

Systematic kinetics of associative reactions of metal carbonyls

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Abstract--Rate constants for associative attack on a wide variety of metal carbonyls by P-donor nucleophiles can be resolved into electronic (σ -basicity) and steric (Tolman cone angle) properties of the nucleophiles. Relative values of the intrinsic reactivities of the complexes to nucleophilic attack can also be obtained. New data for some Ru_3 and Rh_4 clusters are presented and the clusters are shown to be exceptionally susceptible to nucleophilic attack.

INTRODUCTION: LINEAR FREE ENERGY RELATIONSHIPS (LFER) AND STERIC DEVIATIONS

Associative substitution reactions of metal carbonyls with P-donor nucleophiles have been known for over 20 years to depend systematically on the basicity of the entering nucleophile.^{1,2} Linear free energy plots of $\log k_2$ against Δh_{np} were found for a number of mononuclear metal carbonyls^{1,2} where Δh_{np} is a measure of the relative half neutralization potential for titration of the nucleophile against $HClO_4$ in nitrobenzene.³ Reactions of the large nucleophile PCy_3 ($Cy = C_6H_{11}$) were slower than expected from the LFER and this was quite reasonably explained by steric repulsions experienced by the approaching nucleophile.¹ The metal carbonyls usually contained ligands that were capable of easily withdrawing a pair of electrons from the metal as the nucleophile approached.² Thus the NO^+ ligands in $Co(CO)_3(NO)$, $Mn(CO)_4(NO)$, and $Fe(CO)_2(NO)_2$ can become NO^- as the metal-nucleophile bond is made and the metal can thereby avoid having to approach the energetically unfavorable 20-electron configuration. The $(\eta^5-C_5H_5)^-$ ligand can undergo concerted slippage to an $(\eta^3-C_5H_5)^-$ form with the same result.² The much faster reactions of analogous η^5 -indenyl complexes and the effect of substituents in the $(\eta^5-C_5H_5)^-$ ligand offer powerful supporting evidence to this picture.² However, even the binary carbonyls $M(CO)_6$ ($M = Cr, Mo, \text{ or } W$) undergo associative substitution⁴ and LFERs can be obtained from the data.⁵

The binary carbonyl cluster $Ru_3(CO)_{12}$ was also found to give a reasonably good LFER but now the less large nucleophile PPh_3 (cone angle, $\theta = 145^\circ$) also showed a significant deviation, that of PCy_3 ($\theta = 170^\circ$) being much larger.^{5,6} It was suggested that gradients of the LFER could be taken as a measure of the relative amounts of bond making in the transition states while any deviations from the LFER shown by PPh_3 and/or PCy_3 could be taken as a quantitative measure of the steric effects. The greater scatter of the LFER for $Ru_3(CO)_{12}$, together with the large steric deviations of PPh_3 and PCy_3 , were taken as a qualitative

indication of greater steric effects for these reactions since even the relatively small nucleophiles involved in the LFER might be expected to show some steric effects.^{5,6}

THE THREE-PARAMETER EQUATION AND STERIC PROFILES

The approach outlined above was used intermittently until quite recently⁷ when studies of S_N^2 reactions of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{P-X-C}_5\text{H}_4\text{N})^+$ ⁸ and $\text{Ir}_4(\text{CO})_{12}$ ⁹ were found to show regular electronic and steric effects that could be represented by the 3-parameter equation (1) where pK_a is a measure of the basicity of the P-donor nucleophile and α , β , and γ are

$$\log k_2 = \alpha + \beta \cdot \text{pK}_a + \gamma \cdot \theta \quad (1)$$

constants, the last being negative. The data for $\text{Ir}_4(\text{CO})_{12}$ were plotted in terms of Δhnp ⁹ but since this is linearly related to pK_a ³ they can also be plotted against pK_a . This is preferable since β will then be dimensionless. Reactions of complexes that show an LFER will obviously follow eq. (2) and it follows that plots of $\log k_2 - \beta \cdot \text{pK}_a$ against θ can be

$$\log k_2 = \alpha + \beta \cdot \text{pK}_a \quad (2)$$

horizontal if steric effects are small and γ is negligible. If values of γ are significant, plots of $\log k_2 - \beta \cdot \text{pK}_a$ against θ will be linear with a negative gradient, according to eq.(1). There must also be an intermediate type of behavior when $\log k_2 - \beta \cdot \text{pK}_a$ tends to become invariant with θ at lower cone angles but begins to decrease as θ increases and approaches the linearly decreasing region where $\log k_2 - \beta \cdot \text{pK}_a = \alpha + \gamma\theta$. The sharpness or otherwise of the change from the horizontal to the downward sloping linear part of the plots can be taken as a measure of the flexibility of the complex. A sharp change will imply that as soon as steric effects come into play they immediately become quite significant. This will probably be associated with large negative values of γ . A gradual change will indicate that even when steric effects due to the nucleophiles come into play they are not too pronounced because the ligands present can move and give way to the entering nucleophiles. In general, therefore, plots of $\log k_2 - \beta \cdot \text{pK}_a$ (or $\log k_2^\circ$, see below) against θ will be distributed somewhere along curves of the sort shown in Figure 1. These are known as "steric profiles".¹⁰

STERIC PROFILES, STERIC EFFECTS, AND INTRINSIC REACTIVITIES

The systematic nature of a selection of published data, when expressed as steric profiles, was found independently by two groups.^{9,10} Thus, data for $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ and $\text{V}(\text{CO})_6$ all lie on steric profiles such as those shown in Figure 1. The ligand N_4Me_2 is another of those ligands that are capable of concerted withdrawal of a pair of electrons from the metal as the nucleophile approaches,² and $\text{V}(\text{CO})_6$ is a 17-electron molecule of the sort that is known to be very susceptible to nucleophilic attack because of the favorable 2-center, 3-electron interaction between the metal and the incoming nucleophile.¹¹⁻¹³ It is generally possible to obtain values of β from the dependence of $\log k_2$ on pK_a for

nucleophiles of closely similar or identical size. A quantitative measure of the steric effect can then be obtained either from γ (if eq.(1) is obeyed) or from the extent to which the values of $\log k_2 - \beta \cdot pK_a$ for larger ligands such as PPh_3 or PCy_3 fall below the σ -independent value of $\log k_2 - \beta \cdot pK_a$ defined by the data for smaller ligands. This is the value of $\log k_2$ for a particular small nucleophile corrected to what it would be for a standard nucleophile with $pK_a = 0$. This corresponds to a nucleophile of intermediate basicity, the basicities of P-donor nucleophiles ranging from -2 (for $P(OPh)_3$ or $PPhH_2$) to 8.65 (for PMe_3).¹⁴ We believe that it is useful to use a less basic hypothetical nucleophile as a reference standard on the grounds that the rate for a less basic nucleophile is determined more by the complex itself than by the nucleophile. Thus, as the pK_a of the standard decreases, one approaches, though one can never finally reach, a measure of what might be called the intrinsic reactivity of the complex towards an associative reaction. We have chosen to use as a standard a hypothetical very weak nucleophile with $pK_a = -4$. This is less basic than any of the P-donors available¹⁴ and will provide a reasonable estimate of intrinsic reactivities, at least for comparative purposes. This choice has no influence on the estimates of electronic or steric effects. We therefore plot values of $\log k_2 - \beta(pK_a + 4) = \log k_2^\circ$ against σ in order to provide steric profiles after β values have been determined. The value of $[\log k_2^\circ]_{\sigma \rightarrow 0}$ for nucleophiles small enough for there to be no steric effects can be taken as a measure of the intrinsic reactivities.

We have been unable to find any systematic data in the literature for straightforward S_N2 reactions that do not fall somewhere on steric profiles of the sort shown in Figure 1. Values of β are always available. Lower limits of the intrinsic reactivity can always be found from the highest values of $\log k_2^\circ$ at the lowest σ , even when σ -independent values are unavailable. Values of γ are found only occasionally since a linear dependence of $\log k_2^\circ$ on σ is relatively rare. Steric effects, if any, then have to be quantified by the difference between $[\log k_2^\circ]_{\sigma \rightarrow 0}$ and $\log k_2^\circ$ for PPh_3 and/or PCy_3 . Table 1 shows a collection of the parameters β , ΔPPh_3 and/or ΔPCy_3 , and $[\log k_2^\circ]_{\sigma \rightarrow 0}$ that have been obtained from data taken from the literature or available from some recent unpublished work. Figures 2,3, and 4 show examples of some of the steric profiles.

DISCUSSION

Mononuclear carbonyls

The complexes $Co(CO)_3(NO)$, $Mn(CO)_4(NO)$, and $V(CO)_5(NO)$ show a progressively decreasing electronic discrimination (β) towards the nucleophiles in accord with a steadily decreasing amount of bond making in the transition states. A slight steric effect may be operative for the 5-coordinate $Mn(CO)_4(NO)$ but the degree of bond making in reactions of $V(CO)_5(NO)$ is evidently too low for a steric effect to be shown by PPh_3 even though the complex is 6-coordinate. Although the intrinsic reactivities of $Co(CO)_3(NO)$ and $Mn(CO)_4(NO)$ are comparable, that of $V(CO)_5(NO)$ is much higher and this can be ascribed to a much greater

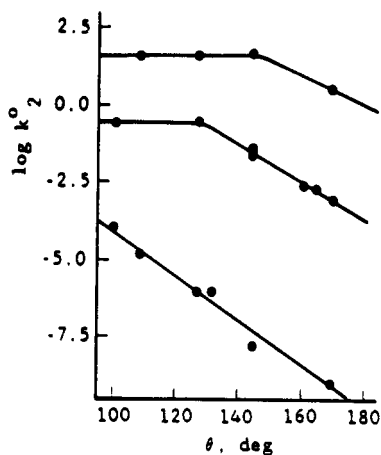


Figure 4: Steric profiles for, from top to bottom, $\text{Rh}_4(\text{CO})_9(\text{PCy}_3)_3$, $\text{Rh}_4(\text{CO})_9(\text{etpb})_3$, and $\text{Ir}_4(\text{CO})_{12}$, respectively.

extent of V-CO bond breaking resulting from the high trans effect of NO,¹⁷ neither of the other complexes having a CO trans to the NO ligand.

The comparison of $\text{V}(\text{CO})_5(\text{NO})$ with $\text{V}(\text{CO})_6$ is interesting. The extent of bond making in the latter is much greater, possibly because bond breaking is more difficult but also because bond making to the 17-electron metal center must be more effective, a bond of order one half being formable without any bond breaking being necessary.¹¹ However, the intrinsic reactivity of $\text{V}(\text{CO})_6$ is lower than that of $\text{V}(\text{CO})_5(\text{NO})$ because bond making is more important for the former and the intrinsic reactivity is defined for a standard nucleophile that is very weak. The high intrinsic reactivity of $\text{V}(\text{CO})_5(\text{NO})$ is due to easy bond breaking whereas the quite high reactivity of $\text{V}(\text{CO})_6$ intimately depends on the presence of a nucleophile and is therefore less intrinsic to the complex itself. Although there might be some relationship between intrinsic reactivities and the rates of CO dissociation processes it must be remembered that the circumstances of bond breaking in associative and dissociative reactions are quite different.

The hexacarbonyls $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or } \text{W}$) have little to help them undergo associative reactions apart from the relatively large number of CO ligands that can evidently delocalise charge from the metal, as the nucleophile approaches, sufficiently for the process to occur. This contrasts with the cases of $\text{Fe}(\text{CO})_5$,²³ $\text{Ru}(\text{CO})_5$,²⁴ and $\text{Ni}(\text{CO})_4$ ²⁵ in spite of the lower steric effects expected. The amount of bond making for reactions of $\text{Cr}(\text{CO})_6$ is very small and even PPh_3 shows no steric retardation.⁵ Bond making is greater for $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ to the extent that the β values are greater, and steric retardation is shown for PPh_3 , the retardation being greater for $\text{Mo}(\text{CO})_6$ than $\text{W}(\text{CO})_6$.⁵

The data for reactions of the $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ and $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$ complexes are also of interest. Their powers of electronic discrimination are quite comparable, in spite of any differences in electronic interactions between the organic ligands and the Rh atoms, and so are their intrinsic reactivities. By definition neither of these parameters involves any steric effects at all and it is only in this steric respect that the two compounds differ appreciably, the effect for the $\eta^5\text{-C}_5\text{Me}_5$ complex being very much larger as shown by the steric profiles (Figure 2) and the value of $\Delta(\text{PPh}_3)$.

TABLE 1 Steric and electronic effects in associative reactions of some metal carbonyls at 25°C (a)

Complex	β	$\Delta(\text{PPh}_3)$	$\Delta(\text{PCy}_3)$	$[\log k_2^\circ]_{\theta \rightarrow 0}$	Data from Ref.
$\text{Co}(\text{CO})_3(\text{NO})$	0.35 ± 0.2 (b)	0	1.6	-5.2 ± 0.1	15
$\text{Mn}(\text{CO})_4(\text{NO})$	0.26	ca. 0.1	-	-5.4	16
$\text{V}(\text{CO})_5(\text{NO})$	0.18 ± 0.05	0	-	-2.1 ± 0.3	17
$\text{V}(\text{CO})_6$	0.37 ± 0.05	0.4	> 5.5	-2.7 ± 0.3	18
$\text{Cr}(\text{CO})_6$	0.053 (c)	0	-	ca. -10 (d)	4
$\text{CpRh}(\text{CO})_2$ (e)	0.19 ± 0.03	0	2.0	-5.3 ± 0.2	1
$\text{Cp}^*\text{Rh}(\text{CO})_2$ (e)	0.16	≥ 4	-	-5.5	19
$\text{Ru}_3(\text{CO})_{11}(\text{PBU}_3)$	0.074 ± 0.011	1.6	-	-2.5	20
$\text{Ru}_3(\text{CO})_{12}$	0.16	1.4	-	-3.5	6
$\text{Ru}_3(\text{CO})_{11}\{\text{P}(\text{OEt})_3\}$	0.21	3.4	-	-4.4	21
$\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ (f)	0.20	≥ 3.5	-	≥ 3.5	22
$\text{Ir}_4(\text{CO})_{12}$	0.30	≥ 4	≥ 5	≥ -4	9
$\text{Rh}_4(\text{CO})_9(\text{etpb})_3$ (g)	0.22	1.0	2.6	-0.5	20
$\text{Rh}_4(\text{CO})_9(\text{PCy}_3)_3$	0.02	0	1.1	+1.6	20

(a) Where necessary, data were adjusted to 25°C by use of appropriate activation enthalpies. (b) Uncertainties are only available when data for several ligands lie on an LFER. (c) Appropriate to 131°C. (d) Extrapolated to 25°C from 131°C. (e) $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$. (f) $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$. (g) $\text{etpb} = \text{P}(\text{OCH}_2)_3\text{CEt}$.

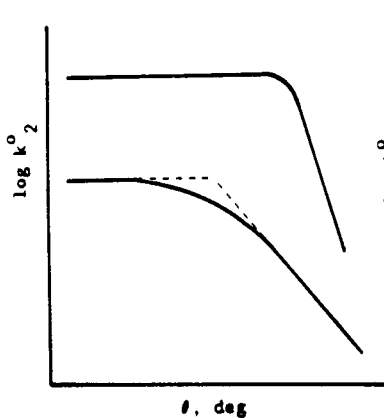


Figure 1

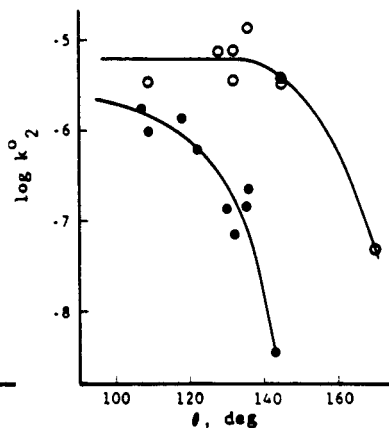


Figure 2

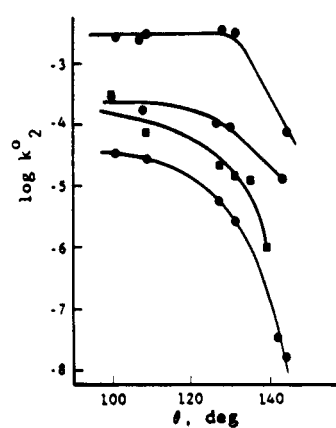


Figure 3

Figure 1: Typical steric profiles for "inflexible" (upper plot) or "flexible" (lower plot) complexes.

Figure 2: Steric profiles for $\text{CpRh}(\text{CO})_2$ (o) and $\text{Cp}^*\text{Rh}(\text{CO})_2$ (*).

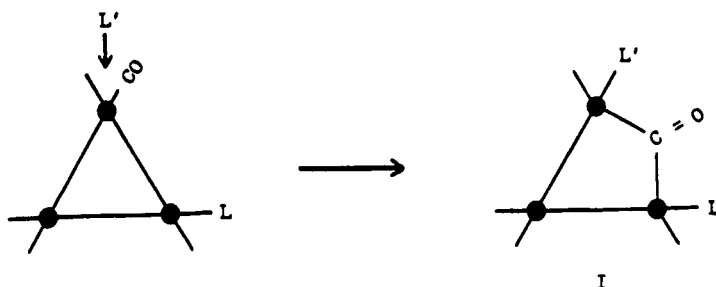
Figure 3: Steric profiles for $\text{Ru}_3(\text{CO})_{11}\text{L}$ (*) (from top to bottom, $\text{L} = \text{P-n-Bu}_3$, CO , and $\text{P}(\text{OEt})_3$, respectively), and $\text{Ru}_3(\text{CO})_{10} \text{dppm}$ ().

Metal carbonyl clusters

The clusters $\text{Ru}_3(\text{CO})_{11}\text{L}$ show a steadily increasing electronic discrimination as L changes along the series $\text{P-n-Bu}_3 < \text{CO} < \text{P(OEt)}_3$ corresponding to an increasing importance of bond making. The steric profile for $\text{Ru}_3(\text{CO})_{11}(\text{P-n-Bu}_3)$ suggests little steric effect until $\theta \geq 130^\circ$ when a fairly pronounced effect sets in. The steric effect for $\text{Ru}_3(\text{CO})_{12}$ is somewhat smaller in terms of $\Delta(\text{PPh}_3)$ but it sets in at lower cone angles, yet more gradually. The steric effect for $\text{Ru}_3(\text{CO})_{11}\{(\text{P(OEt)}_3)\}$ also sets in gradually but is more pronounced. The intrinsic reactivities decrease along the series $\text{L} = \text{P-n-Bu}_3 > \text{CO} > \text{P(OEt)}_3$. These trends suggest that bond making is relatively unimportant for $\text{Ru}_3(\text{CO})_{11}(\text{P-n-Bu}_3)$ and that its high reactivity is genuinely intrinsic in that the complex itself readily adjusts to nucleophilic attack irrespective of the nucleophile itself provided the nucleophile is not too big. This is probably related to the longer Ru-Ru bonds and cluster expansion found for $\text{Ru}_3(\text{CO})_{11}(\text{PR}_3)$ ($\text{R} = \text{Ph}$,²⁶ Cy ,²⁷ and Et ²⁸) compared with $\text{Ru}_3(\text{CO})_{12}$, though the relatively sudden onset of the steric effect suggests a lack of flexibility in the complex. The $\text{Ru}_3(\text{CO})_{11}\{(\text{P(OEt)}_3)\}$ cluster, by analogy with $\text{Os}_3(\text{CO})_{11}\{\text{P(OMe)}_3\}$,²⁹ is probably also expanded compared with $\text{Ru}_3(\text{CO})_{12}$ and its lower intrinsic reactivity appears to suggest that the greater π -acidity of the P(OEt)_3 substituent offsets the effect of the longer Ru-Ru bonds in some way. The greater steric effect, evident in spite of the expanded cluster, emphasises the greater degree of bond making in the transition state, but the gradual onset of the steric effect suggests that the cluster is more flexible even than $\text{Ru}_3(\text{CO})_{12}$. The complex $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ shows a remarkably high intrinsic reactivity for a bis substituted cluster³⁰ but still a high degree of bond making. This may have its origin in steric strain associated with the bridging dppm ligand.³¹

Another feature of reactions of these clusters is the extent to which reaction leads to substitution by $\text{S}_{\text{N}}2$ processes or to fragmentation and formation of mononuclear carbonyls by $\text{F}_{\text{N}}2$ processes.³⁰ A systematic study of product yields for reactions of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{11}(\text{P-n-Bu}_3)$ with P-n-Bu_3 shows³² that $\text{Ru}_3(\text{CO})_{12}$ undergoes mainly $\text{S}_{\text{N}}2$ associative reactions though the $\text{F}_{\text{N}}2$ process becomes significant at lower temperatures. The $\text{Ru}_3(\text{CO})_{11}(\text{P-n-Bu}_3)$ reacts with P-n-Bu_3 almost exclusively by an $\text{F}_{\text{N}}2$ process, and $\text{Ru}_3(\text{CO})_{11}\{(\text{P(OEt)}_3)\}$ also undergoes $\text{F}_{\text{N}}2$ reactions.²¹ It has also been shown that $\text{Os}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{11}(\text{P-n-Bu}_3)$ react with P-n-Bu_3 mainly by $\text{S}_{\text{N}}2$ and $\text{F}_{\text{N}}2$ reactions, respectively.^{30(b)} The $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ undergoes $> 90\%$ $\text{F}_{\text{N}}2$ processes with P-n-Bu_3 but reaction with P(OEt)_3 leads to only ca. 40% $\text{F}_{\text{N}}2$ and ca. 60% $\text{S}_{\text{N}}2$ processes.²² These observations must be related to the extent of strain or bond lengthening in the various M_3 clusters.

Although several transition states or intermediates for such reactions can be envisaged^{6,9,30(b)} one simple one is illustrated diagrammatically by I where



only the ligands in the M_3 plane are shown. Migration of a Ru-Ru electron pair to a terminal CO allows formation of a Ru-L' bond without the necessity of passing through a 20-electron transition state or intermediate. This structure happens to be the same as that proposed for the intermediate in photochemical reactions of $Ru_3(CO)_{11}L$ ($L = CO$)³³ when it is known that only fragmentation occurs subsequently. Different assignments of proposed intermediates to particular processes may turn out to be necessary but which goes with which is not yet ascertainable.

The tetranuclear clusters show that the higher nuclearity leads to much greater susceptibility to nucleophilic attack. The electronic discrimination shown by $Ir_4(CO)_{12}$ is greater than that of $Ru_3(CO)_{12}$ and the intrinsic reactivity is probably at least as great in spite of the lower reactivity expected for a third row transition metal cluster. This, and the very large steric effect, shows that bond making in reactions of $Ir_4(CO)_{12}$ is very high. Only S_N2 processes are observed.

Even the tris substituted $Rh_4(CO)_9(etpb)_3$ shows a high degree of bond making and its intrinsic reactivity is three orders of magnitude greater than that of the unsubstituted $Ru_3(CO)_{12}$. Reactions of $Rh_4(CO)_{12}$ are too fast to measure, even by stopped flow techniques. The cluster $Ru_4(CO)_9(PCy_3)_3$ shows much less bond making (low β and small steric effects) and a much higher intrinsic reactivity than $Rh_4(CO)_9(etpb)_3$. This may originate in a more expanded Rh_4 cluster caused by the three large substituents. Although the tris substituted Rh_4 clusters do undergo some F_N2 processes the unsubstituted $Rh_4(CO)_{12}$ appears to react mainly by S_N2 processes.

CONCLUSIONS

The method, described above, of factorizing kinetic data for associative reactions of P-donor nucleophiles with metal carbonyls into electronic and steric effects is remarkably successful. Quantitative estimates of electronic and steric parameters can be obtained, as can values of relative intrinsic reactivities of the complexes towards nucleophilic attack. Trends in parameters along a series of related mononuclear carbonyls can usually be understood in terms of varying coordination numbers and specific properties of some of the ligands.

Application of the method to reactions of metal carbonyl clusters looks particularly promising. Systematic changes in the kinetic parameters with changing substituents in the clusters are readily apparent and provide an excellent way of characterizing this aspect of the reactivity of clusters. Metal carbonyl clusters appear to be generally very susceptible to nucleophilic attack and the consequences of this attack can either be substitution (by an S_N2 process) or fragmentation (by an F_N2 process). The balance between these two processes provides another characteristic property of a cluster. More data of this sort should be readily available and the relationships between the various kinetic parameters and structural, spectroscopic, and electrochemical properties etc. should provide new insights into the natures of these important compounds.

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