^{14}CO. All that was known at the time was that the X-ray structure showed the solid to contain two bridging and six terminal carbonyls. We were therefore expecting two COs to exchange at a different rate than the other six. Our finding had to await the infrared experiments of Noack [5] which showed that the carbonyl bridged species in solution is in rapid equilibrium with the non-bridged species (4).



$$(OC)_3Co(\mu\text{-}CO)_2Co(CO)_3 \xrightleftharpoons{\text{fast}} (OC)_4Co{-}Co(CO)_4 \tag{4}$$

This rapid scrambling of all COs is the reason our exchange experiments showed that all eight carbonyls are equivalent.

The substitution reactions of manganese pentacarbonyl halides, $Mn(CO)_5X$, were investigated by Angelici [6] and these systems did behave as expected. The six-coordinate complexes react by a dissociation mechanism (5) and (6).

$$Mn(CO)_5X \xrightarrow{k} Mn(CO)_4X + CO\ (\text{slow}) \tag{5}$$

$$Mn(CO)_4X + L \rightarrow Mn(CO)_4LX\ (\text{fast}) \tag{6}$$

It was also found that the rates of reaction decrease for changes in X in the order Cl > Br > I. This too was expected because the less electronegative and more polarizable iodo group puts more electron density on manganese which then can more effectively back bond to the π acid carbonyl groups rendering them more difficult to remove. Consistent with this explanation is the fact that the C–O stretching frequencies in the infrared decrease in energy with changes in X in the order Cl > Br > I. This means that for the resonance structures (7)

$$Mn{-}C{\equiv}O \longleftrightarrow Mn{=}C{=}O \tag{7}$$

the double bonded structure is favored in the iodo compound, and the stronger Mn–C bond means this compound is the slowest to react. We had earlier [7] studied the exchange of ^{14}CO with $Mn(CO)_5X$ and obtained results which suggested the CO *trans* to X exchanged much slower than did the four COs *cis* to X. This is expected because the *trans* CO is more strongly bound, but the fluctional nature of the five-coordinate intermediate makes all COs seem equivalent [8].

Associative (S_N2) Reactions

After our work on $Ni(CO)_4$, it seemed only logical that we should investigate the isoelectronic and isostructural $Co(CO)_3NO$ (Thorsteinson [9]) and $Fe(CO)_2(NO)_2$ (Morris [10]). These three compounds are identical except for the number of protons in some of the nuclei, which meant that we were prepared to have the nitrosyl compounds behave the same as did the parent $Ni(CO)_4$. This was not to be, and we were surprised to find that the nitrosyl compounds readily undergo associative (S_N2) carbonyl substitution reactions. The rate law for substitution is first-order in both the nitrosyl and the nucleophile concentrations (8).

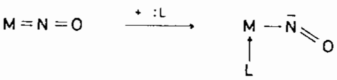
$$\text{Rate} = k[Co(CO_3)NO]\,[L] \tag{8}$$

This means that the mechanism of reaction can be represented by (9) and (10).

$$Co(CO)_3NO + L \xrightarrow{k} Co(CO)_3NOL\ (\text{slow}) \tag{9}$$

$$Co(CO)_3NOL \rightarrow Co(CO)_2NOL + CO\ (\text{fast}) \tag{10}$$

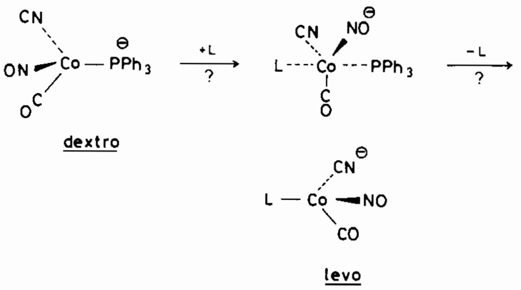
Since these nitrosyls are 'identical' with $Ni(CO)_4$ except for containing one or more NO groups instead of all ligands being CO, we focused our attention on how NO and CO may differ. One difference is that NO is present in these compounds formally as NO^+, whilst CO is neutral. Another difference is that nitrogen is more electronegative than carbon. Both of these differences favor the localization of a pair of electrons on nitrogen, relative to carbon, in the transition state for reaction. This would vacate electrons from a metal orbital, thus freeing it to accept a pair of electrons from the entering nucleophile and provide a low energy path for a displacement reaction. A schematic representation is shown by (11).



$$M{=}N{=}O \xrightarrow{+\,:L} \underset{\substack{\uparrow\\ L}}{M}{-}\bar{N}{\diagdown}O \tag{11}$$

We did not mention a bent nitrosyl at the time, but our designation of the nitrogen in an sp^2 hybrid should have implied it was bent. Positive evidence for a bent nitrosyl was left for my colleague Professor Ibers [11] to discover.

The obvious next question, particularly as these compounds have a tetrahedral structure, was are these classical S_N2 tetrahedral inversion reactions? We decided to try our luck at answering this question, and Panunzi [12] worked diligently on the problem for a few months. What we want to do is shown in (12).

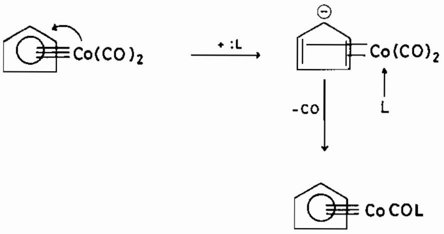


(12)

The anionic complex was made but it could not be resolved. Had we known then about fluctional molecules, we would not even have attempted the resolution.

These nitrosyl compounds which react by an S_N2 mechanism permitted the first quantitative assessment of nucleophilic strengths towards metal carbonyl substrates [9]. From the large amount of qualitative information on reactions of metal carbonyls, it was well known that these metals in their low oxidation states (class b or soft) prefer more polarizable (soft) ligand atoms over less polarizable (hard) ligand atoms. Our studies quantitatively verified the qualitative observations. The kinetic data, as expected, showed a linear free energy relation (LFER) with protonic basicity of the nucleophile for the same ligand atom. That is, except for steric effects, as the basicity of phosphines and phosphites increase the nucleophilic strength of the ligand increases. Of course, for the same base strength a phosphine (soft) is a better nucleophile than an amine (hard). Finally although $Fe(CO)_5$ slowly undergoes dissociative substitution, Wawersik [13] showed that the isoelectronic $Mn(CO)_4NO$ readily reacts by an associative mechanism.

At about the time we were engaged in these nitrosyl studies Williams of the National Science Foundation encouraged Professor E. O. Fischer and me to submit a proposal to initiate a predoctoral student exchange program. The reason being that our researches were complementary, Fischer's group doing syntheses and our group working on kinetics and mechanisms. This was a very worthwhile program for both groups, in particular for the student participants. For example Schuster-Woldan was the first student to arrive on the program and he introduced into our laboratory the Schlenck tube technique of handling air sensitive compounds. He had done some work with $C_5H_5Co(CO)_2$, and he decided to investigate the substitution reactions of this compound as well as the corresponding rhodium and iridium compounds. If one applies my "seat of the pants" approach and views η^5-C_5H_5 as equivalent to three carbonyl groups, then it follows that $(\eta^5\text{-}C_5H_5)Co(CO)_2$ is pseudo-isoelectronic with $Fe(CO)_5$. This might suggest that the cyclopentadienyl compounds of the cobalt triad would react slowly by a dissociation process. Instead substitution takes place readily by a second-order process, suggesting an associative mechanism [14]. From our success explaining substitution reactions of metal nitrosyl carbonyls, we quickly concluded that here too it is perhaps possible to localize a pair of electrons of the cyclopentadienyl ring and permit the attack on the metal by the electron pair of the nucleophile (13).



(13)

This early representation of ours might now more fashionably be designated as η^5-$C_5H_5Cl(CO)_2$ going to η^3-$C_5H_5Co(CO)_2L$. There has been some recent evidence for the formation of such intermediate species [15].

Another important observation made by Schuster-Woldan [14] was that the rates of reaction of η^5-$C_5H_5M(CO)_2$ for the cobalt triad vary in the order Co < Rh > Ir. This is contrary to the order of Co > Rh > Ir for their classical M(III) complexes [1]. We and others found that for metals in their low oxidation states their complexes undergo substitution for different triads at rates such as Co < Rh > Ir, Cr < Mo > W [16], and Ni < Pd > Pt [17]. The second row transition metal systems are the fastest to react in a given triad. This may be one reason that homogeneous catalysts often involve second row transition metal complexes such as the metals Mo, Rh, and Pd.

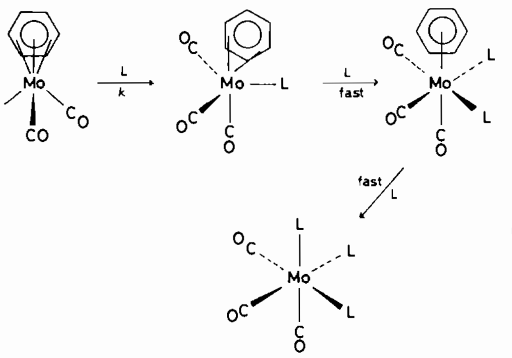
Once we knew that cyclopentadienyl metal carbonyls may undergo associative substitution reactions, it seemed reasonable to expect arene metal carbonyls to react by the same mechanism. This idea was tested by Zingales [18] using (arene)-$Mo(CO)_3$, where arene = toluene, *p*-xylene, and mesitylene. The overall reactions with phosphorus ligands involve the replacement of the arene (14).

TABLE I. Mechanisms of Substitution Reactions of Pseudo-isoelectronic 18-Electron Compounds.

$Cr(CO)_6$	S_N1	$Fe(CO)_5$	S_N1	$Ni(CO)_4$	S_N1
		$Mn(CO)_4NO$	S_N2	$Co(CO)_3NO$	S_N2
$(arene)Cr(CO)_3$	S_N2	$(C_5H_5)Co(CO)_2$	S_N2	$Fe(CO)_2(NO)_2$	S_N2
		$Fe(CO)_3(N_4Me_2)$	S_N2	$MnCO(NO)_3$	S_N2

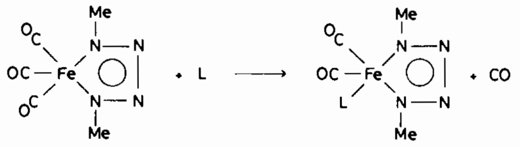
$$(arene)Mo(CO)_3 + L \rightarrow cis\text{-}Mo(CO)_3L_3 + arene \quad (14)$$

The reactions are second-order, with the initial step being rate determining and all subsequent steps being fast (15).



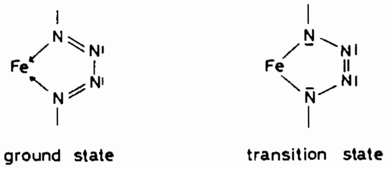
(15)

The work described above was all done before the seventies, and the past decade we have worked only on synthetic oxygen carriers. Thanks to encouragement by Professors Shriver and Trogler, and some students, we have recently started again to do research on metal carbonyls. Pertinent to this discussion of S_N2 reaction is the work just completed by Chang [19] on iron tricarbonyl-1,4-dimethyltetraazadiene, $Fe(CO)_3(N_4Me_2)$. This compound reacts by a displacement process, although it relates to $Fe(CO)_5$. Second-order kinetics are obtained for the substitution reactions (16).



(16)

This is believed to be the first report of a displacement reaction of a metallocycle compound. Again it is possible to write a valence bond structure of the transition state which localizes a pair of ground state electrons onto the transition state (17).



(17)

Iron in the transition state can now accommodate a pair of electrons from the entering nucleophile and allow for a displacement reaction path.

16,18-Electron Rule

Some years ago I met Tolman for the first time at a National Meeting of the American Chemical Society in Washington, D. C. He invited me to have lunch with him because he wanted to try out his 16,18-electron rule on me prior to publication. I fear I was not a very good guest because I could not get too excited about the rule. I may even have said that I saw no reason to publish such a rule because it was generally understood without it having to be stated as a rule. Fortunately Tolman [20] did not heed by advice and as we know the rule has focused attention on the importance of electron counting in these systems, and the rule has been particularly helpful to students and beginning investigators. This and hard and soft have taught me a lesson – if you can formulate a rule or give something a name then by all means do it.

With this in mind, the time is long past when we can state the following rule: *substitution reactions of 18-electron transition metal organometallic compounds may proceed by an associative mechanism provided the metal complex can delocalize a pair of electrons onto one of its ligands.* The previous section summarizes our studies which permit the statement of this rule, and the 18-electron systems and their mechanisms of reaction are listed in Table I.

These examples show that 18-electron complexes will not go to 20-electron intermediates, but will react by dissociation involving a 16-electron active intermediate. Associative reactions may however occur in an 18-electron system if electrons can transfer to one of the ligands, or in a 16-electron system. The latter is true of Werner complexes of platinum-

(II), Vaska's compound, and many other low-spin d^8 square-planar complexes [1, 2]. In these cases the 16-electron substrates react by an S_N2 mechanism involving an 18-electron species (not by S_N1 *via* a 14-electron intermediate).

Acid-induced Substitution Reactions

Some years ago several metal carbonyls and derivatives of metal carbonyls were dissolved in sulfuric acid and in trifluoroacetic acid and the solutions were examined by ^1H NMR and by IR. The results [21] showed that some of the compounds were protonated by the strong acids, and that the C–O stretching frequency in the IR of some of the protonated species increased as much as 140 cm^{-1}. This increase is consistent with there being less back-bonding by the protonated metal than by the metal in the parent compound. It was this observation which suggests a correspondingly weaker M–C bond in the protonated species that aroused our interest.

Brault [22] examined the effect of acid on the rate of exchange of ^{14}CO with $Fe(CO)_5$ and some of its derivatives. The effect is dramatic (18) and (19).

$$Fe(CO)_5 + {}^{14}CO \underset{\text{room temp.}}{\overset{\text{dark}}{\rightleftharpoons}} t_{1/2} = 4 \text{ yrs} \qquad (18)$$

$$Fe(CO)_5 + {}^{14}CO \underset{\substack{CF_3COOH \\ -21\ ^\circ C}}{\overset{\text{dark}}{\rightleftharpoons}} t_{1/2} = 30 \text{ min} \qquad (19)$$

Kinetic studies indicate that the acid-induced exchange proceeds by the dissociation of the conjugate acid (S_N1CA) (20) and (21).

$$Fe(CO)_5 + (CF_3COOH)_2 \overset{\text{fast}}{\rightleftharpoons} [HFe(CO)_5]^+(CF_3COOHOOCCF_3)^- \qquad (20)$$

$$[HFe(CO)_5]^+(CF_3COOHOOCCF_3)^- + {}^{14}CO \rightleftharpoons \text{exchange} \qquad (21)$$

No further studies of this type appear to have been reported, but it should be of interest to assess further the role of protonic and of Lewis acids on the rates and mechanisms of substitution reactions of transition metal organometallic compounds.

Base Catalyzed Substitution Reactions

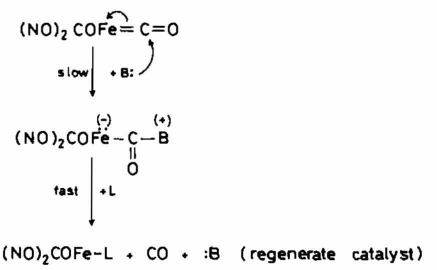
During his studies of the substitution reactions of $Fe(CO)_2(NO)_2$, Morris [23] noticed that the rates and mechanism of reaction were markedly altered by changes in solvent and by the presence of different bases. In toluene and dichloromethane, non-coordinating solvents, the reactions follow a one-term second-order rate law. In the coordinating solvents methanol and tetrahydrofuran (THF) there is a two-term rate law (22).

$$\text{Rate} = k_{sol}[Fe(CO)_2(NO)_2] + k_L[Fe(CO)_2(NO)_2][L] \qquad (22)$$

One term does not depend on the entering nucleophile, whereas the other term is first-order in nucleophile. This suggests a mechanism which involves a solvent path (k_{sol}) and a reagent path (k_L) (23).

$$\begin{tikzcd}
Fe(CO)_2(NO)_2 \arrow[rr, "+L", "k_L"'] \arrow[dr, "+THF", "k_{sol}"'] & & Fe(CO)(NO)_2L \\
& \text{intermediate} \arrow[ur, "+L", "\text{fast}"'] &
\end{tikzcd} \qquad (23)$$

The nature of the intermediate is not known. What is known is that different basis catalyze substitution reactions, also by a two-term rate law where one term depends on the nature and the concentration of the catalyst. Since the effectiveness of the basis decrease in the order $N_3^- > Cl^- > Br^- > I^-$, it is believed that these catalysts function by attack on the carbonyl carbon (hard) and not the metal (soft). Thus the mechanism by the catalysis path is viewed as represented by (24).



(24)

There are many examples of base attack on carbonyl carbons of metal carbonyls. There was even a much more recent report of base catalysis of ligand substitution in metal carbonyls [24]. These reactions are surely to be of importance in certain types of homogeneous catalysis, and they should be the subject of much more study in many different laboratories.

Acknowledgement

I want to thank Professor Croatto for his invitation to contribute to this special volume. I am particularly gratified because of my closeness to Italy, and because perhaps some of my conversations with Professor Belluco the year he spent with us may have helped initiate this journal. My heart felt thanks go out to the fine students whose ideas and work are responsible for our research on metal carbonyls. I am grateful to my colleagues Professors Shriver and Trogler who have helped rekindle my interest in these systems. The research we did was supported by the National Science Foundation for which we are all most thankful.

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