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Associative Substitution Reactions of Metal Carbonyls

FRED BASOLO

Department of Chemistry, Northwestern University, Evanston, Ill. 60201, U.S.A.

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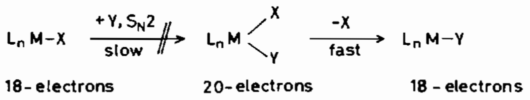
I thank Professor Croatto for kindly inviting me to contribute an article for this special issue commemorating the 100th volume of *Inorganica Chimica Acta*. This journal is of particular interest to me because some of the seminal discussions on the need for such a journal took place in our laboratory the year (1963–64) Professor Belluco did postdoctoral research with us. I am also pleased to be asked to contribute because of my personal and professional ties with the Journal.

Catalysis

The chemistry of metal carbonyls and of other transition metal organometallic complexes largely relates to the magic word catalysis. This was not the case during the time of the pioneering work of Professor Hieber and his school on metal carbonyls. At that time there was little interest in these systems, but all of this has changed with the advent of the importance of metal carbonyls in catalysis [1].

The commercial importance of catalytic properties of transition metal organometallic complexes is firmly established by industrial processes such as the oxo process and the Wacker process, and by the production of *l*-dopa for the treatment of Parkinson's disease and of acetic acid from the reaction between methanol and carbon monoxide. In all such catalytic processes, the active reaction site is the metal. This means the reactants must have access to the metal, and there are two ways this can occur for metal complexes. One is by a dissociative (S_N1) metal–ligand bond cleavage to give a coordinatively unsaturated (CUS) metal complex. Much research has been directed at this problem of creating CUS metal complexes. Some success has been realized [2] by the use of various approaches such as the use of good leaving groups as ligands, the use of bulky ligands to promote dissociation, the use of reagents which react with an annihialate certain ligands, photochemical dissociation, and redox reactions to generate substitution labile metal complex radicals.

The other way by which reactants can get to the metal of a metal complex catalyst is by an associative (S_N2) ligand substitution reaction [3]. This approach of the use of S_N2 reactions for catalysis has not been widely studied. One reason is that transition metal organometallic complexes adhere to the magic electron count of 18-electrons and generally do not react by a 20-electron associative pathway (eqn. 1), but react by a dissociative 16-electron path (eqn. 2):



(1)

$$\underset{\text{18-electrons}}{L_nM-X} \xrightarrow[\text{slow}]{-X,\ S_N1} \underset{\text{16-electrons}}{L_nM} \xrightarrow[\text{fast}]{+Y} \underset{\text{18-electrons}}{L_nM-Y} \qquad (2)$$

In spite of the Tolman [4] 16-, 18-electron rule, we discovered [3] years ago that the presence of ligands such as NO, η^5-C_5H_5, and η^6-C_6H_6 can accommodate a pair of electrons to allow for an active 18-electron intermediate, and permit a low energy pathway for an S_N2 reaction. Recently we have returned to such studies and found other ligands which allow associative substitution reactions to take place, and we are also investigating the properties of such ligands which enhance the rates of substitution. Rapid rates of ligand substitution are essential in catalysis by metal complexes, and it is hoped that the results of our studies will be a useful guide in the preparation of desired catalysts. A summary of the studies in our laboratory on associative CO substitution reactions of metal carbonyls follows.

Nitrosyl Metal Carbonyls

Wojcicki [5] was the first graduate student at Northwestern University to study the kinetics and mechanisms of substitution reactions of metal carbonyls. He investigated CO exchange mostly with binary metal carbonyls, using radioactive ^{14}CO because this was before the days of ^{13}C NMR. Much to our surprise at the time, it was found that $Ni(CO)_4$

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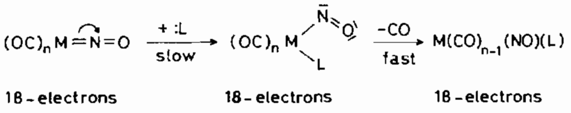
reacts by a dissociative (S_N1) mechanism. We explained this by noting that all the low energy metal orbitals of nickel are filled with electron pairs, thus retarding any nucleophilic attack on the metal. The 16-, 18-electron rule says the same thing, that is, the reaction pathway would avoid a 20-electron species (eqn. 1) and go via a 16-electron path (eqn. 2).

Later we studied the isoelectronic and isostructural nitrosyl metal carbonyls shown in Table I. Metal carbonyls and their corresponding nitrosyl metal carbons are more alike than any other series of analogous compounds. Naturally, we were surprised to find that the presence of one or more NO group in a metal carbonyl causes a change in mechanism of CO substitution from S_N1 for the binary metal carbonyl to S_N2 for the corresponding nitrosyl metal carbonyl. In search of an explanation, before the 16-, 18-electron rule and before the X-ray structure [8] of a bent metal nitrosyl, we suggested [9] a mechanism which localizes a pair of electrons on the nitrosyl group (eqn. 3):



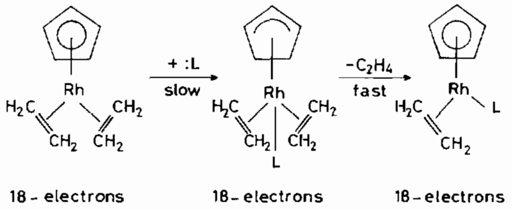
(3)

Using present day language, one sees that the 18-electron count is maintained in the higher coordinated intermediate by localizing a pair of electrons on the nitrosyl group to give a sp^2 bonded N with a bent structure. This is believed to happen to a much greater extent (see section on binary metal carbonyls) with NO than with CO, because of the formal positive charge on NO and because N is more electronegative than is C.

When we were investigating the reactions of nitrosyl metal carbonyls, it was decided to study $V(CO)_5(NO)$. One reason for wanting to do this was that the other nitrosyl metal carbonyls studied were 4- or 5-coordinate, and we wondered if a 6-coordinate system would also undergo associative substitution. Recall [10] that 6-coordinate Werner complexes had been shown to undergo ligand substitution by predominantly bond breaking dissociation processes. The study of $V(CO)_5(NO)$ had to wait some twenty years making it the longest gestation period for any study in our laboratory: finally $V(CO)_5(NO)$ was investigated [7], and the results obtained compared with its corresponding $Cr(CO)_6$ showed no surprises. The nitrosyl compound reacts by an associative S_N2 pathway, except for its reactions with weak nucleophiles such as $P(C_6H_5)_3$ and $N(C_2H_5)_3$. However, even the first-order dissociative path is fast, k (0 °C) = 5×10^{-4} sec^{-1}. This high rate of dissociation is attributed to the large trans labilizing effect of NO. One other point to note is that $V(CO)_4(NO)[P(n\text{-}Bu)_3]$ reacts with $P(n\text{-}Bu)_3$ to form $V(CO)_3(NO)[P(n\text{-}Bu)_3]_2$ entirely by an S_N1 mechanism. This may be caused largely by steric retardation of an associative pathway.

Cyclopentadienyl Metal Carbonyls

Twenty years ago, Schuster-Woldan [11] studied the CO substitution reactions of $(\eta^5\text{-}C_5H_5)M(CO)_2$, where M = Co, Rh, and Ir. He found the reactions readily take place by an associative mechanism, and the rates vary in the order Co < Rh > Ir. This contrasts markedly with corresponding reactions of the pseudo-isoelectronic $Fe(CO)_5$, which are extremely slow and which involve a dissociation mechanism [12]. We explained the difference in reactivity and mechanism in a manner similar to the nitrosyl metal carbonyls *vs.* binary metal carbonyls, by localizing a pair of electrons on the cyclopentadienyl ring in order to permit a low energy nucleophilic attack on the electron-vacated metal orbital. Making use of our concept, but changing our language, Cramer and Seiwell [13] discussed the S_N2 replacement of ethylene from $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$ via an η^3 'slipped' cyclopentadienyl ligand (eqn. 4):



(4)

TABLE I. Mechanisms of CO Substitution of Metal Carbonyls [3].

$Cr(CO)_6$	$(S_N1)^a$	$Fe(CO)_5$	(S_N1)	$Ni(CO)_4$	(S_N1)
$V(CO)_5(NO)$	$(S_N2)^b$	$Mn(CO)_4(NO)$	(S_N2)	$Co(CO)_3(NO)$	(S_N2)
				$Fe(CO_2(NO)_2$	(S_N2)

[a] For high concentrations of good nucleophiles there is also a S_N2 path [6] See section on binary metal carbonyls. [b] For poor nucleophiles there is also a S_N1 path [7].

We have recently investigated [14] the effect of substituents on the cyclopentadienyl group on the rates of reaction of $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ (eqn. 5):

$$(\eta^5\text{-}C_5H_4X)Rh(CO)_2 + PPh_3 \longrightarrow (\eta^5\text{-}C_5H_4X)Rh(CO)(PPh_3) + CO \qquad (5)$$

X = H, NO_2 and PR_3^+; also used pentamethylcyclopentadienyl, indenyl and heptamethylindenyl

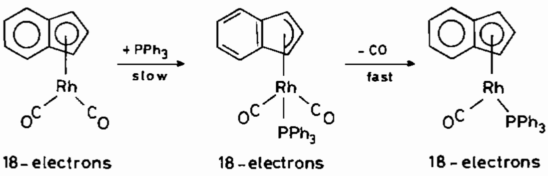
The relative rates of reaction and the CO stretching frequencies are given in Table II.

TABLE II. Relative Rates of CO Substitution of Some Dicarbonylrhodium Compounds and Their Carbonyl Stretching Frequencies.

Compound	$k_{rel.}$	ν_{CO} (cm^{-1})
$Rh(\eta^5\text{-}C_9H_7)(CO)_2$	2.8×10^8	2048, 1993
$Rh(\eta^5\text{-}C_9(CH_3)_7(CO)_2$	6.1×10^5	2021, 1965
$Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$	1.2×10^4	2067, 2011
$[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2^+$	1.1×10^2	2062, 2002
$Rh(\eta^5\text{-}C_5H_5)(CO)_2$	1	2051, 1985
$Rh(\eta^5\text{-}C_5(CH_3)_5)(CO)_2$	2.2×10^{-2}	2020, 1967

If our original suggestion is valid, then it follows that electron-withdrawing substituents (NO_2 and PR_3^+) on the cyclopentadienyl group should speed up the reaction and electron-donating groups (CH_3) should slow down the reaction. The relative rate constants in Table II show this is what was observed. Furthermore, the ν_{CO} values increase for electron-withdrawing groups and decrease for electron-donating groups in a manner expected. The Rh–C bond strengths are believed to inversely correlate changes in ν_{CO} and also inversely correlate the rates of reaction, as is observed. Note that a decrease in the rate of the pentamethylcyclopentadienyl compound may also be in part due to steric retardation.

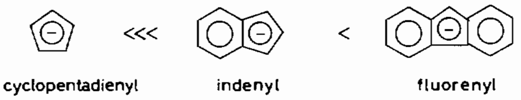
Perhaps the most interesting result is that a fused benzene on cyclopentadienyl has no effect on the values of ν_{CO}, yet it increases the rate of reaction by a factor of 10^8. This is a huge effect, and we have designated it the *indenyl ligand effect* [15]. Others [16] have previously reported the rate enhancement of indenyl over cyclopentadienyl for these reactions; they explained this on the basis of a driving force towards complete aromatization of benzene in the transition state for a mechanism involving $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ bonding of the cyclopentadienyl group (eqn. 6):



(6)

That the rate enhancement is mostly a transition state effect, and not ground state, is in accord with the observation that the ν_{CO} values for the indenyl and cyclopentadienyl compounds are about the same.

The indenyl ligand effect of rate enhancement was successfully applied on some η^5-cyclopentadienyl derivatives of the moiety $Mn(CO)_3$. It was known [17] that $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ does not undergo CO substitution even after three days at 130 °C, so it was decided to attempt the reactions of corresponding indenyl and fluorenyl manganese carbonyls. We were gratified to find [15] that the indenyl and fluorenyl groups do labilize the manganese system, and our studies show that the rates of CO substitution increase with changes in ligand in the order



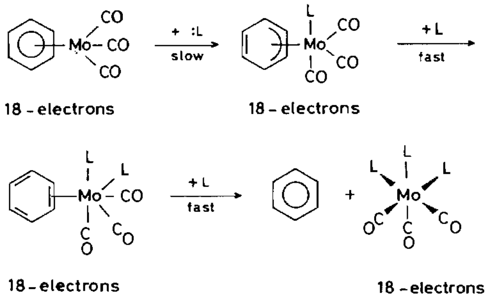
Research now in progress on corresponding N-heterocycles such as pyrrole and indole show [18a] these groups further enhance rates of CO substitution. This is the result anticipated, based on the view that electron withdrawal from the metal towards the ligand is involved in the reaction process. Since N is more electronegative than is C, it follows that replacing C with N in any carbocycle ligand would result in its having a greater attraction for electrons and would be expected to promote associative substitution reactions of the type being discussed. Finally it has been reported [18b] that the 'open cyclopentadienyl' system $(\eta^5\text{-pentadienyl})Mn(CO)_3$ also reacts by an associative $\eta^5 \rightarrow \eta^3$ mechanism.

Arene Metal Carbonyls

Substitution reactions of $(arene)Mo(CO)_3$ (eqn. 7)

$$(arene)Mo(CO)_3 + 3L \longrightarrow Mo(CO)_3L_3 + arene \qquad (7)$$

were found to be first-order in substrate and first-order in nucleophile [19]. The mechanism suggested was similar to that just discussed for associative reactions of cyclopentadienyl metal carbonyls. The mechanism suggested could be represented in terms of step-wise associative reactions with conversions of $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2 \rightarrow \eta^0$, as shown in eqn. 8:

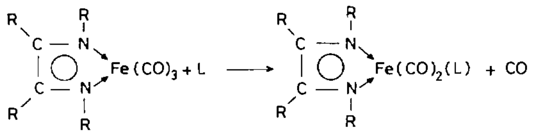


(8)

The rates of reaction decrease in the order toluene ≃ p-xylene > mesitylene for changes in arene, and the values of ν_{CO} also decrease in this order. Such results are expected because methyl substituents on arene increase its electron density, but also one must not overlook the possible steric retardation of the reaction. This system is finally being investigated [20] in considerable detail, and it appears the mechanism proposed (eqn. 8) will have to be modified.

1,4-Diaza (and -Tetraaza)butadiene Metal Complexes

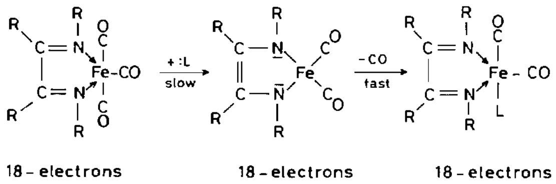
Diazabutadiene (DAB) and tetraazabutadiene (TAB) iron tricarbonyls readily react with phosphine and phosphite ligands [21] (eqn. 9):



(9)

The TAB chelate ligand differs from DAB in that the CR groups are replaced by N. All of these compounds are pseudo-isoelectronic with $Fe(CO)_5$, which is extremely slow to undergo CO substitution, and which does so by a S_N1 process [12].

Again these DAB and TAB ligands are capable of accommodating a pair of electrons, allowing for an associative pathway with nucleophilic attack on the metal (eqn. 10).



(10)

That electron drain towards the chelate ring is important for reaction is supported by the observation that the TAB system reacts 10^5 times faster than does the corresponding DAB system. This is because TAB has four nitrogens in its chelate ring, making it more electron-withdrawing due to the more electronegative nitrogens relative to the two carbons in the DAB chelate ring.

Metal Carbonyl Radicals

The substitution lability of 17-electron organometallic radicals has long been recognized [22], but the mechanisms involved were ill-defined and the rate difference between 17- and 18-electron systems had not been quantified. For example, CO substitution of $Mn(CO)_5$ appears to proceed by a dissociative process [22b], whereas $Re(CO)_5$ reacts by an associative process [22c]. Phosphine substituted $Mn(CO)_5$ also exhibits associative behavior [22d]. All these radicals were prepared as transient species, and their kinetics and mechanisms of reaction were studied *in situ*. For these reasons, and others, we decided to investigate the only known stable solid 17-electron binary metal carbonyl, $V(CO)_6$.

Substitution reactions of $V(CO)_6$ were found [23] to proceed *entirely* by a second-order rate law, first-order in carbonyl and first-order in nucleophile; with even the weak nucleophile $AsPh_3$. This suggests a totally associative pathway (eqn. 11).

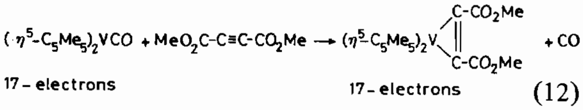
$$V(CO)_6 \xrightarrow[\text{slow}]{+:L} V(CO)_6(L) \xrightarrow[\text{fast}]{-CO} V(CO)_5(L) + CO \qquad (11)$$

17-electrons 19-electrons 17-electrons

It is most unusal for a 6-coordinate complex to react so readily by a 7-coordinate pathway, because most octahedral complexes react predominantly by a bond-breaking or dissociative process [10]. It is important to note that the reaction of the 17-electron $V(CO)_6$ with $P(n\text{-}Bu)_3$ is about *10^{10} times faster* than is the same associative reaction for the corresponding 18-electron $Cr(CO)_6$. This large difference in rate is in accord with the earlier observations [22] that metal carbonyl radicals are substitution-labile.

Why these species have such extreme lability remains a mystery. Surely it is easier for a nucleophile to attack a 17-electron than an 18-electron metal center, but *ten* orders of magnitude better? Thirty-five years ago in his classical review on ligand substitution reactions of Werner metal complexes, Taube [24] called attention to the fact that high-spin octahedral complexes are substitution labile and low-spin complexes are substitution inert. This focused attention for the first time on the importance of electronic structures relative to rates of substitution reactions. However, this does not account for the substitution lability of metal carbonyl radicals, all of which are low-spin. Apparently the hole in the bonding d^5t_{2g} orbital set permits facile nucleophilic attack compared with electronically saturated d^6 (18-electron) organometallic systems. The transition state for reaction is perhaps reached at a relatively long vanadium–nucleophile distance. A two-center three-electron bond is probably crucial for stabilizing the 19-electron transition state or intermediate.

Whatever the reason for such extreme reactivity of organometallic radicals, clearly this is of importance in homogeneous catalysis and in syntheses generally. Advantage is being taken of this by generating reactive radical anions or cations, using appropriate electrochemical [25] or chemical redox reactions [2]. Finally, it has recently been shown [26] that the 17-electron $(\eta^5\text{-}C_5Me_5)_2VCO$ also reacts by a second-order process (eqn. 12):

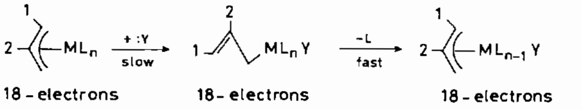


(12)

However, this is not a ligand substitution reaction, but an oxidative addition reaction with V(II) going to V(IV).

π-Allyl Metal Carbonyls

An η^3-allyl ligand in electron count is analogous to NO, with both ligands contributing 3-electrons to the metal of a metal complex. Similar to NO, an η^3-allyl group can localize a pair of electrons on itself by going to an η^1-allyl. This process then can provide an associative pathway for ligand substitution of an $(\eta^3\text{-}C_3H_5)ML_n$ compound (eqn. 13):



(13)

This type of mechanism seems to be involved [27] in CO substitution reactions of $(\eta^3\text{-}C_3H_4X)Fe(CO)_2(NO)$ and of $(\eta^3\text{-}C_3H_5)Fe(CO)_3(X)$.

Muetterties and co-workers [28] observed that $(\eta^3\text{-}C_3H_5)Co(PR_3)_3$ and $(\eta^3\text{-}C_3H_5)Mn(CO)_2(PR_3)_2$ act as catalysts for hydrogenation of alkenes and arenes. They originally proposed that catalysis involved an $\eta^3 \rightarrow \eta^1$-allyl conversion in order to open up a coordination site on the metal. Their subsequent experiments showed the allyl group to be hydrogenated to propane, which does not coordinate to the metal, leaving a coordinatively unsaturated metal complex which functions as the catalyst.

In spite of the availability of an associative pathway (eqn. 13), it has been found that CO substitution of $(\eta^3\text{-}C_3H_4X)Co(CO)_3$ [29] and of $(\eta^3\text{-}C_3H_4X)Mn(CO)_4$ [30] proceed by a dissociation (S_N1) mechanism. Of interest is our observation that substituents in the 1-position of the allyl (see eqn. 13) cause a slight retardation in rate, whereas bulky groups in the 2-position markedly enhance the rate of substitution. This steric rate enhancement is in accord with the structure of the manganese compound, wherein the substituent in the 2-position eclipses one of the CO ligands. This CO ligand is believed to be the one labilized by bulky groups in the 2-position.

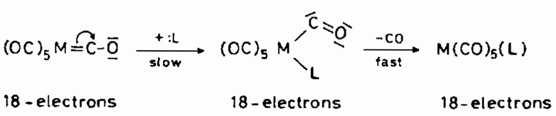
Binary Monometal Metal Carbonyls

The term monometal is used here in order to restrict our discussion to $M(CO)_n$ compounds, and not include metal carbonyl clusters. From our discussion above it is implicit that such 18-electron binary metal carbonyls generally react by a dissociation (S_N1) process, and that particular ligands (or radical compounds) which can accept a pair of electrons from the metal are required to permit an associative S_N2 mechanism.

Experimental facts in need of re-evaluation can be discussed using as an example CO substitution reactions of the metal carbonyls $M(CO)_6$, where M = Cr, Mo, and W. These compounds were found [31] to react by a two-term rate law (eqn. 14).

$$\text{Rate} = k_1[M(CO)_6] + k_2[M(CO)_6][L] \qquad (14)$$

The k_1 path corresponds to reaction by a S_N1 mechanism, whereas the k_2 path involves a S_N2 mechanism. The data show that appreciable contribution of the S_N2 pathway is made only by high concentrations of the best nucleophile used ($P(n\text{-}Bu)_3$). Also the activation parameters for S_N2 reactions with $P(n\text{-}Bu)_3$ are $\Delta H_2^{\ddagger}$ (kcal/mol) = 26(Cr), 22(Mo), 29(W) and $\Delta S_2^{\ddagger}$(e.u.) = −15(Cr), −15(Mo), −7(W). These values compare with the usual values [10] for S_N2 reactions of $\Delta H^{\ddagger} < 20$ kcal/mol and $\Delta S^{\ddagger} < -15$ e.u., suggesting that for S_N2 reactions of $M(CO)_6$ there is perhaps more bond-breaking than bond-making in the transition state. However, it does appear that this process may take place without evoking a 20-electron transition state or intermediate (eqn. 15):

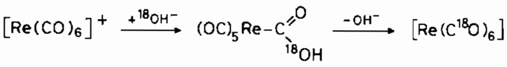


(15)

The bent sp^2 hybrid carbanion here corresponds to the bent nitrosyl (eqn. 3) proposed for facile associative reactions of nitrosyl metal carbonyls. As discussed previously, CO has a much lesser tendency to do this than does NO, which agrees with the fact that only good nucleophiles at high concentration cause this to happen in binary metal carbonyls.

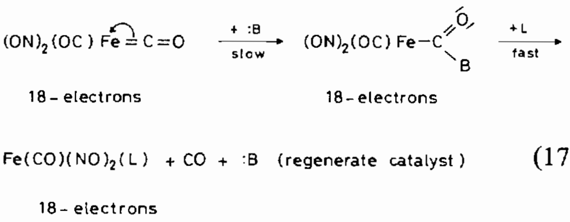
Nucleophilic Attack on Carbon of Metal Carbonyls

Nucleophilic attack at carbon in metal carbonyls has been observed in various ways. One of the earliest examples is that of Muetterties [32] showing there is oxygen exchange between the solvent water and $[Re(CO)_6]^+$ in basic solution (eqn. 16).



$$[Re(CO)_6]^+ \xrightarrow{+^{18}OH^-} (OC)_5Re{-}C(=O)(^{18}OH) \xrightarrow{-OH^-} [Re(C^{18}O)_6]^+ \qquad (16)$$

Our studies [33] of the CO substitution reactions of $Fe(CO)_2(NO)_2$ show that the reactions are catalyzed by bases in a pathway which is second-order, first-order in substrate and first-order in catalyst. Since effectiveness of the base decreases in the order $N_3^- > Cl^- > Br^- > I^-$, it is believed that the catalyst functions by attack on the carbonyl carbon (hard) and not on the metal (soft). The mechanism proposed for this catalysis pathway is shown by eqn. 17:



$$(ON)_2(OC)Fe{=}C{=}O \xrightarrow[\text{slow}]{+\ :B} (ON)_2(OC)Fe{-}C(=O)(B) \xrightarrow[\text{fast}]{+L}$$

18-electrons 18-electrons

$$Fe(CO)(NO)_2(L) + CO + :B \text{ (regenerate catalyst)} \qquad (17)$$

18-electrons

The mechanism of the final fast step is not known.

Conclusions

Not withstanding the 16-, 18-electron rule [4], for ligand substitution reactions of transition metal organometallic complexes the following rule applies: *Substitution reactions of 18-electron metal complexes may proceed by an associative mechanism, provided the metal complex can delocalize a pair of electrons onto one of its ligands and make available a vacant low energy orbital on the metal to permit nucleophilic attack on the metal.* Furthermore, we see that the rates decrease by a factor of 10^{10} for CO substitution from (η^5-carbocycles)-$Rh(CO)_2$ in the order indenyl > heptamethylindenyl > nitrocyclopentadienyl > triphenylphosphonium cyclopentadienyl > cyclopentadienyl > pentamethylcyclopentadienyl. These results show that it is possible to greatly modify the reactivity of such compounds by making appropriate, albeit modest, changes in the ligands present. Advantage can and should be taken of such studies to design more efficient catalysts and to assist in the syntheses of organometallic compounds. The same can be said for the observation that ligand substitution reactions of 17-electron metal complexes react about 10^{10} times faster than do the corresponding 18-electron compounds. These are huge differences in rate which have to be important in studies of reactions of organometallic compounds.

Acknowledgements

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