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Ligand and metal effects on the reactivity of metal carbonyls

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Abstract

The reactivity of metal carbonyl complexes is surveyed. The effect of charge, electron count, row and electronic configuration of the metal are examined for mononuclear carbonyls and more limited information is examined for metal clusters. Ligand effects are also examined for the metal carbonyls. The reactivity of metal carbonyl complexes changes by at least 15 orders of magnitude. This paper provides a framework for understanding such a range of reactivity.

Most of the early work on metal carbonyl complexes focused on the physical properties of this very unusual class of compounds [1]. As the physical properties were defined, interest began to shift to the reactivity. Mechanistic studies began with Basolo and coworkers in the early 1960's [2,3]. Now sufficient data have been collected to note trends in the reactivity of metal carbonyl complexes. The primary focus of this manuscript will be on the substitutional reactivity of binary carbonyl complexes, although in several cases complexes with other ligands will be used. In each case the reactions discussed will be replacement of a carbon monoxide by another ligand.

Substitution of carbon monoxide by another ligand may take place through a dissociative path or an associative path [4].

$$\mathrm{M(CO)}_x \xrightarrow{-\mathrm{CO}} \mathrm{M(CO)}_{x-1} \xrightarrow{+\mathrm{L}} \mathrm{M(CO)}_{x-1}\mathrm{L} \tag{1}$$

$$\mathrm{M(CO)}_x \xrightarrow{+\mathrm{L}} \mathrm{M(CO)}_x\mathrm{L} \xrightarrow{-\mathrm{CO}} \mathrm{M(CO)}_{x-1}\mathrm{L} \tag{2}$$

In addition there is some evidence for interchange mechanisms [4]. Associative mechanisms are commonly observed when a ligand is present that can change its bonding mode with a concomitant two electron decrease in its contribution to the metal or by nucleophilic attack on the carbon of a carbonyl, releasing CO_2. Associative reactions of binary carbonyl complexes are not commonly observed. Dissociation of CO from metal carbonyl complexes occurs at rates from 10^5 s^{-1} to

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10^{-10} s^{-1} [4]. In this manuscript I will try to lay a foundation for the myriad of complexes that undergo CO dissociation, to allow a partial understanding of these diverse rates and to give a basis for predictions.

Reactivity may be affected by either ground state or transition state properties. The usual procedure is to ascribe any reactivity that does not correlate with ground state properties to transition state differences. For examples where sufficient data are available I will comment on the source of reactivity differences.

Metal effects on metal carbonyl reactivity

The effect of metal center on organometallic reactivity has not been clearly defined. In this manuscript we will examine: (1) the effect of charge, (2) the effect of electron count, (3) first row, second row and third row effects, (4) the effect of *d*-electron count and (5) the effect of metal changes within a cluster. There now exist data that indicate each of these may be important in metal carbonyl reactivity.

Effect of charge. The effect of charge on metal–carbon monoxide bonding has been frequently examined with the extent of π-acceptance greater as the charge is lowered. The effect of charge on reactivity is not as clear. $V(CO)_6^-$, $Cr(CO)_6$ and $Mn(CO)_6^+$ are relatively inert to CO dissociation [5]. Similarly $Mn(CO)_5^-$ and $Fe(CO)_5$ are relatively inert, though the fact that $Co(CO)_5^+$ is unknown may indicate that it would have considerable reactivity. The best indication of the expected effect of charge on reactivity is in the greater reactivity of $Ni(CO)_4$ than $Co(CO)_4^-$ (ready substitution [6] versus no reaction in 48 h [7]).

I find it surprising that the effect of charge is not more general. One could argue that the greater reactivity of metal carbonyl halides ($Mn(CO)_5X$ for instance) is evidence for charge, but the inertness of $Mn(CO)_6^+$ suggests that a ligand effect, not charge on the metal is responsible for the reactivity of the metal carbonyl halides.

The failure (in many cases) to see the expected large increase in rate of CO loss with increase in charge must indicate that the destabilization of the ground state is negated by a similar destabilization of the transition state. This suggests that the effect of charge on the bonding of CO in the 16 electron transition state for CO dissociation is similar to that for the 18 electron ground state.

For associative reactions that proceed by nucleophilic attack on the carbon of a carbonyl, the effect of charge is clear. The more highly charged is much more susceptible to attack.

Electron count. One of the most startling effects on metal carbonyl reactivity lies in the enhanced reactivity for seventeen electron complexes [8,9]. Table 1 shows some examples of the relative reactivity of 17- and 18-electron complexes. The reactivity of 17-electron complexes has been a very active area of research in recent years [8–18]. An explanation of this reactivity by formation of two-center, three-

Table 1

Relative reactivity of seventeen and eighteen electron complexes

Formula	17-electron ($k_2 M^{-1}$ s^{-1})	18-electron (s^{-1})
$M(CO)_6$	M = V [10], 2.5×10^{-1}	M = Cr [11], 10^{-12}
$M(CO)_3L_2$	M = Mn, L = PBu_3 [12], 2.1×10^{-1}	M = Fe, L = PPh_3 [13], 5×10^{-11}

Table 2

Reactivity of the group 6 hexacarbonyls, $M(CO)_6$ [4]

$M(CO)_6$	k_{obs} (130 °C)
$Cr(CO)_6$	1.4×10^{-4} s^{-1}
$Mo(CO)_6$	2.0×10^{-3} s^{-1}
$W(CO)_6$	4.0×10^{-6} s^{-1}

electron bonds has been offered [18]. The lack of reactivity of 17-electron complexes where the odd-electron orbital is shielded adds support to this hypothesis [18]. The loss of an electron opens an associative path for ligand substitution that often is ~ 10 orders of magnitude greater than that for the 18 electron complex.

Based on the failure to observe a 19-electron intermediate in the associative reactions of 17-electron species, one may assume that CO dissociation from 19-electron species is very rapid [8,9]. Thus addition of an electron to an 18 electron complex also enhances reactivity.

Row effects. In general the reactivity is greatest for the second row metal and least for the third row metal. Table 2 illustrates this trend for $M(CO)_6$ complexes [4]. This order is different than the order of reactivity observed for classical coordination complexes for which the reactivity decreases down a row for analogous complexes [19]. An explanation has been offered for the organometallic complexes in terms of increased π-bonding interactions for the first row-metal that provides extra stability for first row organometallic complexes [20]. The M–CO bond length for the $M(CO)_6$ species support this ground state interpretation although the differences in bond length are too small to be conclusive [21].

Electron configuration. The effect of *d*-electron configuration on metal carbonyl reactivity (the change of reactivity across a row) has not been examined to any significant extent. Our attention was directed to this area of research in our attempts to understand the relative inertness of mononuclear iron complexes [13]. The order of reactivity, $Ni(CO)_2L_2 > Cr(CO)_4L_2 > Fe(CO)_3L_2$ (L = CO, phosphine base), does not correlate with effective nuclear charge or steric considerations [13]. Further, M–L distance does not correlate with the reactivity toward dissociative loss of L [13], as shown in Table 3.

Metal carbonyls and derivatives. The metal carbonyl compounds offer the best comparative data on rates of reactions [5,10–12,22–24].

Complex	$Co(CO)_4$,	$Mn(CO)_5$ >	$V(CO)_6$ >	$Ni(CO)_4$,	$Ti(CO)_3(P{-}P)_2$ >	$Cr(CO)_6$ >	$Fe(CO)_5$
d-electrons	d^9	d^7	d^5	d^{10}	d^4	d^6	d^8

Table 3

The reactivity of $M(CO)_nL_2$ towards dissociative loss of L (at 30 °C) correlated with M–L bond distance [13]

M	*n*	k (s^{-1}) [a]	M–P (Å) [a]
Ni	2	5.6×10^{-4}	2.22
Fe	3	5.0×10^{-11}	2.24
Cr	4	3.1×10^{-6}	2.42

[a] $L = PPh_3$.

Possible ground state contributions to the reactivity of the binary carbonyls are difficult to assess. The M–CO distances which are known show no significant variation with electron configuration [21]. A sample series is $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ and $V(CO)_6$ with M–C distances of 1.84, 1.82, 1.909 and 1.995 Å, respectively [21,25]. When the differences in metal radii for this series are included, no differences in M–CO bond distance exist that can be attributed to *d*-electron configuration. Calculations also fail to indicate changes in M–CO bond strength with *d*-electron configuration [26–31]. Calculations on $Ni(CO)_4$, $Fe(CO)_5$ and $Cr(CO)_6$ reported from one study show less overlap population for Ni–CO than for Fe–CO and Cr(CO), with Fe–CO and Cr–CO almost equal [26]. Thermochemical data for these complexes which should also assess the ground state energies show the same trend, although the average bond energies would show a different trend [32]. Modified extended Hückel theory was used to calculate enthalpies of activation for the metal carbonyls considering ground state and transition state energies [27]. The values ($Ni(CO)_4$, 22.5 kcal/mol; $Fe(CO)_5$, 42.5 kcal/mol; $Cr(CO)_6$, 59 kcal/mol) do not agree with the observed experimental order [27]. The M–C stretching frequencies also do not correlate well with the observed reactivity order [26]. At the present time there are no experimental data that indicate that the observed correlations of reactivity with *d*-electron configuration for the metal carbonyl complexes (CO substitution reactions) arise predominantly from ground state effects.

Dissociation of other ligands from similar complexes has also been investigated. As indicated previously, our interest arose from consideration of L dissociation in $Ni(CO)_2L_2$, $Fe(CO)_3L_2$ and *trans*-$Cr(CO)_4L_2$ where L = phosphine, phosphite or arsine [13]. In these complexes there was no indication of ground state reasons for the reactivity and the conclusion was that transition state factors must be involved [13]. Although one would anticipate that steric interactions should be important, the per-phosphito complexes show an order of reactivity that is similar to $M(CO)_nL_2$ and $M(CO)_n$ complexes [20,33–36]. Thus $Fe(P(OMe)_3)_5$ does not undergo substitution reactions [35], while $Ni(P(OEt)_3)_4$ and $Cr(P(OMe)_3)_6$ undergo substitution at comparable rates [20,36]. The extra reactivity of $Cr(P(OMe)_3)_6$, in comparison to $Cr(CO)_6$, can readily be ascribed to steric interactions leading to a destabilization of the ground state. It is significant that in the case of per-phosphito complexes, where steric factors should be important, the order of reactivity is not that expected from steric considerations alone.

Cyclopentadienylmetal carbonyl complexes. The cyclopentadienylmetal carbonyls form a series nearly as extensive as the binary metal carbonyls and react with a

Table 4

Rates of substitution reactions of cyclopentadienyl carbonyl complexes, $CpM(CO)_n$

Compound	Rate (°C)	$\Delta H^{\neq}$	$\Delta S^{\neq}$	*d*-electrons	Reference
$CpV(CO)_4$	8.0×10^{-5} (110)	55	36	4	37
$CpMn(CO)_3$	no reaction (140)	–	–	6	38
$CpCo(CO)_2$	4.5×10^{-6} (40)	–	–	8	39
$CpRh(CO)_2$	4.6×10^{-5} (40)	16	−23	8	39
$CpIr(CO)_2$	2.1×10^{-6} (40)	–	–	8	39

Table 5

Substitution reactions of $CpM(CO)_nBr$

Compound	Rate (70 ° C)	$\Delta H^{\neq}$	$\Delta S^{\neq}$	*d*-electrons	Reference
$CpFe(CO)_2Br$	2.76×10^{-4}	31.2	14.1	6	42
$CpRu(CO)_2Br$	1.5×10^{-7}	31.1	−1.4	6	43
$CpMo(CO)_3Br$	3.9×10^{-4}	28.9	10.0	4	44

diversity of rates. The rates of several mononuclear complexes are summarized in Table 4 [37–39].

Substitutions of the d^8 complexes are almost certainly associative as has been demonstrated for the rhodium complex [39]. The structures of $CpV(CO)_4$ and $CpMn(CO)_3$ show very little difference in M–C bond lengths (V–CO, 1.90 and Mn–CO, 1.80 Å) that cannot be accommodated by the different metal radii [40,41]. The M–CO bonds in the cyclopentadienyl complexes appear to be slightly shorter than in the binary carbonyl compounds. This has been explained in terms of less competition for the π-electron density at the metal by the ligand *trans* to CO in the cyclopentadienyl complexes. This ground state contribution is shown in the lower reactivity of cyclopentadienylmetal carbonyls in comparison to binary metal carbonyls of the same *d*-electron configuration.

Cyclopentadienylmetal carbonyl halide complexes. There have been a number of studies of the reactivity of $CpM(CO)_nX$ complexes [42–44]. The primary focus was on the effect of the X group, but some data are available for comparison of metal center effects. These are shown in Table 5 for X = Br.

These complexes involve metals in the +2 oxidation state and the rate of CO loss in a dissociative reaction would be expected to be more facile than zero valent metals. This would be justified by comparison of $Fe(CO)_5$ and $CpFe(CO)_2Br$, but is obviously not general because substitution of $CpRu(CO)_2Br$ and $CpMo(CO)_3Br$ are not more rapid than substitution of the binary carbonyls, $Ru(CO)_5$ and $Mo(CO)_6$, respectively. This is another indication that the effects of charge and oxidation state on reactivity of metal carbonyl complexes are not simple.

The order of reactivity for the iron and ruthenium complexes is reversed for the M^{II} species in comparison to M^0 complexes. The ability of the first row metal to π-bond must be inhibited by the +2 charge leaving the order as that typical for coordination complexes.

Summary. The summary of the reactions as described earlier indicates two separate effects: (1) the effect of *d*-electron configuration and (2) an effect of the row (or size) for a given *d*-electron configuration.

Table 6 is composed of associative and dissociative reactions for quite different classes of compounds. These data indicate several features which appear to be general. (1) Organometallic complexes with a d^{10} configuration are relatively labile. (2) Complexes with 5, 7 or 9 *d* electrons are very labile. (3) Complexes with a d^6 configuration are relatively inert. (4) Dissociative reactivity apparently follows the order $d^{10} > d^4 > d^6 > d^8$ for a homologous series. (5) Complexes of 8 *d*-electrons which react by associative mechanisms are of moderate reactivity.

The comparison of analogous compounds shows no evidence that the observed dependence of the rate on the metal center arises from ground state properties. Thus

Table 6

Rates of reactions of 30 °C for different organometallic complexes compared to the number of *d*-electrons

Compound	Rate	ln *k*	*d*-electrons	Reference
$CpMn(CO)_3$	very slow at 140 °C		6	38
$CpV(CO)_4$	$4.7\times10^{-13}\ s^{-1}$	−28	4	37
$Cr(CO)_6$	$1\ \times10^{-12}\ s^{-1}$	−28	6	11
$Fe(CO)_3(PPh_3)_2$	$1\ \times10^{-11}\ s^{-1}$	−25	8	13
$Cr(CO)_4(PPh_3)_2$	$5\ \times10^{-11}\ s^{-1}$	−24	6	45
$CpRu(CO)_3Br$	$3\ \times10^{-10}\ s^{-1}$	−22	6	43
$CpFe(CO)_2I$	$5\ \times10^{-8}\ s^{-1}$	−17	6	42
$CpMo(CO)_3I$	$6.2\times10^{-8}\ s^{-1}$	−17	4	44
$Ni(P(OEt)_3)_4$	$1.0\times10^{-6}\ s^{-1}$	−14	10	20
$CpCo(CO)_2$ [a]	$1\ \times10^{-6}\ s^{-1}\ M^{-1}$	−14	8	39
$Mn(CO)_4NO$ [a]	$3\ \times10^{-4}\ s^{-1}\ M^{-1}$	−8	8	46
$Ti(CO)_3(PP)_2$	labile at room temperature		4	24
$Co(CO)_3NO$ [a]	$1\ \times10^{-3}\ s^{-1}\ M^{-1}$	−7	10	47
$Ni(CO)_4$	$1\ \times10^{-2}\ s^{-1}$	−5	10	6
$V(CO)_6$ [a]	$2.5\times10^{-1}\ s^{-1}$	−1	5	10
$Mn(CO)_3(PBu_3)_2$ [a]	$1\ \times10^{2}\ s^{-1}$	5	7	12

[a] Associative reaction.

a primary factor in the metal center reactivity is the transition state. This is similar to the conclusions regarding substitutional reactivity of Werner complexes, suggesting that similar interpretations may be possible.

Metal effects in clusters. Data to ascertain metal effects on cluster reactivity are not extensive. Trinuclear clusters such as $M_3(CO)_{12}$ [48] and $(\mu_3\text{-RC})M_3(CO)_{10}H$ [49,50] exhibit a reactivity order $M = Fe > Ru > Os$, that is different than that observed for mononuclear carbonyls. The $M_4(CO)_{12}$ species provide the only other series where the reactivity of all three are known, but possible mechanistic differences complicate this series [51,52]. These complexes undergo ligand substitution by associative pathways with the reactivity order $Rh_4 > Co_4 > Ir_4$.

In each of the clusters above several metal atoms are changing and in some cases the geometry changes. To provide more consistent data on the effect of changing a metal atom, we have examined the substitutional reactivity of the clusters $MFe_2(CO)_{12}$ and $M_2Fe(CO)_{12}$ ($M = Fe$, Ru, Os) [53,54]. Each of these clusters reacts by a CO dissociative pathway, with dissociation almost certainly occurring from the iron center. The rate constants for $MFe_2(CO)_{12}$ are shown in Table 7. The metal M affects the reactivity of $MFe_2(CO)_{12}$ to a small extent in the order $Ru > Fe > Os$, even though dissociation occurs from the iron center. Since the

Table 7

Relative rates for CO dissociation from $MFe_2(CO)_{12}$ [53,54]

$MFe_2(CO)_{12}$	Relative rate
$Fe_3(CO)_{12}$	9.5
$RuFe_2(CO)_{12}$	42
$OsFe_2(CO)_{12}$	1

structures are unchanged the metal M must be affecting the adjacent iron centers. The order of reactivity is wrong for steric interactions; an electronic effect is indicated [54]. The relatively small rate differences and lack of data on ground state properties do not allow assignment to ground state or transition state effects.

Ligand effects

The term ligand effect has been used for many different experiments. For this manuscript ligand effect will describe the change in rate associated with a change in a non-participating ligand attached to a metal. The ligands that are most often used with metal carbonyl complexes involve σ-donation and π-acceptance in their bonding and may have differing steric requirements. There have been many attempts to separate σ, π and steric influences, from early efforts with carbonyl stretching frequencies to more involved current concepts [55–58]. While these efforts provide useful comparisons, they fail to accommodate the dynamic nature of bonding. σ and π interactions of a ligand may change as the electron density at the metal changes; even steric interactions may not be constant since some ligands fit together better.

As discussed earlier in the section on metal effects, a kinetic effect may arise from the ground state or from the transition state. Ground state ligand effects (ligand influences) should be observed in spectra or structures; effects that do not correlate with the ligand influence are usually assigned to the transition state.

A non carbonyl ligand affects the bonding of the remaining carbonyls, with the *trans*-CO most affected. This is illustrated in Table 8. Obviously the oxidation state of the metal has the largest effect on the CO stretching frequency. For a given metal, however, the CO stretching frequency of the *cis*-CO's appears to mirror the M–CO bond length changes that result from changes in the ligand. Note that a ligand has a much larger effect on the *trans*-CO than on the *cis*-CO's. The ligands represented in Table 8 are either weaker π acceptors or stronger σ donors (or both). Such ligands appear from structures and spectra to strengthen the metal–CO bonds with the most significant strengthening for the CO *trans* to the ligand. This represents the ground state effect of a ligand with weaker π acceptance/stronger σ donation.

We have suggested that a donor ligand stabilizes the sixteen electron transition state formed in a reaction proceeding by a dissociative mechanism [63,64]. This simple postulate is useful in interpreting the ligand effects in mononuclear, dinuclear and polynuclear metal carbonyl complexes.

Table 8

Structural influence of ligands on cis and trans carbonyls.

Compound	M–C(*trans*)	M–C(*cis*)	ν(asymmetric stretch)
$Cr(CO)_6$ [59]	1.909(7)	1.909(7)	1985 cm^{-1}
$Cr(CO)_5P(OPh)_3$ [60,61]	1.861(4)	1.893(4)	1960 cm^{-1}
$Cr(CO)_5PPh_3$ [60,61]	1.845(4)	1.880(4)	1945 cm^{-1}
$Mn(CO)_5Cl$ [62]	1.807(9)	1.892(6)	2042 cm^{-1}

Table 9

First order rate constants at 30 °C for the substitution reactions of chromium carbonyl compounds

Compound	Substituting ligand	$k_1(s^{-1})$	Ref.
$Cr(CO)_6$	$P(C_6H_5)_3$	1×10^{-12}	11
$Cr(CO)_5PR_2R'$	PR_2R'	2×10^{-11}	65
$Cr(CO)_5P(C_6H_5)_3$	^{13}CO	3×10^{-10}	61
$Cr(CO)_5I^-$	$P(C_6H_5)_3$	$\ll 10^{-5}$	66
$Cr(CO)_5Br^-$	$P(C_6H_5)_3$	2×10^{-5}	66
$Cr(CO)_5Cl^-$	$P(C_6H_5)_3$	1.5×10^{-4}	66

Table 10

First order rate constants at 30 °C for substitution of rhenium carbonyl compounds

Compound	Substituting ligand	$k_1(s^{-1})$	Ref.
$Re(CO)_6^+$	^{14}CO	N.R. [a] 60 h	67
$HRe(CO)_5$	$P(C_6H_5)_3$	N.R. 60 d	68
$Re(CO)_5I$	$P(C_6H_5)_3$	4×10^{-8}	69
$Re(CO)_5Br$	$P(C_6H_5)_3$	5×10^{-7}	69
$Re(CO)_5Cl$	$P(C_6H_5)_3$	2×10^{-6}	69

[a] No reaction.

Mononuclear complexes. Most data on ligand effects in mononuclear complexes are for octahedral complexes of group 6 or group 7 metals. Some data are shown in Tables 9 and 10 for CO dissociation. Dissociation of phosphines from metal carbonyl complexes shows similar trends as shown by the data in Table 11 [70]. For CO dissociation from complexes with a ligand that is a weaker π-acceptor/stronger σ-donor than CO, dissociation occurs *cis* to the ligand [63]. This is reasonable in light of the discussion above since the CO *trans* to such a ligand is bound more strongly to the metal than are the *cis*-CO's. Thus the stereochemistry is readily understood from ground state considerations. However, the labilization cannot be accounted for by ground state changes, since the evidence suggests a slight strengthening of the *cis*-CO–metal bond. The labilization must result from lowering the energy of the transition state by the presence of a weaker π-acceptor/stronger σ-donor. Results from phosphine dissociation where the leaving group is *trans* to the ligand, indicate that the stabilization does not depend on the location of the ligand [70]. All of these results are consistent with our postulate that a donor ligand stabilizes the sixteen electron transition state in a dissociative process.

Table 11

Ligand effect for dissociation of PPh_3 from *trans*-$Cr(CO)_4LPPh_3$ [70]

L	Relative rate [a]	$Cr-PPh_3$ (Å)
PBu_3	2400	2.345(3)
$P(OPh)_3$	130	2.393(1)
$P(OMe)_3$	81	2.362(2)
CO	1	2.422(1)

[a] At 130 °C.

Table 12

Relative rates of associative substitution on $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ [71–73]

Cp′	k
$\eta^5\text{-}C_9H_7$	3.8×10^8
$\eta^5\text{-}C_9Me_7$	6.1×10^5
$\eta^5\text{-}C_5H_4NO_2$	1.2×10^4
$\eta^5\text{-}C_5H_4Cl$	4.0×10^2
$\eta^5\text{-}C_5H_4PPh_2$	1.1×10^2
$\eta^5\text{-}C_5H_5$	1
$\eta^5\text{-}C_5Me$	2.2×10^{-2}

Table 13

Ligand effects on CO dissociation from $Ir_4(CO)_{11}L$ [74]

L	Relative rate
CO	1
$P(OPh)_3$	8
$AsPh_3$	54
PPh_3	82
PBu_3	170

Very little data concerning ligand effects on associative reactions of metal carbonyls exist. The most comprehensive data are for $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ and are shown in Table 12 [71–73]. These data show that electron-withdrawing groups stabilize the $\eta^3\text{-}C_5H_4X$ transition state in a ring-slippage mechanism.

Dinuclear and polynuclear complexes. For those dinuclear and polynuclear complexes that react by CO dissociation, the effect of a weaker π-acceptor/stronger σ-donor ligand is the same as for mononuclear complexes. Data for $Ir_4(CO)_{11}L$ are shown in Table 13 [74].

It is often difficult to determine the site of CO dissociation from a metal cluster complex. We suggest that the effect of the first substitution on subsequent substitutions as a useful measure of whether the site of substitution is the site of CO dissociation. Substitution of phosphine on $MnRe(CO)_{10}$ to produce $MnRe(CO)_8L_2$ proceeds in two steps that occur at approximately the same rate. This led us to the conclusion that CO dissociated from manganese, but that the first phosphine substituted on rhenium. The manganese would be relatively unaffected by substitution on rhenium and the second substitution would occur at approximately the same rate. Substitution on manganese would result in an enhanced second substitution. Enhanced reactivity for $(CO)_4(PPh_3)MnRe(CO)_5$ has recently been observed [75]. Similar rationale was part of the conclusion that CO dissociation occurs from iron in the mixed metal clusters $RuFe_2(CO)_{12}$ and $OsFe_2(CO)_{12}$ [53,54].

Conclusion

In the past 25 years tremendous advances have been made in understanding of metal carbonyl reactivity. The effect of charge and oxidation state on the metal in CO substitution are not as straightforward as expected. The ground state weakening of the M–CO as charge and oxidation state are increased must be offset by a similar increase in the energy of the transition state resulting in very small rate changes. Odd electron complexes with either 17 or 19 electrons react at least 10 orders of magnitude more rapidly than similar 18 electron complexes. Electron configuration has a large effect on CO substitution with the order of reactivity: $d^{10} > d^4 > d^6 > d^8$ for 18 electron complexes. Changing a metal atom in a cluster complex affects the reactivity of the other metal centers. Dissociative reactions are accelerated by the presence of a stronger σ-donor/weaker π-acceptor that stabilizes the 16 electron transition state. In this paper we have tried to draw conclusions that are supported by most of the data about the effects of metal and ligand on carbonyl substitution. There, of course, exist exceptions to the general trends.

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