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Early kinetic studies on CO substitution reactions of metal carbonyls

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Abstract

Research done in our laboratory, spanning the period 1956–1970, on CO substitution kinetics and mechanisms of metal carbonyls is highlighted. In today's language of organometallic chemistry, it was shown that (1) 18-electron binary metal carbonyls react by a dissociative (S_N1) process, while 16-electron systems react by associative (S_N2) mechanisms, (2) metal carbonyls of 18-electrons with certain ligands (NO, η^5-C_5H_5) react by an associative process via a pair of electrons localized on the ligand in the reaction pathway, e.g. for η^5-C_5H_5, ring slippage of $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$, (3) insertion of CO in an alkyl metal bond was described mechanistically as alkyl migration, and (4) the ligand substitution lability of organometallic complexes of the 2nd row transition metal of a given triad was discovered.

Although Mond [1] discovered metal carbonyls ($Ni(CO)_4$) a century ago, those of us who work with metal carbonyls know the "father" of metal carbonyl chemistry was the late Professor Walter Hieber [2]. His pioneering research and contributions to the reactions and syntheses of metal carbonyls has dominated this area of chemistry, and even today one working in the field often has to refer to the early publications of Hieber and coworkers. Most of his work dealt with what he called "real chemistry" (reactions and syntheses), leaving others to be concerned with the "philosophy of chemistry" (bonding theories and mechanisms of reactions). Yet he realized that the philosophy of chemistry is important, and in his later years even worked on the kinetics and mechanisms of CO exchange reactions of metal carbonyls [3].

Hieber was largely responsible in my developing an interest in the kinetics and mechanisms of CO substitution reactions of metal carbonyls. In 1955 I listened to his plenary lecture at the International Conference on Coordination Chemistry in Amsterdam. His talk was in German, which I do not understand, but it was clear

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from his slides that a great deal of very elegant work on metal carbonyl chemistry had been done over the years in his laboratory. However, during the discussion, it appeared that questions of kinetics and mechanisms of reactions of metal carbonyls had not been addressed.

Keep in mind that in 1955, unlike at present, there was little interest in metal carbonyl chemistry. For example, all of our work at that time had to do with reactions of transition metal coordination compounds, now often called "Werner complexes". Organotransition metal chemistry, which now includes metal carbonyls, had not yet been so sanctified and I viewed metal carbonyls as just a special type of metal complex (a view I still hold of transition metal organometallic compounds, including Zeise's salt, ferrocene, etc.). Since we were engaged in research on the kinetics and mechanisms of reactions of metal complexes [4], it was only natural to want to extend this work to the related metal carbonyls.

Studies of metal complexes were largely limited to octahedral (Co^{III} complexes) and to square planar (Pt^{II} complexes) ligand substitution reactions, whilst the metal carbonyls were expected to also permit investigations of tetrahedral ($Ni(CO)_4$) and trigonal bipyramidal ($Fe(CO)_5$) substitutions and possibly to allow one to test the relative reactivities of bridging versus terminal ($Co_2(CO)_8$)CO substitutions. Clearly there was much that could be learned from such studies at a time when there was little interest in metal carbonyl chemistry. In this article I just give an overview of our early kinetic studies on CO substitution reactions of metal carbonyls, until about 1970 when we terminated this work for a decade to do research on synthetic oxygen carriers [5].

When I returned to Northwestern University, after the ICCC in Amsterdam, I was anxious to have some graduate students decide to work on the kinetics and mechanisms of CO exchange and/or substitution reactions of metal carbonyls. This seemed to me like an ideal Ph.D. dissertation problem because when I first discussed this with students no such work had been reported so the research was almost 100% certain to generate new fundamental information about these reactions suitable for a thesis and for important publications. Shortly before our first paper on the subject appeared, Keeley and Johnson [6] reported the half-lives of ^{14}CO exchange with some metal carbonyls, and Meriwether and Fine [7] reported on the kinetics and mechanism of phosphine replacement of $Ni(CO)_2(PR_3)_2$ with other phosphines.

In spite of the suitability of such a problem, some of the graduate students initially chose to work on some aspect of ongoing research in our laboratory with the aqueous solution chemistry of Werner complexes rather than the toxic, volatile metal carbonyls foreign to our research group. Finally an adventurous brave graduate student, Andrew Wojcicki, decided to study the kinetics and mechanisms of CO exchange of several metal carbonyls. He did such an outstanding job that soon there was no difficulty in interesting students and postdoctorates to select problems involving metal carbonyls.

$Ni(CO)_4$. Wojcicki [8] started his research on ^{14}CO exchange with the simplest members of first row transition series of binary metal carbonyls (note this was before the days of ^{13}C NMR). He found, as reported earlier [6,9] that the rates of exchange of $Cr(CO)_6$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ are extremely slow at room temperature, but at 0 °C $Ni(CO)_4$ and $Co_2(CO)_8$ exchange at rates convenient to permit a kinetic study (see Day [10] for our later correction of kinetic data on

$Ni(CO)_4$). In both cases the rate law was first order in carbonyl concentration, but zero order in CO concentration. For $Ni(CO)_4$ this came as somewhat of a surprise, because our experience with four-coordinate Pt^{II} complexes was that these undergo ligand substitution by an associative (S_N2) mechanism. Since coordination numbers greater than four are common place, we expected an associative replacement of CO in $Ni(CO)_4$ with expansion of coordination number but found a dissociation (S_N1) mechanism. Confronted with such a dilemma, we turned to the milestone review of Taube [11] which taught us the importance of the electron configuration of metal complexes (albeit in terms of valence bond theory) in considerations of ligand substitution reactions. This clearly pointed to the difference between a tetrahedral (sp^3) Ni^0 complex and a square planar (dsp^2) Pt^{II} complex, wherein the Pt^{II} complex has a low energy vacant p orbital suitable for nucleophilic attack. Since no such vacant orbital is available to Ni^0 complexes, it seems reasonable that reaction takes place by a dissociative process. In today's language of Tolman's [12] 16–18-electron rule, these observations would be discussed as represented in eq. 1 and 2.

$$\underset{\text{16-electron}}{\mathrm{Rh(CO)Cl(PPh_3)_2}} \xrightarrow[\text{slow}]{+{}^{14}\mathrm{CO}} \underset{\text{18-electron}}{\mathrm{Rh(CO)({}^{14}CO)Cl(PPh_3)_2}} \xrightarrow[-\mathrm{CO}]{\text{fast}} \underset{\text{16-electron}}{\mathrm{Rh({}^{14}CO)Cl(PPh_3)_2}} \qquad (1)$$

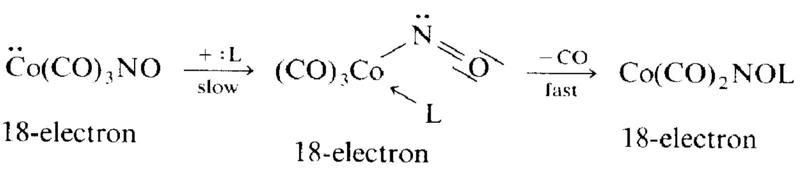
$$\underset{\text{18-electron}}{\mathrm{Ni(CO)_4}} \xrightarrow[\text{slow}]{-\mathrm{CO}} \underset{\text{16-electron}}{\mathrm{Ni(CO)_3}} \xrightarrow[\text{fast}]{+{}^{14}\mathrm{CO}} \underset{\text{18-electron}}{\mathrm{Ni(CO)_3({}^{14}CO)}} \qquad (2)$$

(These 16-electron Angoletta and Vallarino [13] compounds $M(CO)Cl(PPh_3)_2$ (M = Rh, Ir) are used here in order to comply with the present usage of organometallic complexes versus corresponding Pt^{II} amine complexes, which points to this arbitrary distinction made between similar coordination compounds.) The studies of Gray and Wojcicki [14], with an assist from Angelici, showed that all three of the ligands in this Rh system exchange rapidly presumably by an associative mechanism.

When Tolman was preparing his 16–18-electron paper he introduced himself to me at a Washington, D.C. National ACS Meeting and invited me to lunch, for which DuPont picked up the tab. He surprised me by having read all our papers, and being excited about how shuttling between 16–18-electrons explained why CO substitution of metal carbonyls takes place by either associative or dissociative mechanisms. I was less than impressed, because it sounded much the same as what we and others had been saying, except his language was different. Fortunately, he did not take my advice, and now we all know how useful his 16–18-electron rule is, particularly for beginning students to understand.

$Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$. A few years later Thorsteinson [15] examined the CO substitution of $Co(CO)_3NO$ and Morris [16] did the same for $Fe(CO)_2(NO)_2$. Both nitrosyls are isoelectronic and isostructural with $Ni(CO)_4$, the three compounds are as much alike as any three different compounds could possibly be. So again we were in for a complete surprise, when it was found that the nitrosyl compounds react by associative mechanisms. Why should NO in place of CO in such closely related systems make a marked difference in the mechanism of CO

substitution? Our explanation, put in today's 16–18-electron terms, is illustrated by eq. 3.

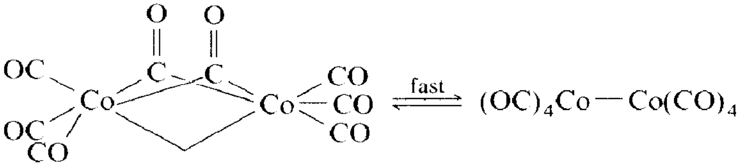


(3)

(−) (+)

The ground state, formally Co(CO)$_3$(NO), may form an active intermediate with an electron pair from cobalt localized on nitrogen to given an sp^2 bent nitrosyl and vacate a low energy orbital on cobalt to permit nucleophilic attack, e.g. maintaining throughout the reaction pathway 18-electrons at the metal. Three years later [17], the X-ray structure was reported of a stable bent metal nitrosyl.

$Co_2(CO)_8$. Returning to our story [8] about ^{14}CO exchange with Co$_2$(CO)$_8$, we were naive enough then to spend considerable time trying to detect a difference in reactivity between the six thermal COs and the two bridging COs. However, the results shows that all eight of the COs exchanged at the same rate. The futility of our study was recognized two years later when it was reported [18] that in solution Co$_2$(CO)$_8$ rapidly equilibrates (eq. 4):



(4)

The fluxional nature of organometallic compounds has now been long recognized [19].

$Fe(CO)_5$. The CO substitution inertness of Fe(CO)$_5$ is well known [6,20], and because its reactions are so extremely slow it has yet to be subjected to a detailed kinetic study. This slow reaction may result from the fact that the transition state/active intermediate for reaction, Fe(CO)$_4$, is high-spin [21] and this electron spin change from low-spin Fe(CO)$_5$ corresponds to a spin forbidden process [22]. In spite of this, Brault and Poë [23] observed that a 1,2-dichloroethane solution of Fe(CO)$_5$ with added CF$_3$COOH readily exchanges with ^{14}CO. The rate of exchange is dependent on concentrations of carbonyl and of acid, but not on the concentration of CO. This suggests a mechanism involving a rapid pre-equilibrium (eq. 5), followed by a rate determining dissociation (eq. 6).

$$\mathrm{Fe(CO)_5 + H^+ \xrightleftharpoons{\text{fast}} [HFe(CO)_5]^+} \qquad (5)$$

$$\mathrm{[HFe(CO)_5]^+ \xrightarrow[\text{slow}]{-CO} [HFe(CO)_4]^+ \xrightarrow[\text{fast}]{+^{14}CO} [HFe(CO)_4(^{14}CO)]^+} \qquad (6)$$

The attempt to activate Fe(CO)$_5$ was made based on a report [24] that several organometallic compounds in strong acids form metal–proton bonds, and protonated metal carbonyls may have ν(CO) values as much as 140 cm^{-1} higher than the parent carbonyl. This suggests the M–CO bond strength is weakened in the protonated species, in accord with the dramatic labilization found for $Fe(CO)_5$ in strong acid solutions.

$Mn(CO)_5X$ ($X = Cl, Br, I$). An early observation of the now often found correlation between the rates of CO substitution and the C–O stretching frequencies of metal carbonyls was reported for reactions of $Mn(CO)_5X$ ($X = Cl, Br, I$) by Angelici [25]. The reactions of $Mn(CO)_5X$ with a variety of ligands to form $Mn(CO)_4LX$ are first-order in substrate but zero-order in nucleophile concentrations, suggesting a dissociative mechanism. The rates of reaction decrease in the order $Cl(178) > Br(19) > I(1)$ (relative rates in parentheses), and the highest frequency IR bands of CO decrease in the order $Cl(2070) > Br(2064) > I(2056)$ (values of $\nu(CO)$ cm^{-1} in parentheses). Since iodine is the least electronegative and most polarizable of the halogens, it leaves more electron density on Mn which then has the greatest tendency to donate electrons to the π-acid CO and makes the strongest Mn–CO bond of the three carbonyl halides. This nicely accounts for $Mn(CO)_5I$ being the slowest to undergo CO substitution.

Since both ground state and transition state stabilities are important factors in rates of chemical reaction, it is perhaps not surprising that the rates of CO substitution of $Mn(CO)_5X$ were later discussed in terms of *cis*-labilization of X [26a]. Our earlier explanation of the relative rates of reaction of $Mn(CO)_5X$, considered only the relative ground state stabilities. The *cis*-labilization concept suggests that ligand X in the basal plane of a square pyramidal transition state ($Mn(CO)_4X$) lowers its energy, and enhances the rate of reaction.

The research of Wawersik [27] on CO substitution of $Mn_2(CO)_{10}$ should perhaps also be mentioned here. He observed a first-order rate law, and CO retardation of the rate, so he proposed a simple Mn–CO dissociative mechanism. This was later challenged, suggesting a pathway involving homolytic cleavage of the Mn–Mn bond as the rate determining step. This mechanism was proven incorrect by showing that no metal–metal crossover takes place during CO substitution [26b].

Migratory insertion reaction. The early important discoveries [27] of insertion reactions in organometallic complexes was soon followed by the elegant experiment [28] showing that the labeled CO added to convert $CH_3Mn(CO)_5$ into $(CH_3CO)Mn(CO)_5$ is not the acetyl CO but one of the other five terminal COs. The term insertion reaction, while describing accurately the overall result, may be mechanistically misleading. Mawby [29] designed an experiment to test if the reaction is mechanistically insertion or methyl migration. This was done by decarbonylating *trans*-$(CH_3CO)Mn(CO)_4PPh_3$ and determining the isomeric structure of the $CH_3Mn(CO)_4PPh_3$ product. The product was the *cis* isomer which, applying the law of microscopic reversibility, requires the reverse process to proceed by methyl migration and not CO insertion that would have given the *trans* isomer. Unfortunately it was later shown [30] that although the conclusion reached was correct, the experiment was flawed because at the conditions used the starting *trans*-acetyl isomerizes to the *cis*-acetyl prior to decarbonylation. Now it is agreed these reactions are best described as migratory insertion reactions.

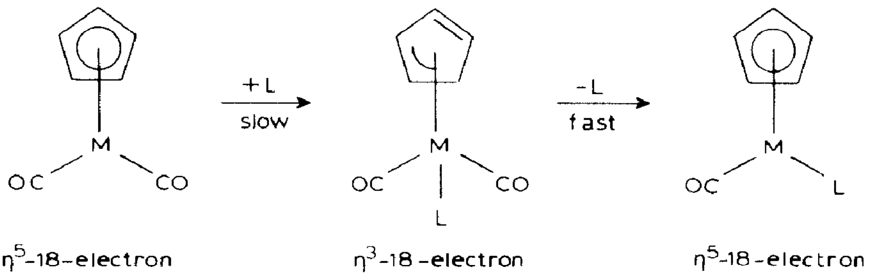
Mawby [31] and Butler [32] investigated the reactions of $CH_3Mn(CO)_5$, $(\eta^5$-$C_5H_5)Fe(CO)_2CH_3$, and $(\eta^5$-$C_5H_5)Mo(CO)_3CH_3$ with a variety of ligands to form the corresponding metal acetyl compounds. In all cases, the rates of reaction were found to depend on ligand concentration but a limiting rate was reached at higher ligand concentrations. The results were explained on the basis of a solvent and/or nucleophile assisted mechanism (eq. 7):

$$\begin{tikzcd} & (CH_3CO)Mn(CO)_4(\text{solvent}) \arrow[dd, shift left, "\text{fast}\\+\text{L}"] \\ CH_3Mn(CO)_5 \arrow[ur, "+\text{ solvent}\\\text{slow}"] \arrow[dr, "+\text{ L, slow}"'] & \\ & (CH_3CO)Mn(CO)_4L \arrow[uu, shift left] \end{tikzcd} \tag{7}$$

Migratory CO insertion into transition metal alkyl bonds is one of the most fundamental and extensively studied reactions in organometallic chemistry and homogeneous catalysis [33]. Yet one of the more recent publications [34] on the mechanism of this reaction largely resembles that reported earlier (eq. 7).

$\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ ring slippage mechanism. In the mid-sixties Professor E.O. Fischer and I has support for the collaborative exchange of predoctoral students in their final year of thesis research. Fischer's laboratory was very experienced in the syntheses and reactions of transition metal organometallic compounds, whilst our laboratory was engaged in studies of their kinetics and mechanisms of reactions. This was an ideal collaboration, beneficial to our students and to our research, but it terminated after a few years when funding for the project stopped.

Schuster-Woldan arrived in our laboratory having just prepared for the first time the compounds (η^5-C_5H_5)M(CO)$_2$(M = Co, Rh, Ir) and some of their phosphine derivatives. Viewing a cyclopentadienyl ligand as three CO ligands, I looked upon these compounds as being pseudoisoelectronic with Fe(CO)$_5$. Since we knew Fe(CO)$_5$ is extremely slow to react, I was not prepared to learn that the compounds (η^5-C_5H_5)M(CO)$_2$ readily react with phosphines and phosphites to give (η^5-C_5H_5)M(CO)L. Schuster-Woldan [35] investigated the kinetics of these CO substitution reactions, and he obtained a second-order rate law with activation parameters consistent with an associative mechanism. The challenge was how could this happen, since all low energy metal orbitals in these compounds are filled with pairs of electrons? Fortunately, this observation was made just at the time when we had explained the unique behavior of an NO ligand [15] which can localize a pair of electrons on N to vacate a metal orbital for nucleophilic attack. An analogous explanation was given of localizing a pair of electrons on the cyclopentadienyl ring in order to permit nucleophilic attack on the metal. Our suggestion of an η^4-diene with carbanion structure for the ring was wrong, but our concept of localizing a pair of electrons on the ring was and is correct. Later the correct η^3-allyne-ene structure for the ring was proposed [36], and soon afterwards the first X-ray structure was reported [37] of (η^3-C_5H_5)M bonding. In modern terms, we now describe the associative CO substitution, as an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ mechanism (eq. 8).



(8)

This ring slippage mechanism is now well known [38] to be an important fundamental aspect of transition metal organometallic chemistry.

Substitution lability of 2nd-row transition metal organometallic complexes. One other most important observation made by Schuster-Woldan [35] was that the rates of CO substitution of the (η^5-C_5H_5)M(CO)$_2$ (M = Co, Rh, Ir) compounds vary in the order Co < Rh > Ir. This was not expected because we had studied the rates of Cl substitution of $[M(NH_3)_5Cl]^{2+}$ (M = Co, Rh, Ir) and found the usual monotonic decrease in rates [4] for the triad of Co > Rh > Ir. It was also reported [9,39] that the rates of CO exchange for $M(CO)_6$ (M = Cr, Mo, W) vary in the order Cr < Mo > W. A little later Meier [40] found that $M[P(OC_2H_5)_3]_4$ (M = Ni, Pd, Pt) react with relative rates of Ni < Pd > Pt (sorry these are not organometallic complexes, as they do not have a M–C bond). Thus it began to appear early on that for low valent metal complexes, where back π bonding is important, the 2nd row metal of a given transition metal triad is the most substitution labile. Now it is well known [41] that in homogeneous catalysis, where ligand substitution lability is a must, most commercial catalysists are 2nd row transition metal catalysts. An early attempt [40] to account for the lability of 2nd row metal complexes suggested stabilization of the M–L bond for the 1st row metal by predominately π back bonding and for the 3rd row by largely σ bonding, thus leaving the 2nd row as the most labile (this was during the days when Professor R.W. Parry said "ashes to ashes, dust to dust if σ bonding can't do it, then π bonding must."). A similar explanation [42] was given in terms of the low electronegativity of 1st row metals as one factor, and a good matching of the orbital energies of 3rd row metals with the ligand as another factor. The latest word [43] on this, to my knowledge, is the detailed molecular orbital calculations based on density functional theory to estimate the first CO ligand dissociation energy ΔH of $M(CO)_n$ for the three binary metal carbonyl triads $M(CO)_6$ (M = Cr, Mo, W), $M(CO)_5$ (M = Fe, Ru, Os), and $M(CO)_4$ (M = Ni, Pd, Pt). For each triad of transition metals, the calculated ordering of the M–CO bond strengths (including relativistic effects) is $3d > 5d > 4d$. This makes us experimental metal carbonyl chemists happy, because it is what we have known for many years.

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