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Associative reactions of metal carbonyl clusters: systematic kinetic studies of some ruthenium and other clusters

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Abstract

Rate constants for associative reactions of metal carbonyl clusters with a range of P-donor nucleophiles of various basicities and sizes can always be fitted successfully to the equation $\log k_2 = \alpha + \beta(\mathrm{p}K'_a + 4) + \gamma(\theta - \theta_{th})\lambda$. The evolution of this equation, and the use of the electronic

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parameter pK'_a and steric parameter θ assigned to particular P-donor nucleophiles, is outlined. λ is a switching function which is zero when $\theta \leqslant \theta_{th}$, (the steric threshold) and becomes unity when $\theta > \theta_{th}$. The data can be fitted to the equation by a least-squares programme developed initially by Professor W.P. Giering. The significance of the parameters α (defined as the standard reactivity of the carbonyl), β (the susceptibility of the carbonyl to the σ basicity of the nucleophiles), θ_{th} (the Tolman cone angle of the nucleophile where steric effects begin to be apparent, i.e. the steric threshold) and γ (the sensitivity of the rates to the cone angles of the nucleophiles when $\theta > \theta_{th}$) are discussed in detail and their interrelationships considered. In particular the sharpness of the steric threshold is taken to imply that a substrate carbonyl undergoes an isomerization reaction when approached by the nucleophile. This produces a so-called transition state isomer (TSI) that contains a roughly conical opening into which all nucleophiles with $\theta \leqslant \theta_{th}$ can fit without steric difficulty. When $\theta > \theta_{th}$ the nucleophiles can attain the same metal–P-donor bond distance in the transition state if the TSI opens up further, so that γ is a measure of the flexibility of the TSI. Alternatively the flexibility of the TSI may be so low that it cannot accommodate large nucleophiles unless they penetrate less deeply into the space in the TSI.

The application of this systematic kinetic approach to the delineation of the dynamic character of metal carbonyl clusters is illustrated by examples, many of them unpublished, that involve $Ru_3(CO)_{11}L$ clusters (where the effect of varying the P-donor substituent is probed), some Rh_4 and Ir_4 clusters, some high nuclearity Ru and Fe clusters, and a variety of osmium clusters. Not only are the clusters characterizable in this way but also the actual mechanistic paths followed, and the products formed, can undergo major changes which depend mainly on the size of the nucleophiles.

Keywords: Associative reactions; Metal carbonyl clusters; Kinetics; Ruthenium; Rhodium; Iridium; Osmium; Iron

1. Introduction

The kinetic and mechanistic behaviours of metal complexes define the dynamic character of each individual complex and this is as important as their crystallographic structures and their spectroscopic and other properties in describing their overall natures. This is as true for metal carbonyl clusters as for traditional Werner-type coordination complexes, or mononuclear metal carbonyls which were the first to receive detailed kinetic study [1]. Most mononuclear metal carbonyls undergo substitution reactions mainly or entirely via CO-dissociative processes [1,2] and these can be studied systematically as a function of the nature of the metal atom, the coordination number and the nature of any other "spectator" ligands [3]. However, it has been known for many years [1,2] that mononuclear metal carbonyls that contain certain types of ligand prefer to react via associative paths, particularly with P-donor nucleophiles. The kinetic data for such reactions provide additional information about the nature of the complexes because the systematic dependence of the rates on the nature of the nucleophiles involved is a characteristic of each individual complex. In this they resemble the d^8 complexes of Pt(II), the substitution reactions of which are overwhelmingly associative in nature [4], and susceptible to systematization in terms of $n(Pt)$ values of the nucleophiles [4,5].

2. Associative reactions of metal carbonyls: early studies

The occurrence of associative reactions of a metal carbonyl was first observed by Heck [6] in 1963 who showed that $Co(CO)_3(NO)$ underwent substitution reactions with PPh_3 at rates proportional to $[PPh_3]$. This observation was followed by work in Basolo's laboratory where it was shown that the rates of reactions of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with a number of P-donor ligands L were also first order in [L] [7]. This discovery was extended in a seminal way by the observation that the values of $\log k_2$ varied linearly with a parameter Δ(hnp) that provided a quantitative measure of the proton basicity of the nucleophiles. These values of Δ(hnp) are the half-neutralization potentials found when titrating the P-donor ligands against $HClO_4$ in nitromethane [8], and they decrease with increasing basicity of L. Since they provide a measure of the free energy of attachment of the ligand to the proton, and since $\log k_2$ is proportional to the free energy $\Delta G^{\neq}$ of attaching the nucleophile to the metal in the transition state, the linear plots of $\log k_2$ vs. Δ(hnp) are a type of linear free-energy relationship (LFER).

An important supplementary observation was that the value of $\log k_2$ for the large nucleophile PCy_3 ($Cy \equiv C_6H_{11}$) fell considerably below the LFER defined by the smaller nucleophiles, thus showing the importance of steric effects in some reactions of this complex. Systematic studies of reactions of $Co(CO)_3(NO)$ led to similar results [9].

The occurrence of these associative reactions required some explanation in the light of the largely dissociative paths followed by binary metal carbonyls in their substitution reactions. It is now agreed [10] that the key factor is the ability of the NO^+ and $\eta^5\text{-}C_5H_5$ ligands to withdraw an electron pair from the metals during the approach of the nucleophile. In so doing they are converted to reasonably stable NO^- and $\eta^3\text{-}C_5H_5$ forms respectively. Transition states can therefore be formed that involve metal–L bond making and no metal–CO bond breaking without contravention of the 18-electron rule which is closely obeyed by most metal carbonyls. This concept has been used, explicitly or implicitly, ever since. Basolo has considerably extended such studies over the years and has reviewed his work quite recently [10].

3. Quantitative separation of electronic and steric effects

The quantitative separation of electronic and steric effects was first undertaken following a study [11] of reactions of the carbonyl cluster $Ru_3(CO)_{12}$, associative reactions of which had been detected earlier by Candlin and Shortland [12]. A moderately well-defined LFER was exhibited by smaller nucleophiles but the larger PPh_3 and PCy_3 showed clear steric deviations. It was suggested that the gradients β of this LFER, and of other LFERs derivable from data then available, could be taken as a quantitative measure of the relative extents of metal–L bond making in the transition states for reactions of the various complexes involved. Thus the values of β indicated decreasing bond making along the series $Fe(CO)_2(NO)_2 >$ $Co(CO)_3(NO) > Mn(CO)_4(NO) > (\eta^5\text{-}C_5H_5)Rh(CO)_2 \approx Ru_3(CO)_{12} > W(CO)_6 \approx$

$Mo(CO)_6 > Cr(CO)_6$. Steric effects were also quantified by $\Delta(PCy_3)$ and/or $\Delta(PPh_3)$, the deviations from the LFER of the values of $\log k_2$ for these larger nucleophiles, and this method of data analysis was continued up to 1984 [13].

Meanwhile, in relation to these steric effects, a very useful quantitative measure of the size of P-donor ligands had been suggested, namely the Tolman cone angle θ [14], and Kochi and co-workers [15] showed that data for associative reactions of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_2(p\text{-}NO_2C_5H_4N)^+$ with P-donor nucleophiles gave an excellent fit to

$$\log k_2 = \alpha + \beta\, pK_a + \gamma\theta \qquad (1)$$

where the electronic parameters used for the P donors were estimated values of pK_a for the corresponding phosphonium ions in aqueous solution, a parameter that is linearly related to Δ(hnp). The use of pK_a, rather than Δ(hnp), is to be preferred because it leads to dimensionless values of β. Use of Δ(hnp) leads to units of reciprocal volts for β which, although satisfactory for comparative purposes, leads to numbers that have no absolute significance. The dimensionless values have the virtue that they provide a direct comparison of the strengths of the partial metal–L bonds in the transition state with the strengths of the fully formed H^+—L bonds in the phosphonium ion. While these bonds are not as closely comparable as would be the metal–L bonds in the transition states and in the fully formed M—L products, the strengths of the latter are not available and comparison with the fully formed H^+—L bonds is the best that can be done. In addition, a new parameter γ became available to provide a quantitative measure of the steric effect in units of receprocal degrees.

A similar equation to Eq. (1) was soon found [16] to describe the data for associative reactions of the carbonyl cluster $Ir_4(CO)_{12}$ and a linear plot of $\log k_2 - \beta\Delta(\text{hnp})$ against θ was obtained over a 70° cone angle range. However, as these workers pointed out, a more general type of behaviour must involve a change from Eq. (1) to

$$\log k_2 = \alpha + \beta\, \Delta(\text{hnp}) \qquad (2)$$

since those complexes that show a linear dependence on Δ(hnp) or pK_a, irrespective of the size of the nucleophiles, would show a horizontal plot of $\log k_2 - \beta\, pK_a$ against θ. In other words, a general indication of the steric effects would involve a horizontal region of the plot of $\log k_2 - \beta\, pK_a$ vs. θ at low values of θ and this would change to a linear downward slope with increasing θ when θ became large enough. Examples of this behaviour were found to be shown by previously published data.

Almost simultaneously Giering and co-workers [17] had independently come to the same conclusion and essentially identical exemplarary plots were shown. Plots of $\log k_2$ vs. pK_a for isosteric nucleophiles (i.e. nucleophiles with the same cone angle), or for nucleophiles small enough not to show any steric effects, were called electronic profiles and plots of $\log k_2 - \beta\, pK_a$ against θ were termed steric profiles. They also quantified the change from no steric effect to a finite steric effect by the steric threshold θ_{st} and defined an intrinsic reactivity as being the value of $\log k_2$ for the quite small nucleophile $P(OMe)_3$ ($\theta = 107°$). This turns out not to be a good measure of an intrinsic reactivity of a complex because $P(OMe)_3$ is quite a strong base ($pK_a = 2.6$) and the strength of the metal–P bond in the transition state will be relatively large. The stability of the transition state will be determined significantly by the nature of the nucleophile and not solely by the nature of the complex as should be the case when measuring an intrinsic property of the complex. An alternative way of characterizing the reactivity of the complex is to define a standard reactivity [18] as being $\log k_2^0 = \log k_2 - \beta(pK_a + 4)$, i.e. the value of $\log k_2$ for a hypothetical nucleophile that is small enough ($\theta < \theta_{st}$) to exhibit no steric effects, and weak enough ($pK_a = -4$, i.e. weaker than any commonly used nucleophiles) that the metal–P bond strength in the transition state will be relatively small, and the value of the standard reactivity will be relatively close to the intrinsic reactivity, i.e. to the reactivity of the complex when stabilization of the transition state by bond formation is negligible. In principle the standard reactivity will only approach closely to the intrinsic reactivity when β decreases to zero but relative intrinsic reactivities will be given by the relative standard reactivities for those complexes that have equal values of β.

4. Recent developments: appropriate parameters for electronic and steric properties of P-donor nucleophiles

4.1. Electronic parameters

Although the electronic parameters pK_a or Δ(hnp) for the P-donor nucleophiles proved useful in the initial development of the data analysis they have been superseded recently by other more appropriate parameters. However, before these are considered, it has to be emphasized that the successful use of pK_a values described above suggests that it is only the σ-donor capacity of the nucleophiles that is important. Any π acidity that is characteristic of some P-donor ligands is not operative in the transition states, possibly because of the greater lengths of the only partial metal–P bonds formed. This means that any electronic parameter that might be used in the analysis of electronic effects in associative reactions should reflect only the σ-donor capacity of the nucleophiles. It is well known that C—O stretching frequencies in metal carbonyls are profoundly affected by the nature of any substituents present. Tolman [14c] suggested that the Al C—O stretching frequencies in the complexes $Ni(CO)_3L$ provided a good standard measure of the net electron donor capacity of the ligands L, i.e. the combined effects of σ donation of electrons to the metal and withdrawal of π electrons from the metal. These were expressed by the values $\chi = \nu_{C-O}(L) - \nu_{C-O}(P\text{—}t\text{-}Bu_3)$ since the ligand P—t-Bu_3 is the most effective net electron donor and ν_{C-O} in $Ni(CO)_3(P\text{—}t\text{-}Bu_3)$ is the smallest value observed. Tolman's values of χ have been replaced by a more extensive and precise set obtained by Bartik et al. [19]. Giering and co-workers [20,21] noted that pK_a values are related to χ by

$$pK_a = -(0.68 \pm 0.03)\chi - (0.047 \pm 0.010)\theta + (18.9 \pm 1.6) \tag{3}$$

provided that the P-donor ligands are only those that could be classified as simple σ donors, no evidence for any π-acid capacity being apparent. This evidence for π acidity was provided in other cases by the fact that the χ values for the suspected π acids deviated from the correlation shown by Eq. (3), the χ values being too high. The term -0.047θ in Eq. (3) was ascribed to the fact that the pK_a values were derived for the phosphonium ions $L{-}H^+$ in aqueous solution. Smaller $L{-}H^+$ ions would be more stabilized by hydration than would the larger ions, and their pK_a values would be higher as a result. The values of χ are, of course, not affected by hydration and the electronic parameter that is needed for correlations of the associative rate constants should not reflect hydration effects either because the kinetics are followed in non-solvating (generally non-polar) organic solvents. This suggests that the parameter χ would be better to use to define the σ donicity of those ligands that are σ donors only, and that it should be designated χ_d in these cases [21]. The σ donicity of those ligands that are also π acids can be expressed by χ_d values calculated from

$$\chi_d = \frac{-pK_a - 0.047\theta + 18.9}{0.68} \tag{4}$$

which is a rearranged version of Eq. (3), making use of experimental values of pK_a. This means that there are two classes of χ_d values: those for σ donors only which are identical with the χ values, and those for ligands that are π acids as well as σ donors which are derived from experimental pK_a values adjusted for the hydration effects according to Eq. (4). It has also to be remembered that some of the pK_a values quoted in the literature are not actually experimental values but have been derived indirectly. Thus interpolation between the values for PR_3 and $P(OR')_3$ is used to obtain values for $PR_2(OR')$ and $PR(OR')_2$. The provenance of all available pK_a values has been analyzed [22].

Because at least some of the χ_d values are so well defined by precise $\nu_{C{-}O}$ measurements, it seems that they should be preferred over pK_a values for use as electronic parameters in equations analogous to Eqs. (1) and (2). However, if this is done, β will be in units of centimeters and the numerical values will bear little relation to physical reality in the same way as those in units of reciprocal volts that were obtained when the electronic parameter Δ(hnp) was used. It is preferable therefore to use values of the parameter pK_a' [23] which can be obtained for σ donors from

$$pK_a' = 18.93 - 0.0464 \times 145 - 0.673\chi \tag{5}$$

and, for σ-donor and π-acid nucleophiles, from

$$pK_a' = pK_a + 0.0464(\theta - 145) \tag{6}$$

The numbers 18.93, 0.673 and 0.0464 correspond to the similar numbers in Eq. (3) but are given to slightly more significant figures that result from our analysis of the appropriate data [22]. The values of pK_a' for σ-donor nucleophiles still have the virtue of incorporating the precision of the measurements of χ, and the values of pK_a' for σ-donor and π-acid nucleophiles still necessarily have the same dependence on experimental or derived values of pK_a, and on the hydration corrections, that the corresponding χ_d values have. The term $\theta - 145$ in Eq. (6) is used so that the values of pK'_a are close to the values of pK_a, the correction for the unwanted dependence of pK_a on the size of the ligands being made relative to the very commonly used and intermediate-sized ligand PPh_3 which has a cone angle of 145° [14]. The term 0.0464×145 is required in Eq. (5) so that the combination of Eqs. (5) and (6) is equivalent to Eq. (3).

4.2. Steric parameters

Tolman's cone angles have the virtue of simplicity and have been very widely used in probing for steric effects on kinetic and thermodynamic data, but it has to be conceded that they are a very crude measure of the "size" of a P-donor ligand. Refinements have been proposed by Fergusson et al. [24] to take into account the fact that the ligands can be considered as irregular conic cogs, and the concept of ligand profiles was introduced. However, these ligand profiles are obtained from crystallographic data, and the sizes and conformations of the ligands in the crystal do not necessarily bear a close relation to those of the free ligands in solution or in the transition states of associative reactions. The data provided by the method of Fergusson et al. are quite compatible with Tolman's cone angles but they are available for relatively few ligands and are not therefore generally useful. Desanto et al. [25a] and Coville and co-workers [25b] have also provided a useful critique of various ways of quantifying ligand sizes, but again no data of such wide application as Tolman's are available.

Tolman's original cone angles were revised significantly by him on the basis of experimental data, and even his finally chosen values have been subjected to suggested modifications. In particular, Stahl and Ernst [26] proposed major increases of over 20° to the cone angles of $P(OMe)_3$ and $P(OEt)_3$. These increases were based partly on some thermodynamic data for reactions involving addition of several P-donors to a Ti(II) complex, and partly on conformations of the POR moieties in these ligands found crystallographically. No compressed conformation corresponding to that assumed by Tolman has ever been seen in a crystal structure [26]. There are, however, important difficulties raised by these proposed changes. Firstly the data found for associative reactions of $Ir_4(CO)_{12}$ [16] include values of $\log k_2$ for $L \equiv P(OEt)_3$ as well as for etpb (i.e. $P(OCH_2)_3CEt$), the latter ligand having a quite unambiguous cone angle of 101° by virtue of the very precise conformation that it is forced to adopt [14,26]. The data for $P(OEt)_3$ fit very well to Eq. (1) when the Tolman cone angle of 109° is used but not at all when the value of 134° proposed by Stahl and Ernst is used. This is typical of the problems raised when modifications are proposed on the basis of a lack of fit to one set of data without considering how the changes will affect the goodness of fit to (possibly numerous) other sets of data. Another problem that is raised is that one does not know what to do with all the other OR-containing ligands whose conformations could also lead to possible proposed changes. In fact, the data analysis proposed by Stahl and Ernst can be improved [22] so as to lead to increases of only 10° in the cone angles of $P(OMe)_3$

and $P(OEt)_3$ and these have much less serious implications. Giering and co-workers [27] use a cone angle of 136° for P—*n*-Bu_3 and some similar ligands but the effect of this change is small.

A much more fundamental objection to the use of Tolman's cone angles is that there seems to be no physical reason why kinetic or thermodynamic free-energy parameters should depend linearly, as in Eq. (1), on the size of the ligand as measured by a cone angle. Recently another approach has been proposed by Brown and Lee [28]. They have estimated ligand repulsion energies E_R by molecular mechanics calculations on the molecules $Cr(CO)_5L$ and suggest that these would be much more appropriate than Tolman's cone angles in analyzing steric effects on kinetic and thermodynamic behaviour. Although the E_R values have a greater physical significance in this context than the cone angles, it does not yet appear [23,28,29] that they lead to better fits of kinetic data to appropriate equations analogous to Eq. (1). Part of this may be due to the use of $\delta(^{13}CO)$ by Brown and Lee as the electronic parameter for P donors acting as nucleophiles even though this parameter includes effects due to π acidity as well as σ donicity [30]. If π acidity were important in the transition states of associative reactions, then $\delta(^{13}CO)$ would not be an appropriate parameter to allow for it. This is because π acidity would be expected to reinforce the effects of σ donicity in the transition states whereas π acidity counteracts the σ donicity effects on $\delta(^{13}CO)$. If π acidity is not important in the transition states, then an electronic parameter that includes it is equally inappropriate. One of the very useful results of the calculations of E_R values by Brown and Lee is that, for quite a large group of ligands, there is a good linear correlation between E_R and Tolman's cone angles. To this extent it becomes possible to say that plots of kinetic and thermodynamic parameters against cone angles are equivalent to plots against an energy parameter. It remains to be seen whether the E_R values will replace the empirically very successful use of Tolman's cone angles in the analysis of kinetic data for associative reactions involving P-donor nucleophiles in particular. To the extent that the latter, and the pK_a' electronic parameters, lead to a good fit of a very wide range of such data (see below) they can be considered to have taken on a validity of their own, independent of their precise origin. In this sense they resemble the correlations observed in Pt(II) kinetics between $\log k_2$ values for a given complex and *n*(Pt), a parameter derived from reactions of a standard complex [4,5], i.e. any given complex is being compared with a chosen standard complex. For reactions of metal carbonyls we can imagine that any given complex is being compared with a hypothetical Platonic standard complex for which reactions with all P-donor nucleophiles have been studied.

5. The importance of the steric threshold

Giering and co-workers [21] have suggested that the onset of steric effects on the rates of reactions involving P-donor nucleophiles is quite sudden. This enabled them to propose that the data should be represented by

$$\log k_2 = a(\chi_d) + b(\theta - \theta_{st})\lambda + c \tag{7}$$

or, as we would prefer it [23], by

$$\log k_2 = \alpha + \beta(\text{p}K'_a + 4) + \gamma(\theta - \theta_{th})\lambda \tag{8}$$

These equations are very closely related in view of the connection between χ_d and pK'_a discussed above and Eq. (8) allows for a better definition of the standard reactivity. They both incorporate the very important feature that λ is a switching function which is zero when the cone angle is less than or equal to the steric threshold θ_{th} or unity when θ exceeds θ_{th}, and steric effects are measured by the gradient γ of the steric profile obtained by plotting $\log k_2^0 = \log k_2 - \beta(\text{p}K'_a + 4)$ against θ. The fact that the data analyzed by Giering and co-workers [21] fit well to Eq. (7) or (8) confirms the sharpness of the steric thresholds in those cases and shows that our earlier assumption [18] that the onset of steric effects might be more gradual was incorrect. This has an important practical consequence in that Eqs. (7) and (8) allow objective computer analysis of data, whereas no analytical expression suitable for computer analysis is available if the onset of the steric effects is more gradual.

6. The protocol for stereoelectronic analysis of the kinetic data

The first step in the data analysis is to plot values of $\log k_2$ against pK'_a. The exactly isosteric nucleophiles $P(p\text{-}XC_6H_4)_3$ ($X \equiv$ H, MeO, Me, Cl, F etc.) have a wide range of pK'_a values [23] and the values of $\log k_2$ for these nucleophiles, when plotted against pK_a', will immediately provide a value of β. Any positive deviations of $\log k_2$ for smaller nucleophiles, or negative deviations for larger nucleophiles, will provide an indication of steric effects. The series of almost isosteric nucleophiles $P(OPh)_3$ ($\theta = 128°$), $P(O\text{–}i\text{-}Pr)_3$ ($\theta = 130°$) and $P\text{–}n\text{-}Bu_3$ ($\theta = 132°$) can provide similar information and, if both sets of nucleophiles have been used, the β values should be the same. When steric effects are small (i.e. all nucleophiles have $\theta \leqslant \theta_{th}$), the data should lie on a linear plot of $\log k_2$ against pK'_a which will also provide a value of β.

When an initial value of β has been obtained, it is possible to obtain the steric profile by plotting $\log k_2^0$ against θ. In favorable circumstances an initial value of θ_{th} can be obtained from the intersection of the horizontal ($\theta \leqslant \theta_{th}$) and downward-sloping ($\theta > \theta_{th}$) parts of the steric profile, and an initial value of γ can be obtained from the slope of the latter. The data can then be refined by use of Giering's least-squares computer program which minimizes the squares of the deviations of $\log k_2$(expt) from $\log k_2$(calc). (We are very grateful to Professor Giering for providing us with a copy of his program.) The program requires initial input of values of θ_{th} and the optimization of the fit by varying θ_{th} until a minimum r.m.s. deviation is obtained. This provides values of the standard reactivity, β and γ, together with estimates of their standard deviations but not, unfortunately, of the standard deviation of θ_{th}. Initial plotting of the data is always advisable in giving a graphical indication of the success of the model in accounting for the data, and an indication of any values of $\log k_2$ that show a very poor fit, for some reason, and that had better be ignored. When the best fit is finally obtained the corresponding steric profile can be plotted to illustrate the goodness of fit [21–23].

In choosing nucleophiles to use in such a study it is important to avoid using only nucleophiles which show a linear correlation between pK'_a and θ (i.e. $pK'_a = a\theta + b$). This is often approximately true for a number of nucleophiles (e.g. PPh_nR_{3-n}) but obviously not for groups of isosteric or near-isosteric nucleophiles. The correlation would prevent determination of separate electronic and steric effects [27].

Availability of data for a judiciously chosen set of nucleophiles can therefore lead to analysis according to Eq. (8). Over 50 sets of data have been analyzed successfully in this way [22,23], thus demonstrating the general validity of the model and of the electronic and steric parameters used (see above). The analyses provide values of the parameters θ_{th}, standard reactivity, β and γ which are characteristic of the dynamic natures of the carbonyls as reflected in their associative reactions with P-donor nucleophiles. Two representative steric profiles are shown in Figs. 1 and 2, that in Fig. 1 being based on the very first set of such data published [7].

The method has been used by Giering and co-workers [27,31] to correlate a large number of physiochemical data. They have also introduced [27] another potentially

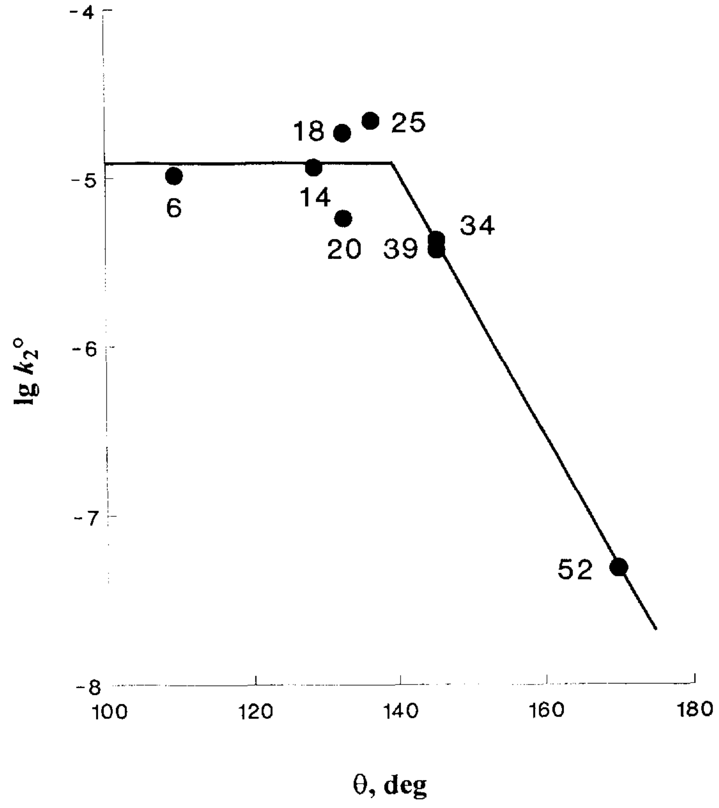


Fig. 1. The steric profile [22] for reactions of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with P-donor nucleophiles in toluene (standard reactivity, -4.9 ± 0.1; $\theta_{th} = 139°$; $\beta = 0.17 \pm 0.02$; $\gamma = -0.078 \pm 0.009$ deg^{-1}; r.m.s. deviation, 0.16). The ligand numbering, here and in other figures, is taken from Appendix A.

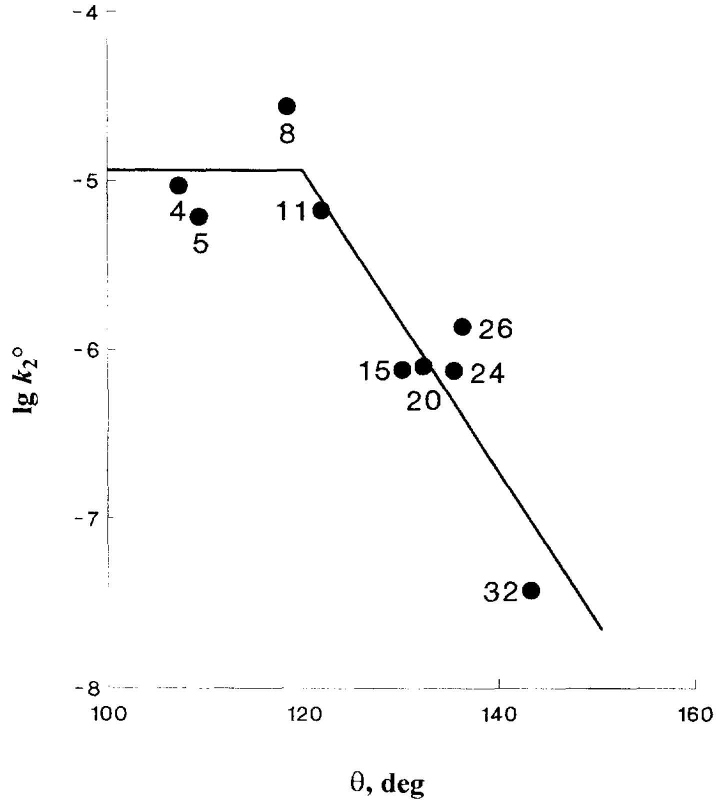


Fig. 2. The steric profile [22] for reactions of $(\eta^5\text{-}Me_5C_5)Rh(CO)_2$ with P-donor nucleophiles in toluene (standard reactivity, -4.9 ± 0.03; $\theta_{th} = 120°$; $\beta = 0.09 \pm 0.05$, $\gamma = -0.093 \pm 0.017\ \text{deg}^{-1}$; r.m.s. deviation, 0.30).

important parameter that is related to the number of aryl groups attached to the P atom in P-donor ligands, and that gives rise to the term aryl effect. This effect appears to be surprisingly independent of any substituents in the aryl rings and its physical origin remains obscure. In some correlations it is evidently quite important but it is not yet clear that it leads to significant changes in the other parameters considered here although the possibility that it might must be borne in mind.

7. The implications of the derived parameters

The value of β is directly related to the varying amounts of stabilization induced in the transition state by the series of P-donor nucleophiles used and referenced to the corresponding fully formed H^+—P bonds as measured by pK_a'. Relative values of β provide a measure of the relative extents of bond making where the extent of bond making is given by the ratio of the strength of an M···P bond in the transition state to the strength of the fully formed M—P bond in the absence of steric effects. This is only true to the extent that the M—P bonds do not vary very much from complex to complex since a smaller proportion of a larger M—P bond energy could be larger than a larger proportion of a smaller M—P bond energy. However, to a first approximation, smaller values of β can be taken to reflect smaller extents of bond formation, and larger values larger extents, i.e. earlier and later transition states respectively. For the following reasons this extent of bond formation can be taken as constant for the various nucleophiles which react with a given complex. Although it might be thought that the extent of bond making, defined in this way, could increase with increasing basicity of the nucleophiles, this has not so far been demonstrated. If it did occur, the value of β found from a set of nucleophiles with $\theta < \theta_{th}$ (where there would be no steric difficulty for those nucleophiles with higher pK_a' values to form stronger and shorter bonds) would be expected to be greater than the value found, for example, from a set of isosteric nucleophiles with $\theta > \theta_{th}$ (where forming stronger and shorter bonds would be sterically inhibited). This type of behaviour would correspond to the presence of "cross-terms" involving both pK_a' and θ in a more general equation than Eq. (8) and no such behaviour has been observed.

Recent measurements [32] of volumes of activation for associative reactions of a wide variety of P-donors with $(\mu\text{-H})_2Os_3(CO)_{10}$ to form the adducts $(\mu\text{-H})(H)Os_3(CO)_{10}L$ are relevent to this point. The steric threshold is about 150° [32,33] and the values of $\Delta V^{\neq}$ for *para*-substituted triphenylphosphine nucleophiles $P(p\text{-}XC_6H_4)_3$ ($\theta = 145°$), which cover a range of pK_a' from -1.39 to 5.13, are constant at -20.0 ± 0.4 cm^3 mol^{-1}. If the more basic of these nucleophiles had shorter Os···P bonds in the transition states, the values of $\Delta V^{\neq}$ would have been expected to decrease perceptibly with increasing pK_a'.

The existence of the rather sharply defined steric threshold, quantified by the parameter θ_{th}, also has important implications. Metal carbonyl complexes, including in particular metal carbonyl clusters, exist as closely packed polytopal arrays of CO (and other) ligands with the metal atom(s) contained inside the ligand polytope [34]. This suggests that any expansion of the ligand polytope caused by the approach of a nucleophile would be dependent on the size of that nucleophile, and it seems difficult therefore to accept that there would be any region of the steric profile where no dependence on θ would occur. This was why it was believed [35] that steric profiles would curve down gradually as θ decreased so that there would not be a sharp steric threshold. The fact that well-defined horizontal regions of steric profiles do occur must therefore be addressed. It has recently been proposed [23] that, at some stage during the approach of the nucleophile, a sudden and precise change in the geometry of the carbonyl is induced. This results in the formation of a relatively high energy isomeric form (the transition state isomer; TSI) of the carbonyl which contains a well-defined and roughly conical space in the ligand polytope. The space made available will be larger than that required by the smaller nucleophiles but, as θ increases, there will come a stage where the nucleophile will just fit into the space and the cone angle of this nucleophile will define the steric threshold. Accommodation of larger nucleophiles must be accompanied by a further opening up of the TSI if the same amount of metal–L bond making is to be maintained. This will increase the energy of the transition state to an extent that depends on how much θ exceeds θ_{th} and that reflects the flexibility of the TSI. The parameter γ will therefore be a quantitative measure of this flexibility, becoming more negative as the flexibility decreases. An alternative possibility is that the larger nucleophiles can only be accommodated at the cost of lengthening the M···L bond in the transition state (i.e. the TSI is totally inflexible) and the transition state will be less stabilized as a result. The measurements [32] of $\Delta V^{\neq}$ mentioned above strongly suggest that, in the reactions of $(\mu\text{-H})_2Os_3(CO)_{10}$, the TSI does open up further to accommodate nucleophiles with cone angles between the steric threshold of 150° and 157° while maintaining the same Os···L bond length. However, the distorted TSI is unable to accommodate nucleophiles with even larger cone angles and these can only form Os···L bonds of greater length which stabilize the transition states to a smaller extent. It seems therefore that both effects can contribute to the value of γ and that Os···L bond lengthening for the largest nucleophiles is not easily detected by changes in β in this case. The situation is described, in cartoon form, in Fig. 3.

The significance of the values of θ_{th} has also to be considered in relation to the amount of bond making indicated by β. In a case where the same value of θ_{th} is found for two complexes that have significantly different β values, the space opened up in the TSI of the complex with the higher β value would have to be larger than that opened up in the other TSI. This follows because, if the space were equally large, there would be an earlier onset of the steric effect when bond making is greater and the M···L bond length is shorter. Only if the space is larger can the steric threshold for greater bond making be the same as when there is less bond making. On the contrary, if there are two complexes with similar β values but significantly different values of θ_{th}, the complex showing the smaller value of θ_{th} would be expected to have the smaller opening. These conclusions are likely to be valid only to a first approximation, but they may be useful as a starting point in considering the implications of data for particular systems.

The standard reactivity is an unambiguously defined parameter but its usefulness is limited. Only when $\beta \rightarrow 0$ does it correspond to the intrinsic reactivity which defines the energy necessary to form the TSI without any assistance from bond making. When two complexes have the same values of β, then their relative intrinsic reactivities are given by the relative values of the standard reactivities. When complexes have different finite values of β, care has to be taken to assess what happens to the relative reactivities when the basicities of the nucleophiles are reduced below $pK_a' = -4$. It is quite possible that electronic profiles for nucleophiles with $\theta \leqslant \theta_{th}$ will cross over at pK_a' values below -4 so that a complex that has a higher standard reactivity than another, but also a higher β value, will have a lower intrinsic reactivity. The cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ mentioned above has a very high value of β (0.47) [33] and even the hypothetical nucleophile with $pK_a' = -4$ can be shown to contribute very substantially to the stabilization of the transition state so that the standard reactivity is much greater than the intrinsic reactivity.

Although a full analysis of the various electronic and steric parameters found for mononuclear and dinuclear complexes will have to be considered elsewhere, it is

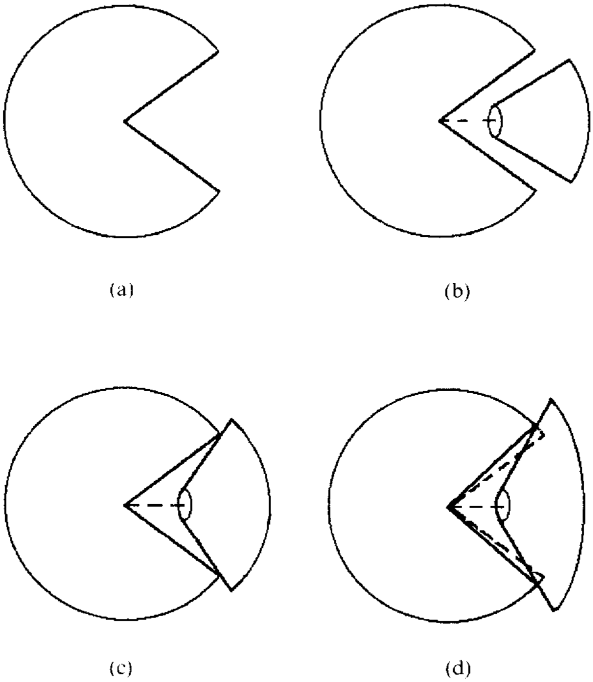


Fig. 3. A cartoon representation of (a) a TSI with an open space made available for approach of a nucleophile to its electrophilic centre. (b) The TSI with a smaller P-donor nucleophile ($\theta < \theta_{th}$) attached to the electrophilic centre. The nucleophile is shown as a truncated cone (as any P-donor ligand must be when isolated from its standard metal centre [14]) which forms a partial bond to the electrophilic centre without any steric interaction. (c) The TSI with an attached nucleophile ($\theta = \theta_{th}$) such that a partial bond of the same length as in (b) can just be formed without unfavorable steric interaction. (d) The TSI with a larger attached nucleophile ($\theta > \theta_{th}$) which has forced the TSI to open up further so that a partial bond of the same length as in (b) and (c) can be formed, albeit at some energy cost. The opening shown by the broken lines is of the same size as those in the undistorted TSIs in (a)–(c). If the TSI is too inflexible to open up further in this way, then larger nucleophiles of this sort will only be able to form longer and therefore weaker bonds than they would otherwise do.

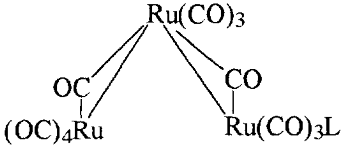
worth examining, for illustrative purposes, the data found for the (Cp)– and (Cp*)–Rh(CO)$_2$ complexes for which the steric profiles are shown in Figs. 1 and 2 (Cp$\equiv$C$_5$H$_5$ and Cp*$\equiv$Me$_5$C$_5$.) The major difference is the much smaller value of θ_{th} for the Cp* complex, a much earlier onset of steric effects being expected in view of the greater steric congestion caused by the methyl substituents on the Cp* ring. This is so even though the amount of bond making is greater for the Cp complex (as expected, perhaps, from the lower electron donation from the Cp ligand) and this would be expected to lower the value of θ_{th}. The flexibility of the TSI for the Cp* complex is slightly lower but the standard reactivities are the same. Since β for the Cp complex is greater, this implies that the intrinsic reactivity of the Cp complex is lower than that of the Cp* analogue. The methyl substituents in the Cp* ring must therefore facilitate the formation of the TSI, i.e. they must encourage the slippage process [10].

8. Results of stereoelectronic data analysis for some metal carbonyl clusters

The kinetic behaviour of metal carbonyl clusters has been reviewed [36] but little attention was given to systematic studies of associative reactions. However, sufficient data for a substantial number of metal carbonyl clusters are now available for the type of stereoelectronic analysis described above to be possible and parameters for a selection of clusters are shown in Table 1.

8.1. Ru_3 clusters: $Ru_3(CO)_{12}$

$Ru_3(CO)_{12}$ was the first cluster shown [11,12] to undergo associative reactions with P-donor nucleophiles in addition to reacting via a CO-dissociative path. According to its standard reactivity it is four orders of magnitude more susceptible to nucleophilic attack than $Mo(CO)_6$ (standard reactivity, −7.5). ($Tc_2(CO)_{10}$ was not found to react by an associative path [45]). It has been proposed that this susceptibility to nucleophilic attack is due to the cluster's ability to undergo Ru–Ru bond breaking concurrently with Ru–L bond making so as to form an intermediate



I

such as **I** in which each Ru atom has maintained its 18-electron configuration in a way that only clusters can. Subsequent loss of a CO ligand and reformation of the Ru–Ru bond will lead to substitution although an alternative possibility would be fragmentation of **I**, an outcome that is well known in reactions of several Ru_3 and Os_3 clusters with P donors that are more nucleophilic [36,46].

$Ru_3(CO)_{12}$ shows another, very unusual feature which is that the value of β found for nucleophiles with $\theta \leqslant 132°$ is considerably lower (0.16) than that found for the $P(p\text{-}XC_6H_4)_3$ nucleophiles ($\theta = 145°$; $X \equiv CF_3$, Cl, F, H, Me or MeO) [47]. This will be discussed later.

8.2. Substituted Ru_3 clusters

The Ru_3 clusters that contain one or two P-donor substituents are also found to react via associative paths, in addition to dissociative paths, and systematic data are available for some of these in Table 1. This enables one to examine the effect of a series of substituents on the associative reactions of the clusters, just as substituent

Table 1
Kinetic parameters for associative reactions of some metal carbonyl clusters with P-donor nucleophiles[a]

Cluster (number of nucleophiles used)	Reference	θ_{th} (deg)	Standard reactivity	β	γ (deg^{-1})	R.M.S. deviation
$Ru_3(CO)_{12}$[b] (12)	[22]	120	-3.4 ± 0.2	0.15 ± 0.02	-0.03 ± 0.01	0.25
$Ru_3(CO)_{12}$[c] (6)	[22]			0.347 ± 0.013		0.059
$Ru_3(CO)_{11}$ $P(OEt)_3$ (5)	[37]	123	-4.2 ± 0.1	0.22 ± 0.02	-0.18 ± 0.01	0.07
$Ru_3(CO)_{11}$ PMe_3 (6)	[38]	123	-3.1 ± 0.1	0.15 ± 0.02	-0.125 ± 0.006	0.07
$Ru_3(CO)_{11}$ $P(OPh)_3$ (6)	[39]	118	-4.2 ± 0.2	0.25 ± 0.03	-0.107 ± 0.015	0.14
$Ru_3(CO)_{11}$ $P(n\text{-}Bu)_3$ (7)	[40]	129	-2.4 ± 0.1	0.07 ± 0.02	-0.114 ± 0.010	0.09
$Ru_3(CO)_{11}$ PCy_3 (8)	[40]	123	-3.2 ± 0.2	0.23 ± 0.03	-0.100 ± 0.015	0.22
$Ru_3(CO)_{10}\{P(n\text{-}Bu)_3\}_2$ (4)	[40]	$\leqslant 101$	$\geqslant -3.2$	0.03 ± 0.02	-0.019 ± 0.007	0.09
$Ru_3(CO)_{10}$ $(PCy_3)_2$ (5)	[40]	$\leqslant 101$	$\geqslant -2.6$	0.09 ± 0.02	-0.009 ± 0.004	0.09
$Ru_3(CO)_{10}$ (μ-dppm) (6)	[41]	$\leqslant 101$	$\geqslant -2.9$	0.17 ± 0.05	-0.053 ± 0.015	0.31
$(\mu\text{-}H)_2Os_3(CO)_{10}$ (11)	[33]	150	-1.19 ± 0.28	0.44 ± 0.05	-0.20 ± 0.02	0.34
$Os_3(CO)_9(\mu_4\text{-}C_4Ph_4)$ (9)	[29]	156	-2.5 ± 0.1	0.26 ± 0.02	-0.21 ± 0.01	0.12
$Rh_4(CO)_{10}$ $(PCy_3)_2$ (4)	[42]	140	$+1.60 \pm 0.01$	0.050 ± 0.001	-0.041 ± 0.001	0.001
$Rh_4(CO)_9(etpb)_3$ (8)	[42]	120	$+0.15 \pm 0.11$	0.12 ± 0.02	-0.042 ± 0.050	0.08
$Rh_4(CO)_9\{HC(PPh_2)_3\}$ (4)	[43]	121	$+0.64 \pm 0.01$	0.40 ± 0.01	-0.155 ± 0.001	0.004
$Ir_4(CO)_{12}$[d] (8)	[16]	$\leqslant 101$	$\geqslant -3.4$	0.31 ± 0.05	-0.091 ± 0.010	0.30
$Ir_4(CO)_{11}$ (PPh_3) (4)	[44]	$\leqslant 101$	$\geqslant 2.1$	0.30 ± 0.03	-0.104 ± 0.010	0.114
$Ru_5C(CO)_{15}$[e] (7)	[50a]	117	$+2.86 \pm 0.18$	0.21 ± 0.04	-0.07 ± 0.01	0.13
$Fe_5C(CO)_{15}$[f] (4)	[50b]	$\leqslant 101$	$\geqslant 0.9$	0.33 ± 0.10	-0.07 ± 0.02	0.15
$Ru_5C(CO)_{15}$[g] (9)	[50a]	148	-2.30 ± 0.13	0.59 ± 0.03	-0.233 ± 0.012	0.12
$Ru_6C(CO)_{17}$ (14)	[23]	119	$+1.51 \pm 0.26$	0.41 ± 0.04	-0.20 ± 0.01	0.41

[a] The data analysis was carried out as described in the text. Where the results are different from published data, the values here are from later analysis [22]. The standard reactivities have been adjusted to 25°C but the other parameters are appropriate to the temperature of measurement, usually 50°C or less. Values of β and γ are not appreciably sensitive to temperature (see for example [16]).

[b] In chlorobenzene with $\theta \leqslant 140°$.

[c] In chlorobenzene with $\theta = 145°$.

[d] Plus additional data for $P(O\text{—}i\text{-}Pr)_3$.

[e] Data for addition reactions of ligands with $\theta \leqslant 130°$.

[f] Data for addition reactions of ligands with $\theta \leqslant 128°$.

[g] Data for concerted substitution reactions with $\theta > 136°$.

effects on dissociative reactions can be studied [22,37,40,48]. The clearest substituent effect that is evident is the inverse correlation shown between the standard reactivity and β for the $Ru_3(CO)_{11}L$ clusters. This reflects the fact that, the more intrinsically susceptible a cluster may be towards nucleophilic attack, the less it will need assistance from metal–nucleophile bond making during its associative reactions and the less discriminating it will be towards different nucleophiles. The correlation is shown in Fig. 4 to be linear for $L \equiv P\text{—}n\text{-}Bu_3$, $L \equiv PMe_3$, $L \equiv CO$, $L \equiv P(OEt)_3$ and $L \equiv P(OPh)_3$, but the data for $L \equiv PCy_3$ show that this cluster has a higher value of standard reactivity than would be inferred from its β value. Least-squares analysis shows that the linear relationship is governed by the equation $SR = -1.62 - 10.8\beta$ (where SR is the standard reactivity) with a correlation coefficient of 0.983. This has the interesting implication that there is an isokinetic relationship of a novel kind in that a nucleophile with a pK_a' of 7 (i.e. $pK_a' + 4 = 10.8$) will react with all those clusters at the same rate, a fact that is clearly illustrated in Fig. 5. This figure also

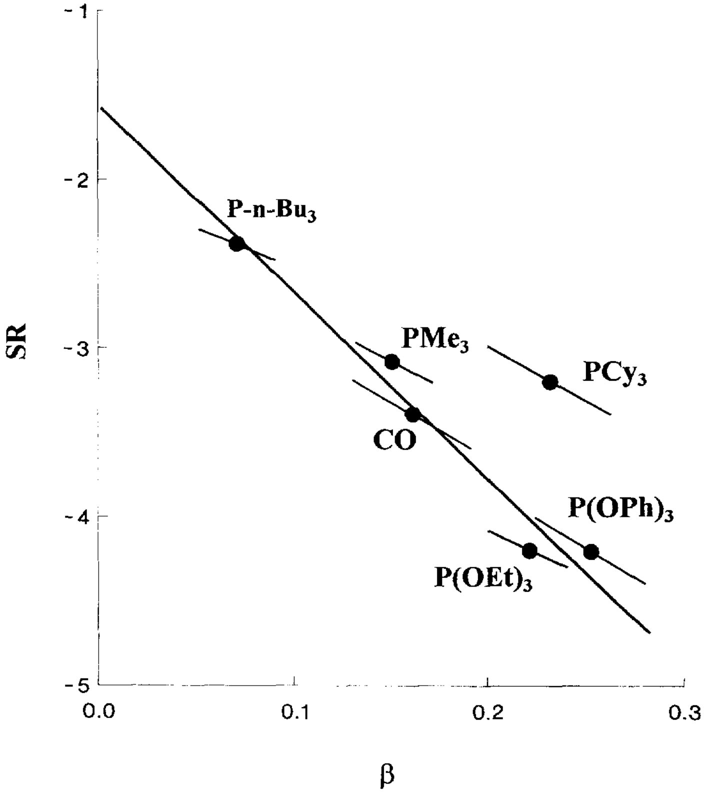


Fig. 4. The correlation of standard reactivity SR for the clusters $Ru_3(CO)_{11}L$ with the corresponding value of β. The line is the least-squares line drawn through the data for all the ligands L except for $L \equiv PCy_3$, and $SR = -1.62 - 10.8\beta$ ($R = 0.983$). The uncertainties of each point represent the covariant uncertainties of standard reactivity and β (Table 1), high standard reactivities corresponding to low values of β.

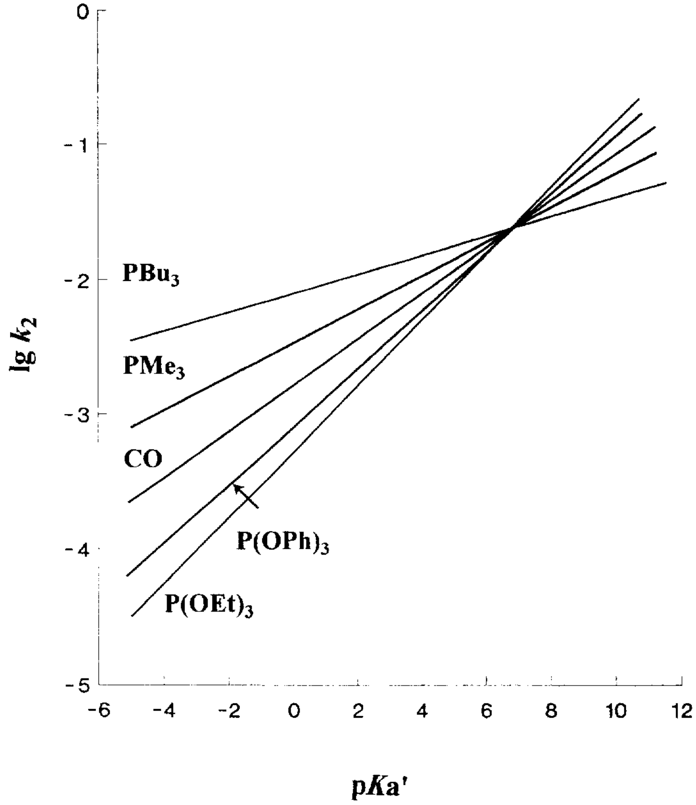


Fig. 5. Electronic profiles for the clusters $Ru_3(CO)_{11}L$ drawn so that the standard reactivities and β values fit the least-squares equation $SR = -1.62-10.8\beta$ (see Fig. 4 and the text).

shows that the standard reactivity and the intrinsic reactivity of these clusters varies as $L \equiv P\text{—}n-Bu_3 > PMe_3 > CO > P(OPh)_3 > P(OEt)_3$. There is also a reasonably good inverse correlation between the values of θ_{th} and β, especially if an uncertainty of $\pm 2°$ is assumed for the θ_{th} values. An earlier onset of steric effects might be expected as the degree of bond making becomes more pronounced. The values of γ do not appear to correlate with any of the other parameters although they do increase (become less negative) as $\theta(L)$ increases from 109° to 128° after which they remain constant. An increase in the flexibility of the TSI with increasing size of the substituent is unexpected at first sight.

The electronic and steric effects of the P-donor substituents on the standard reactivities of the clusters are interesting. Since some of the substituents show π acidity as well as σ-donor properties the parameter $\delta(^{13}CO)$ [30], which measures the net electron donicity of the substituents, might be the best to use [22]. The data for $L \equiv P(OPh)_3$ and $L \equiv P\text{—}n-Bu_3$, which are nearly isosteric, show that the standard reactivity increases with increasing net electron donicity of the substituent, and the standard reactivities for $P(OEt)_3$ and PMe_3 are lower than expected from their

$\delta(^{13}CO)$ values to an extent that increases with decreasing cone angle. In fact the data for these four substituents fit well to the equation $SR = -4.8 + 0.4\delta(^{13}CO) + 0.04\theta$, showing quantitatively that the standard reactivity increases both with increasing net electron donicity and with increasing size of these substituents. The former effect shows that greater electron donicity encourages Ru–Ru bond breaking to a greater extent than it discourages Ru–L bond making, while the latter effect shows that larger substituents encourage cluster opening to form the TSI as would be expected. However, the standard reactivity for $L \equiv PCy_3$ is lower than expected which shows that, when the substituent is large enough, steric destabilization of the TSI can offset destabilization of the ground state cluster. When $L \equiv CO$ the standard reactivity is much greater than would be expected from its small size and low net electron donicity compared with the behaviour of the P-donor substituents.

The data for the clusters $Ru_3(CO)_{10}L_2$ ($L \equiv P\text{–}n\text{-}Bu_3$ or PCy_3) show that the extra substituent decreases the extent of bond making in the transition state and suggest early and rather flexible transition states, even though the steric effects come into play with the smallest nucleophiles. The standard reactivities are probably not particularly different from those of the corresponding monosubstituted clusters but, because of the low β values, this implies that the intrinsic reactivities are enhanced by the second substituent, i.e. Ru–Ru bond breaking and cluster opening are facilitated. The cluster with the bridging dppm substituent has a significantly later transition state with more bond making and a less flexible TSI [41].

As mentioned above, a general feature of the associative reactions of Ru_3 clusters is that they often lead to fragmentation with eventual formation of mononuclear products. This was observed qualitatively in the earliest systematic kinetic study where $P(OEt)_3$, etpb and $P\text{–}n\text{-}Bu_3$ induced fragmentation [11]. A later, more detailed study [46a] showed that fragmentation occurs exclusively via associative F_N2 pathways and that the relative importance of F_N2 and S_N2 pathways can vary appreciably with the nature and number of the substituents present in the cluster. $Ru_3(CO)_{11}(P\text{–}n\text{-}Bu_3)$ is particularly susceptible to fragmentation, presumably owing to the unique lengthening of the Ru–Ru bonds cis to the substituents in the monosubstituted clusters [49]. F_N2 reactions of $Ru_3(CO)_{10}(dppm)$ have also been observed [41].

8.3. *Rh_4 and Ir_4 clusters*

No systematic nucleophile dependence studies have been carried out on $Rh_4(CO)_{12}$ but its associative reactions with PPh_3 are known [43] to be about 10^8 times faster than those of $Ru_3(CO)_{12}$ [11]; so it is extremely susceptible to nucleophilic attack. Even its substituted derivatives $Rh_4(CO)_{10}(PCy_3)_2$ and $Rh_4(CO)_9(etpb)_3$ [42] have standard reactivities that are four to five orders of magnitude greater than that of $Ru_3(CO)_{12}$ and the relative rates of reaction with PPh_3 are as follows: $Ru_3(CO)_{12}$, 1; $Rh_4(CO)_{12}$, 2×10^8; $Rh_4(CO)_{10}(PCy_3)_2$, 3×10^5; $Rh_4(CO)_9(etpb)_3$, 5×10^3; $Rh_4(CO)_9[HC(PPh_2)_3]$, 1×10^2. $Rh_4(CO)_{10}(PCy_3)_2$ has a very high standard reactivity and a correspondingly low degree of help from bond making (very low β) whereas the standard reactivity of $Rh_4(CO)_9(etpb)_3$ is lower and the β value is higher.

The flexibilities of the TSIs are both high. $Rh_4(CO)_9[HC(PPh_2)_3]$ also has a high standard reactivity but it is accompanied by a high β value, and the TSI is relatively inflexible; so bridging ligands seem to behave, compared with monodentates, in the same way in the Ru_3 and Rh_4 clusters.

$Ir_4(CO)_{12}$ reacts associatively with PPh_3 10^{11} times more slowly than $Rh_4(CO)_{12}$ does, and 500 times more slowly than $Ru_3(CO)_{12}$, but it reacts with P–*n*-Bu_3 about 10^5 times more rapidly than does $Os_3(CO)_{12}$ [46b]. It is clear that reactivity increases greatly on going from $M_3(CO)_{12}$ to $M_4(CO)_{12}$ for both second- and third-row transition metals, and that third-row metal clusters are much less reactive than second-row metal clusters.

$Ir_4(CO)_{12}$ has quite a high value of β and a moderately high flexibility of its TSI. Substitution of PPh_3 into this cluster does not affect β or γ appreciably [44], but the reactivities are all increased by a factor of about 20. This is similar to the Rh_4 clusters where introduction of PPh_3 increases the rates of associative reactions with PPh_3 by 50 times [43].

The clusters $Rh_4(CO)_{10}L_2$ ($L \equiv PCy_3$ or PPh_3) both undergo associative fragmentation reactions [42] but $Rh_4(CO)_9L_3$ ($L \equiv$ etpb [42] or $HC(PPh_2)_3/3$ [43]) and the Ir_4 clusters do not [16,44]. The factors causing such behavior deserve further investigation.

8.4. *High nuclearity carbonyl clusters*

The first high nuclearity carbonyl cluster to receive systematic kinetic study [23] was $Ru_6C(CO)_{17}$ which has the Ru atoms arranged octahedrally around the encapsulated C atom [50]. It shows a very high susceptibility to nucleophilic attack which always leads to substitution. It is about 10 times more reactive than $Rh_4(CO)_9[HC(PPh_2)_3]$ but has a very similar and high β value and an exceptionally large negative value of γ. Its standard reactivity is about five orders of magnitude greater than that of the smaller $Ru_3(CO)_{12}$ cluster and about the same as that of $Rh_4(CO)_{10}(PCy_3)_2$. However, its intrinsic reactivity will be less than that of the latter cluster because of its higher β value. The values of γ and β show that increasing the size of the nucleophiles involved produced a decrease of 10^{10} in the rates but the increase in their basicities produced an increase of "only" 10^6. Both effects are very large although they often oppose each other in determining the actual rates. The θ_{th} value is low but not uncommonly so.

The high nuclearity carbonyl cluster $Ru_5C(CO)_{15}$ can easily be obtained from $Ru_6C(CO)_{17}$ [51] and has a square-based pyramidal arrangement of Ru atoms with the C atom lying just below the basal plane but being within bonding distance of all the Ru atoms [50]. Its kinetic behaviour showed several new features [52]. Nucleophiles with cone angles of 133° or less react rapidly to form $Ru_5C(CO)_{14}L$ in two successive stages, the first of which is strictly first order in [L] while the second is independent of [L]. The spectra of the products of the first stage are similar to those of the adducts $Ru_5C(CO)_{15}L$ ($L \equiv$ NCMe, MeOH, halides or CO), the structure of the adduct with NCMe having been shown crystallographically to have an Ru_4 butterfly structure with the wing tips being bridged by an $Ru(CO)_3NCMe$ moiety

[50]. The two stages are therefore as follows:

$$Ru_5C(CO)_{15} + L \rightarrow Ru_5C(CO)_{15}L \tag{9}$$

$$Ru_5C(CO)_{15}L \rightarrow Ru_5C(CO)_{14}L + CO \tag{10}$$

Nucleophiles with cone angles of 136° or greater react more slowly than the smaller nucleophiles to give $Ru_5C(CO)_{14}L$ but do so in a single step that is first order in [L]. The two types of associative process, adduct formation and concerted single step substitution, are characterized by two very different sets of kinetic parameters (Table 1) with electronic profiles being shown in Fig. 6. The two types of reaction must occur via nucleophilic attack at two quite different sites on the cluster. Adduct formation is believed to involve attack at a basal Ru atom with concurrent breaking of an apical–basal Ru–Ru bond. The other path is not so clearly definable but could involve breaking a basal–basal Ru–Ru bond to form a different adduct that loses CO rapidly so that it is not detectable. It may well be that the two different values of β found for reactions of $Ru_3(CO)_{12}$ with smaller and larger nucleophiles (see

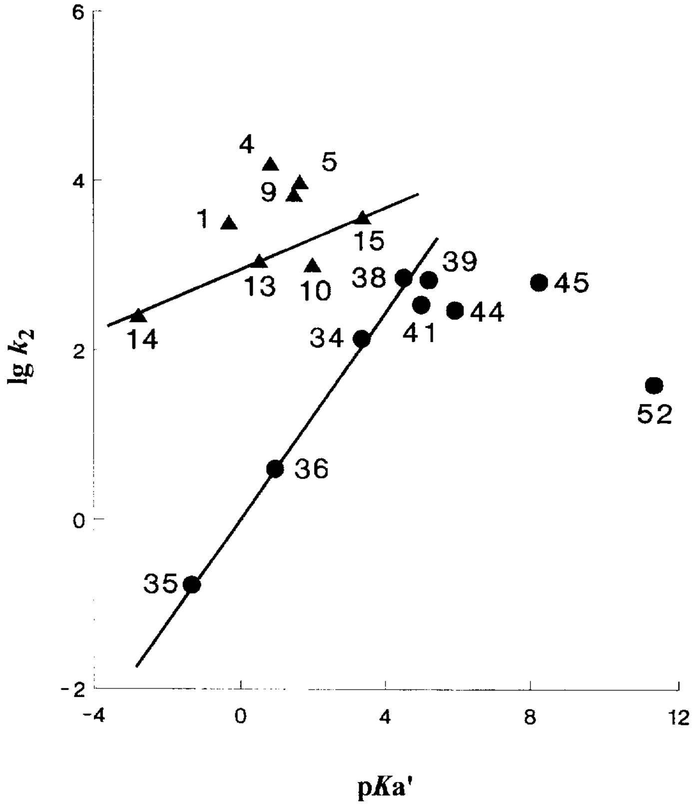


Fig. 6. The electronic profile for reactions of $Ru_5C(CO)_{15}$ in heptane: ▲, nucleophiles with $\theta \leq 130°$; ●, nucleophiles with $\theta \geq 145°$. The data for nucleophiles 13–15 have been adjusted to what they would have been if they had all had $\theta = 128°$ by using the value of $\gamma = -0.068$ deg^{-1} as found later.

above) indicates a similar duality of sites for nucleophilic attack, the only difference being that the loss of CO from both sorts of adduct formed is faster than the rate of formation of the adducts.

$Fe_5C(CO)_{15}$ also reacts with smaller nucleophiles via adduct formation followed by CO dissociation but larger nucleophiles do not react cleanly and appear to lead to fragmentation of the cluster [52b]. The mechanistic change brought about by going from smaller to larger nucleophiles occurs at a lower cone angle ($\theta \leqslant 128°$) than for $Ru_5C(CO)_{15}$ and the steric threshold for the adduct formation reactions is much lower as well, possibly because of the greater extent of bond making indicated by the β value (Table 1). The reactions of the Fe_5 cluster are significantly slower than those of the Ru_5 cluster.

8.5. *Osmium clusters*

The archetypal osmium hydride cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ has given rise to some very rich chemistry [53] but it has received almost no systematic kinetic study. The reversible addition of CO has been studied together with the loss of H_2 under CO to form $Os_3(CO)_{12}$ [54]. The loss of hydrogen occurs unexpectedly from $(\mu\text{-H})_2Os_3(CO)_{10}$ directly as well as from $(\mu\text{-H})(H)Os_3(CO)_{11}$. The kinetic and thermodynamic parameters allowed a full energy profile to be constructed for the overall conversion of $(\mu\text{-H})_2Os_3(CO)_{10}$ to $Os_3(CO)_{12}$. It was also possible to estimate that the enthalpy for rearrangement of the di-μ-hydrido cluster into the form that it takes up in the $(\mu\text{-H})(H)Os_3(CO)_{11}$ adduct is about 35 kcal mol^{-1}. Combination of this value with the activation enthalpy for CO addition leads to an estimated maximum of about 40% in the extent of Os···CO bond formation in the transition state. This value was supported by kinetic [33] and thermodynamic [55] data for addition of $P(OPh)_3$. These lead [33] to an estimated maximum of 50% Os···$P(OPh)_3$ bond formation in the transition state. In both cases the data also allowed for a negligible amount of bond formation but this was concluded to be most unlikely because of the very high value of β (Table 1) obtained from systematic studies with 15 different P-donor nucleophiles [33]. The steric profile obtained for reaction in heptane is shown in Fig. 7. The high value of θ_{th} suggests that the TSI is exceptionally open, and this allows for the high degree of Os···P bond making discussed above.

There are seven nucleophiles (apart from $P(m\text{-tol})_3$ and $P(o\text{-tol})_3$) that are classified as being pure σ donors which have $\theta < \theta_{th}$. It was these and the larger σ-donor nucleophiles that were used to derive the steric profile and the π-acid nucleophiles etpb, $P(OEt)_3$, $P(OPh)_3$ and $P(O\text{–}i\text{-Pr})_3$ lie above the profile by about 1.0, 0.9, 0.6 and 0.1 logarithmic units respectively. These data can be taken to suggest that π-acidity effects are detectable in the transition states of these reactions. This is not unreasonable in view of the high degree of bond making and the consequently short Os···P bonds. They can be detected only because of the relatively large number of σ-donor nucleophiles with $\theta < \theta_{th}$ which allow the estimation of α (or the standard reactivity) without using data for nucleophiles that are π acids. Because most smaller nucleophiles that are usually used, and that fall below θ_{th}, are π acids, the values

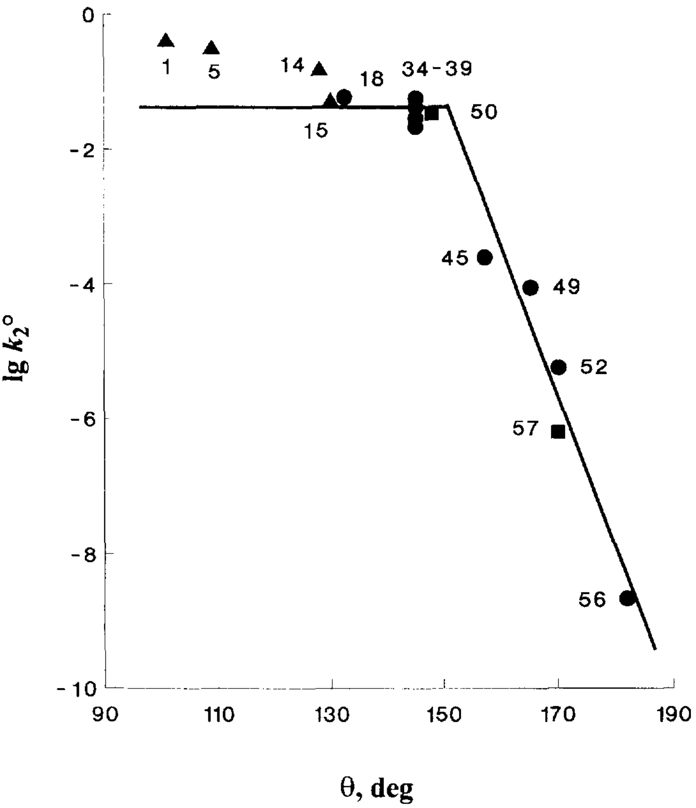


Fig. 7. The steric profile for reactions of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with L in heptane, to form $(\mu\text{-}H)(H))Os_3$-$(CO)_{10}L$. The profile was calculated by using data only for the σ-donor nucleophiles (●). Nucleophiles 50 and 57 (■) were not used in the calculations and their cone angles were taken to be 148° [25b] and 170° respectively, the latter conforming to the correlation between E_R and θ found by Brown and Lee [28].

found for the standard reactivity may often be enhanced by π bonding without its being obvious. Reactions in chlorobenzene [32] also indicate transition state stabilization by the π acids etpb, $P(OMe)_3$ and $P(OBu)_3$, but not by $P(OPh)_3$ or $P(O\text{—}i\text{-}Pr)_3$. On the contrary, the nucleophile $PPh_2(OEt)$ also lies above the steric profile and this is not believed to be a strong π acid [20,21]. The conclusions regarding π-acidity effects are therefore only tentative, and more examples must be found if they are to be firmly established.

Volumes of activation have also been measured for reactions of 18 P-donor nucleophiles with $(\mu\text{-}H)_2Os_3(CO)_{10}$ [32]. These are of particular interest because they relate to the dimensions of the transition states rather than to their energies. As mentioned above, the results for the isosteric nucleophiles $P(p\text{-}XC_6H_4)_3$ show that the length of the Os···P bonds in the transition states are effectively constant in spite of the wide range of nucleophile basicity. In addition, the volumes of activation obey

$$\Delta v^{\neq} = -11.5 - 0.78\tan^2\left(\frac{\theta}{2}\right) \tag{11}$$

over the range $\theta = 101$–157°. This is exactly what would be expected from a constant amount of penetration of the nucleophile into the open space in the TSI, since the values of $\tan^2(\theta/2)$ are directly related to the relative volumes of the cones that have penetrated to a constant distance into the open space. The negative value of the intercept at $\theta = \tan^2(\theta/2) = 0$ is surprising in its implication that the TSI is actually smaller than the ground-state undistorted cluster in spite of the open space created into which the nucleophiles move. The structural implications of this remain to be elucidated but the effect is quite small, the net decrease corresponding to only 5% of the total volume of the cluster. A further feature of Eq. (11) is that it applies to nucleophiles the cone angles of which extend beyond the log k_2 steric threshold by about 10°. This implies that in this region the loss of volume due to penetration of the nucleophile into the TSI is not appreciably affected by any increase in volume caused by the distortion of the TSI that is required in order to accommodate these nucleophiles while maintaining the same Os···P bond lengths. However, for nucleophiles with $\theta = 162$–170°, the TSI is unable to undergo sufficient further distortion to allow them to penetrate to the same extent as the smaller nucleophiles, the values of $\Delta V^{\neq}$ become rapidly less negative, and the decreasing rates with increasing θ in this region can be ascribed to a steady increase in the Os···P bond lengths rather than to larger activation energies required by larger distortions of the TSI. The change from large nucleophiles that can be accommodated in the TSI with the same bond lengths as smaller nucleophiles, but with distortion of the TSI, to even larger nucleophiles that are forced to form longer Os···P bonds because the TSI is unable

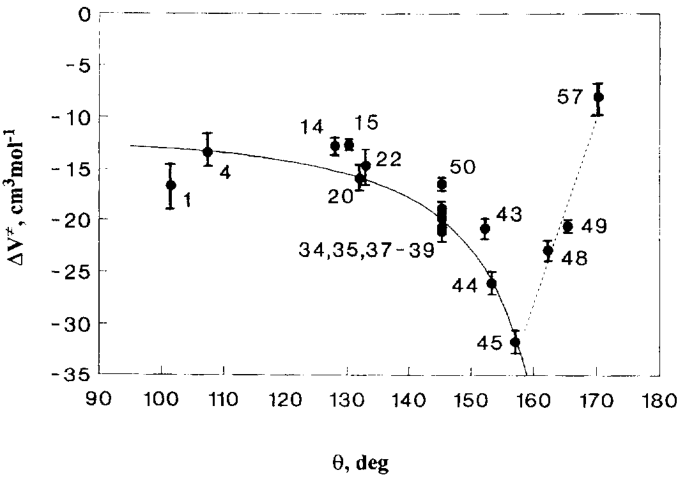
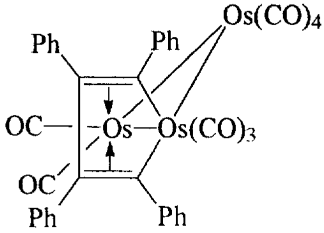


Fig. 8. Correlation of values of $\Delta V^{\neq}$ and θ for reactions of $(\mu\text{-H})_2Os_3(CO)_{10}$ with L in chlorobenzene to form $(\mu\text{-H})(H)Os_3(CO)_{10}L$. The full curve is drawn according to Eq. (11).

to undergo any further distortion, is quite sharp at about 160°, and this represents a new type of steric threshold that manifests itself in these volume measurements. A plot of $\Delta V^{\neq}$ vs. θ is shown in Fig. 8, where the full curve represents the values of $\Delta V^{\neq}$ calculated according to Eq. (11).



II

Reactions of cluster **II**, $Os_3(CO)_9(\mu_4\text{-}C_4Ph_4)$, show some very interesting features. The cluster is formed as one of a series of products generated successively when $Os_3(CO)_{12}$ reacts with C_2Ph_2 under CO, the kinetics of each step having been studied [56]. Of particular interest is the unusual F_N2 reaction that it undergoes with CO to form $Os_2(CO)_6(\mu_4\text{-}C_4Ph_4)$ and $Os(CO)_5$. This is a very facile process for an Os cluster and proceeds smoothly at 50 °C with $k_2 = 0.5$ l mol^{-1} s^{-1}, $\Delta H^{\neq} = 8.2 \pm 1.3$ kcal mol^{-1} and $\Delta S^{\neq} = -35 \pm 4$ cal K^{-1} mol^{-1}. Reaction with PPh_3 appeared to form $Os(CO)_4(PPh_3)$ and $Os_2(CO)_5(PPh_3)(\mu_4\text{-}C_4Ph_4)$ very rapidly at room temperature [56], and the kinetics of reaction with this and a large number of other P-donor nucleophiles have been studied by stopped-flow techniques [29]. The reactions follow two distinct paths. When $\theta \leqslant 143°$, i.e. with PCy_2H and 16 other smaller nucleophiles down to $\theta = 101°$, substitution occurs at the $Os(CO)_4$ moiety. A crystallographic study [57] of the product of reactions with etpb and $P(OPh)_3$ shows that the P-donor occupies an equatorial position trans to the Os that is part of the tetraphenylosmacyclopentadienyl ring. When $\theta \geqslant 145°$, i.e. $L \equiv$ four $(p\text{-}XC_6H_4)_3P$ and five larger nucleophiles up to $P\text{—}t\text{-}Bu_3$ ($\theta = 182°$), the reactions follow F_N2 paths and the IR spectra indicate that two pairs of products are formed, namely (a) $Os_2(CO)_5L(\mu_4\text{-}C_4Ph_4)$ and $Os(CO)_4L$ and (b) $Os_2(CO)_6(\mu_4\text{-}C_4Ph_4)$ and $Os(CO)_3L_2$. Both pairs appear to be formed in all cases but the former appears to be more predominant for higher basicities of the nucleophile.

The distinction between the substitution and fragmentation reactions is obviously very fine in steric terms, separation of only 2° in formal cone angle being sufficient to cause a change from one outcome to another. It is solely dependent on the size of the nucleophiles, the range of basicities overlapping extensively, i.e. smaller nucleophiles have $pK_a' = -2.79\text{–}8.57$ and larger nucleophiles have $pK_a' = 0.87\text{–}12.2$.

The kinetics of the fragmentation reactions fit Eq. (8) very well and the parameters obtained are included in Table 1. Although there are no exactly comparable data, the standard reactivity seems to be very high for an Os cluster, the simple need to use stopped-flow techniques reflecting this quite clearly. The value of θ_{th} shows that steric effects come into play later than with any other carbonyl studied so far, and the TSI must be very open. When compared with the data for the concerted reactions of $Ru_5C(CO)_{15}$ and for $(\mu\text{-}H)_2Os_3(CO)_{10}$, the earlier onset of steric effects with those clusters may be because the extent of bond making is considerably greater. All these clusters where the onset of steric effects is late have very large negative values of γ, values that lead to changes of about 40% in the rate constants for each degree of difference in cone angle. Thus further opening of the already very open TSI is very difficult. The only other cluster to show such a large negative value of γ is $Ru_6C(CO)_{17}$ which has an earlier onset of steric effects, presumably because of the greater steric congestion, even in the undistorted form of this hexanuclear complex with 17 CO ligands.

The kinetics of the substitution reactions are much more complex and proceed in three stages. The first stage, given by

$$Os_3(CO)_9(\mu\text{-}C_4Ph_4) + L \underset{k_{-L}}{\overset{k_{+L}}{\rightleftharpoons}} Os_3(CO)_9L(\mu\text{-}C_4Ph_4) \qquad (12)$$

involves reversible formation of an adduct with the P-donor nucleophile, a process that has, to our knowledge, not been observed elsewhere, and values of k_{+L}, k_{-L} and $K_{+L} = k_{+L}/k_{-L}$ can be obtained. The second stage is much slower to an extent that the reactions in Eq. (12) establish a pre-equilibrium. However, the data also require the use of double-exponential analysis to fit the absorbance–time changes. The value of k(obs) from the first of the two exponentials depend on [L] according to

$$k(\text{obs}) = \frac{kK_{+L}[L]}{1 + K_{+L}[L]} \qquad (13)$$

where k is the rate constant for loss of the equilibrium mixture established in Eq. (12). The values of K_{+L} found from the first and second stages agree well with each other. The rate constants from the second of the double-exponential absorbance change (i.e. the rate constant for the third stage overall) are independent of [L]. These kinetics suggest two possible sequences for the second and third stages. Firstly $Os_3(CO)_9L(\mu\text{-}C_4Ph_4)$ loses CO in the second stage to form an isomeric (probably axial) form of the final product and the third stage is the isomerization to the final equatorially substituted product (see above). Alternatively, the nucleophile could attack $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ in the second stage to form an adduct that is different from, and thermodynamically more stable than, that in Eq. (12) (although formed more slowly), and this adduct loses CO in the third stage to form the final product. It is not possible at this time to distinguish between these two proposals.

Finally, some reactions of an Os_6 "raft" cluster have been studied [58]. The parent cluster $Os_6(CO)_{21}$ is unfortunately too insoluble for its reactions to be monitored spectroscopically in solution. $Os_6(CO)_{20}(NCMe)$ can, however, be prepared [59] and is sufficiently soluble in chlorinated solvents for kinetic study. These "raft" clusters are so called because the six osmium atoms are arranged in a plane. An inner triangle of osmium atoms (with three CO ligands on each osmium) has each side bridged by $Os(CO)_4$ or $Os(CO)_3L$ moieties [59]. They have an electron count of 90 and a low-lying empty molecular orbital that suggests they should be very susceptible to nucleophilic attack or even to two-electron reduction [60]. This is fully borne out by the kinetic studies. Thus, although previous studies [61] of the acetonitrile-substituted Os_3 clusters $Os_3(CO)_{12-n}(NCMe)_n$ ($n=1$ and 2) had shown that the acetonitrile ligands were displaced by P donors via a simple dissociative process, this is not what was observed with $Os_6(CO)_{20}(NCMe)$. Reactions with P donors proceed via the formation of a cluster–(P-donor) adduct in a pre-equilibrium

$$Os_6(CO)_{20}(NCMe)+L \underset{k}{\overset{K}{\rightleftharpoons}} Os_6(CO)_{20}L(NCMe) \tag{14}$$

that is too rapidly set up even for stopped-flow kinetic detection. The adduct then loses NCMe in a dissociative step

$$Os_6(CO)_{20}L(NCMe) \rightarrow Os_6(CO)_{20}L+NCMe \tag{15}$$

to form the substituted product. This is therefore another example where reversible addition of a P-donor ligand to a cluster has been detected through kinetic studies. The adducts are, unfortunately, too short lived for spectroscopic characterization with normal spectrophotometers. Substitution reactions of the initially formed $Os_6(CO)_{20}L$ clusters lead to a variety of different disubstituted products at rates that are all much greater than corresponding reactions of $Os_3(CO)_{11}L$ clusters [46b].

9. Summary

Systematic kinetic studies of associative reactions of metal carbonyls and, in particular, metal carbonyl clusters provide data that can be successfully analyzed according to Eq. (8). The standard reactivity α, θ_{th}, β and γ characterize the dynamic nature of each cluster by its responses to the electronic and steric natures of the nucleophiles. Associative reactions of clusters may generally be allowed because of their ability to adjust to the approach of a nucleophile by breaking one of their metal–metal bonds, so avoiding an excessive electron count. Nucleophilic attack is highly favored by the larger clusters studied so far but other factors than simple nuclearity are likely to be important. Adduct-forming reactions have been detected as initial steps in substitution reactions and equilibrium constants can sometimes be obtained.

The existence of sharp steric thresholds leads to the concept of TSIs which are formed by opening up the clusters to provide a rather well-defined space into which smaller nucleophiles can fit without any steric repulsion. Nucleophiles that exceed the steric threshold can only approach the electrophilic centre to the same extent as smaller nucleophiles if the space in the TSI is enlarged with a concomitant increase in activation energy. Alternatively, if the flexibility of the TSI is sufficiently low, larger ligands will not be able to approach the electrophilic centre in the TSI as closely as smaller ligands, and this will also increase the activation energies. Measurement of volumes of activation can provide very intimate insights into the detailed natures of the transition states.

Steric effects can be exceedingly important in determining rates of reactions and, in some cases, quite small changes in nucleophile cone angle can bring about major changes in mechanism and/or in the products formed.

It is also possible to study the effects of P-donor substituents on the susceptibility of the clusters to the electronic and steric natures of the nucleophiles and an inverse correlation between standard reactivity and extent of bond making required in the transition states is found.

It is therefore clear that systematic variation in the nature of the nucleophiles involved in such reactions reveals both important quantitative features of particular reactions and unexpectedly major changes in mechanism and/or products formed on going from one group of nucleophiles to another. The likelihood is high that this will continue to be observed as more studies are carried out, particularly on carbonyl clusters of higher nuclearity.

Acknowledgments

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Appendix A

The electronic and steric parameter for P-donor ligands are given in Table A1.

Table A1
Electronic and steric parameters for P-donor ligands[a]

Ligand number	L	θ_T[b] (deg)	χ[c] cm^{-1}	pK_a[d]	pK_a'[e]
1	etpb	101	31.20	(1.74)	−0.30
2	PF$_3$	104	54.7[f]	(7.84)	5.9
3	**PPhH$_2$**	106	20.85	(−2.0)	−1.83
4	P(OMe)$_3$	107	24.10	(2.60)	0.83
5	P(OEt)$_3$	109	21.60	3.31	1.64
6	P(O–*n*-Bu)$_3$	109	20.85	(3.31)	1.64
7	P(CH$_2$CH$_2$CN)$_2$H	117	—	0.41	−0.89
8	**PMe$_3$**	118	8.55	8.65	6.45
9	PPh(OMe)$_2$	120	19.45	(2.64)	1.48
10	PPh(OEt)$_2$	121	18.10	(3.1)	1.99
11	**PPhMe$_2$**	122	10.60	6.50	5.07
12	**PCl$_3$**	124	48.00	—	−20.1
13	**PPh$_2$H**	126	17.35	0.03	0.53
14	P(OPh)$_3$	128	30.20	−2.0	−2.79
15	P(O–*i*-Pr)$_3$	130	19.05	4.08	3.38
16	**PPhCl$_2$**	131	36.40	—	−12.3
17	P(CH$_2$CH$_2$CN)$_3$	132	22.35	1.36	0.76
18	**PEt$_3$**	132	6.30	8.69	7.96
19	**P(*n*-Pr)$_3$**	132	5.40	8.64	8.57
20	**P(*n*-Bu)$_3$**	132	5.25	8.43	8.67
21	PPh$_2$(OMe)	133	16.30	(2.69)	2.09

Table A1 (*continued*)

Ligand number	L	θ_T[b] (deg)	χ[c] cm^{-1}	pK_a[d]	pK_a'[e]
22	$PPh_2(OEt)$	133	15.60	(2.91)	2.35
23	$PPh(OPh)_2$	134	24.10	(−0.42)	−0.91
24	$P(OCy)_3$	135	18.00	(3.93)	3.46
25	**$PPhEt_2$**	136	9.30	6.25	5.94
26	**PPh_2Me**	136	12.10	(4.57)	4.06
27	**PPh_2Cl**	137	24.65	(−4.1)	−4.39
28	$PPh_2(OPh)$	139	18.95	(1.15)	0.87
29	**PPh_2Et**	140	11.30	(4.9)	4.6
30	**$PPh_2(n\text{-}Bu)_3$**	140	11.10	(4.6)	4.73
31	$P(O\text{–}o\text{-}tol)_3$	141	29.05	−1.83	−2.02
32	**$P(i\text{-}Bu)_3$**	143	5.70	7.97	8.36
33	**PCy_2H**	143	9.10	4.55	6.08
34	**PPh_3**	145	13.25	2.73	3.28
35	**$P(p\text{-}F_3CC_6H_4)_3$**	145	20.2	(−1.39)	−1.39
36	**$P(p\text{-}ClC_6H_4)_3$**	145	16.80	1.03	0.87
37	**$P(p\text{-}FC_6H_4)_3$**	145	15.70	1.97	1.63
38	**$P(p\text{-}tol)_3$**	145	11.50	3.84	4.46
39	**$P(p\text{-}MeOC_6H_4)_3$**	145	10.50	4.57	5.13
40	**$P(p\text{-}Me_2NC_6H_4)_3$**	145	5.25	8.65	8.67
41	**$PPh_2(i\text{-}Pr)$**	151	10.85	(5.15)	4.90
42	$P(O\text{–}o\text{-}PhC_6H_4)_3$	152	29.15	(−2.0)	−1.68
43	**$PPh_2(CH_2Ph)$**	152	12.30	—	3.92
44	**PPh_2Cy**[g]	153	—	(5.05)	5.6
45	**$P(NMe_2)_3$**	157	5.95	—	8.20
46	**$PPh_2(t\text{-}Bu)$**	157	8.95	—	6.18
47	**$P(i\text{-}Pr)_3$**	160	3.45	(9.7)	9.88
48	**$PPhCy_2$**[g]	162	—	(7.38)	8.3
49	**$P(CH_2Ph)_3$**	165	10.35	(4.3)	5.23
50	**$P(m\text{-}tol)_3$**	165	11.1	3.3	4.7
51	**$P(m\text{-}ClC_6H_4)_3$**	165	18.40	(1.03)	−0.18
52	**PCy_3**	170	1.40	9.7	11.26
53	**$PPh(t\text{-}Bu)_2$**	170	4.95	—	8.87
54	**$PPh_2(o\text{-}MeOC_6H_4)$**	171	10.30	—	5.27
55	$P(O\text{–}t\text{-}Bu)_3$	172	12.95	(4.5)	5.75
56	**$P(t\text{-}Bu)_3$**	182	0	11.40	12.20
57	**$P(o\text{-}tol)_3$**	194	10.5	3.08	5.03

[a] Ligands characterized by Giering and co-workers [20,21] as being σ donors only are given in bold type; other ligands are π- acids as well as σ donors. No pK_a value is available for $P(NMe_2)_3$ and it has been assumed to be only a σ donor.

[b] Tolman cone angles [14].

[c] χ values given to two decimal places are from Bartik et al. [19] except those for $P(p\text{-}F_3CC_6H_4)_3$ and $P(p\text{-}tol)_3$ which are from Giering and co-workers [21]. Those given to only one decimal place are from Tolman [14c].

[d] pK_a values in parentheses are estimated by various methods which have been reviewed [22]. Otherwise they are based directly on experimental data for the particular ligands with appropriate extrapolations so that they are valid for equilibria in aqueous solutions [8].

[e] pK_a' values for σ donors are calculated from Eq. (5) where values of χ are available. Otherwise, they and those for π-acid and σ-donor ligands are estimated from Eq. (6).

[f] This value was estimated by comparison [22] of the relative σ-donor parameters for PEt_3, PF_3 and PPh_3 [62] with the pK_a values for PEt_3 and PPh_3.

[g] The pK_a values for these ligands were estimated by interpolation between the values for PPh_3 and PCy_3. The pK_a' values were obtained from the mean of those found (a) from Eq. (6) and the use of the pK_a values, and (b) those found from the interpolated χ values and the use of Eq. (5).

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