Use of QALE to generate potential energy surfaces in transition states: associative reactions of Ru$_3$(CO)$_{12}$ with P-donor nucleophiles †

Claudia Babij, Hanwen Chen, Lezhan Chen and Anthony J. Poë*

Lash Miller Chemical Laboratories, University of Toronto, 80 St. George Street, Toronto, Canada M5S 3H6. E-mail: apoe@chem.utoronto.ca

Previous studies of associative reactions of Ru$_3$(CO)$_{12}$ have been greatly extended to include a total of 23 P-donor nucleophiles with widely differing electronic and steric properties. Application of standard QALE methodology (QALE = quantitative analysis of ligand effects) enabled the rate constants to be analyzed according to the electronic and steric properties of the nucleophiles. It was unexpectedly found necessary to include what has become known as the aryl effect in this analysis, together with a positive contribution to the rates due to the π-acidity of phosphite nucleophiles. Also the analysis was found to be quite sensitive to the cone angle taken for P(*n*-Bu)$_3$ and the value 136°, favoured by Giering and Prock, was found to be superior to Tolman's value of 132°. The individual contributions of the various effects to the rate constants for each ligand are presented as absolute contributions to $\Delta G^\ddagger$ or fractional contributions to the rate constants. σ-Basicity and steric effects are represented graphically by a three-dimensional 'logk_2 surface' to which the aryl and π-acidity effects can be added and appear as peaks. This logk_2 surface can be converted into a free energy or potential energy surface by a simple scale change for the *y*-axis. However, a free energy surface would be difficult to represent, unless *minus* $\Delta G^\ddagger$ was plotted on the *y*-axis, because 'negative spikes' would represent a graphical problem.

Introduction

The metal carbonyl cluster Ru$_3$(CO)$_{12}$ was the first carbonyl cluster to be shown to undergo associative substitutions with P-donor nucleophiles.[1,2] It was also the first[2a,b] to show a rough linear free energy relationship (LFER) when values of logk_2 were plotted against Δhnp,[3] a measure of the σ-basicity of the nucleophiles. The fact that data for the large nucleophiles PPh$_3$ and PCy$_3$ lay well below the LFER also showed that steric effects could be operative in these reactions. The gradient of the LFER was taken as a measure of the extent of bond making in the transition states, and similar data for other nucleophilic substitutions were subsequently examined for relative degrees of bond making and quantitative contributions from individual steric effects.[4]

A still more general and quantitative approach to steric and electronic effects of P-donor and other ligands was based[5–7] on the seminal work of Tolman,[8] and this has been elaborated systematically since then.[9,10] The concepts of sharp steric thresholds[11] and the so-called aryl effect[12] were introduced, as well as, more recently, π-acidity effects and an extension of an apparent aryl effect to ligands that do not actually contain aryl groups attached to the P-donor atoms.[9b] This general approach is known as QALE (quantitative analysis of ligand effects[9]) and is represented by eqn. (1)

$$\text{property} = a\chi_d + b(\theta - \theta_{st})\lambda + cE_{ar} + d\pi_p + e \quad (1)$$

for a very wide variety of physical measurements on substituted complexes and free ligands, and for the kinetics and thermodynamics of many types of reaction. χ_d is a measure of the σ-basicity of the nucleophiles, θ is a measure of their Tolman cone angles, and θ_{st} is a steric threshold, above which steric effects become evident. The inception of steric effects is controlled by the switching function λ, which is zero when $\theta < \theta_{th}$ and unity when $\theta > \theta_{th}$. E_{ar} is a term related to the number,

n = 1–3, of aryl groups attached to the P-donor atom and n was taken by Giering and Prock (*i.e.* G & P) *et al.* to be 1, 2 or 2.7.[12a] π_p is a measure of the π-acidity of the nuceophiles, and e is a constant.

An analogous equation,[13] specifically related to kinetics of associative reactions of metal carbonyls, is shown in eqn. (2),

$$\log k_2 = a + \beta(pK_a' + 4) + \gamma(\theta - \theta_{th})\lambda + \delta E_{ar} + \phi(pK_a'(\pi)) \quad (2)$$

where pK_a' is a measure of the σ-basicity of the P-donor nucleophile and is closely related to the parameter χ_d in eqn. (1).[10a,c] It is, however, a logarithmic term which leads to a dimensionless β coefficient and this allows for a meaningful quantitative comparison of the extent of bond making in the transition state with the strength of a complete H$^+$–P bond formed under defined conditions. $pK_a'(\pi)$ is a measure of its π-acidity (defined and discussed below) and the coefficient ϕ is also dimensionless. This means that the extent of σ-bond making can be directly compared with the stabilization of the transition state by π back-bonding. This contrasts with the coefficients a and d in eqn. (1) that have quite different units. a is a measure of the standard reactivity, SR, of the metal carbonyl, defined as the value of logk_2 for a small ($\theta < \theta_{th}$) and weakly basic ($pK_a' = -4$) nucleophile with no aryl or π-acidity effects. The other parameters are defined above in connection with eqn. (1).

In the process of developing this approach by applying the relatively simple eqn. (3)

$$\log k_2 = a + \beta(pK_a' + 4) + \gamma(\theta - \theta_{th})\lambda \quad (3)$$

to substituted Ru$_3$ carbonyl clusters[10c,14] it was discovered that the original data for the unsubstituted cluster Ru$_3$(CO)$_{12}$ did not fit at all well, and this became even more of a problem when the precisely isosteric nucleophiles P(*p*-XC$_6$H$_4$)$_3$ (X = CF$_3$, Cl, F, Me, MeO, NMe$_2$) were used to provide an unambiguous measure of β, the contribution of σ-donor effects to the rates.[15] The slope of the dependence of logk_2 on (pK$_a'$ + 4) was much greater (0.30) than that found (0.13) for the nearly isosteric nucleophiles ($\theta \approx 130°$) P(OPh)$_3$, P(O-*i*-Pr)$_3$, and P(*n*-Bu)$_3$.

Agreement between β values obtained for reactions of other carbonyl clusters from these two sets of nucleophiles had previously been rather good.[7,10a,15] The only case where pronouncedly different values had been obtained[10b] was for reactions of the cluster $Ru_5C(CO)_{15}$, but this was shown to be because the reactions of the $\theta \leq 130°$ nucleophiles [$\beta = 0.209(1)$, where the number in parenthesis is the uncertainty (standard deviation) in the last digit] proceeded by a quite different path from those of the larger $P(p\text{-}XC_6H_4)_3$ nucleophiles ($\beta = 0.592(24)$).

In order to resolve the difficulties posed by these contradictory results we have studied reactions of $Ru_3(CO)_{12}$ with some additional nucleophiles, and have applied the more inclusive eqn. (2) to the analysis of the data. This has shown that this archetypal cluster is remarkable in being sensitive to both aryl and π-acidity effects, and these have been accurately quantified. The contributions of the various effects to the values of $\Delta G^{\ddagger}$ or k_2 by individual nucleophiles have also been precisely established and can be compared. The effects of σ-basicity and nucleophile size are represented graphically by a three-dimensional 'logk_2 surface' which can easily be converted to a potential or free energy surface. The aryl and π-acidity effects can be added and appear as peaks.

Experimental

General

Unless stated otherwise, all chemical manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Triratheniumdodecacarbonyl (Strem) was used as received. Chlorobenzene (Baker Analyzed reagent or Caledon) was dried over activated molecular sieves or was pre-dried over calcium chloride and distilled over calcium hydride. Decalin was washed with 4 M H_2SO_4 and water, dried over $MgSO_4$, distilled under reduced pressure, and stored over molecular sieves. Toluene was dried over an appropriate drying agent and distilled prior to use. Liquid phosphorus ligands (triphenyl phosphite, triethyl phosphite, triisopropyl phosphite, tri-n-butylphosphine, diethylphenylphosphine, and diphenylethylphosphine) were obtained from commercial sources and purified by distillation under low pressures of argon or nitrogen immediately before use. Trimethylphosphine (1.0 M in toluene, Aldrich) was used as received. Etpb ($P(OCH_2)_3CEt$, Strem) was sublimed immediately before use. Tripyrrolylphosphine was prepared as described elsewhere[16] and sublimed immediately before use. Tripyrrolidinylphosphine was prepared as described elsewhere.[16] Tri(p-dimethylaminophenyl)phosphine (Organometallics Inc.) and tri-isopropylphosphine (Strem) were used as received. Other ligands were obtained and used as described elsewhere.[10]

Kinetic studies

Standard spectrophotometric techniques[10] were used to monitor reactions. IR spectra were obtained using a Nicolet 10DX FTIR or a Nicolet Magna-IR 550 FTIR spectrophotometer. UV-vis spectra were obtained using a Cary 2300 spectrophotometer. Reactions with most P-donor nucleophiles were monitored directly in a thermostated UV-vis cuvette and/or by standard sampling techniques followed by measurement of IR spectra. Reactions with trimethylphosphine, tripyrrolylphosphine, tripyrrolidinylphosphine, and tri(p-dimethylaminophenyl)phosphine were monitored directly in a temperature controlled IR cell (Wilmad Glass). The reactions in the initial kinetic studies were carried out in decalin but most of the $P(p\text{-}XC_6H_4)_3$ nucleophiles were not sufficiently soluble in decalin and reactions were therefore generally carried out in chlorobenzene, with some reactions in toluene. Runs were performed at 51.2 °C using a pseudo-first-order excess of P-donor nucleophiles over the triratheniumdodecacarbonyl cluster.

Results

Course of reactions in chlorobenzene and toluene

IR spectral changes for reactions with all P-donor nucleophiles, apart from the triaryl phosphines, clearly showed the successive formation of $Ru_3(CO)_{12-x}L_x$ ($x = 1$–3), but the spectral windows in chlorobenzene and toluene are narrow and it was not possible to observe the growth of bands below 1970 cm^{-1}. Reactions with $P(n\text{-}Bu)_3$ led to appreciable amounts of mononuclear products as observed previously.[2b,c,17] Monitoring the reaction with PPh_3 by UV-vis spectroscopy showed that the $Ru_3(CO)_{12}$ cluster reacted directly to form $Ru_3(CO)_9(PPh_3)_3$ without evidence of formation of intermediate species. This could not be established by IR spectroscopy because the product bands were obscured by strong absorptions due to chlorobenzene. IR spectral changes for reactions with all $para$-substituted triarylphosphines and with PMe_3 were similar to those for reaction with PPh_3. UV-vis spectral changes were generally clean, as evidenced by a sharp isosbestic point (Fig. S1 in ESI †). IR spectral changes for reactions with $P(p\text{-}ClC_6H_4)_3$ and $P(p\text{-}MeC_6H_4)_3$ in toluene were similar to those for reaction with PPh_3 in chlorobenzene.

Course of reactions in decalin

IR spectral changes for reactions with all P-donor nucleophiles, apart from PPh_3, were quite complex but clearly showed initial formation of $Ru_3(CO)_{11}L$ followed by further reactions to form $Ru_3(CO)_{10}L_2$ and $Ru_3(CO)_9L_3$. Substituted five-coordinate mononuclear products[2b,17] were sometimes formed together with the substituted trinuclear clusters. Reaction with PPh_3 resulted in the loss of $Ru_3(CO)_{12}$ and the direct formation of $Ru_3(CO)_9(PPh_3)_3$, characterized by bands at 1984s, 1973s, and 1948m, and no intermediate species were observed. This confirmed the results of UV-vis monitoring of the reactions in chlorobenzene mentioned above. IR spectra of a selection of clusters, formed either in $situ$ or obtained after isolation, are shown in Table S1 of the ESI. †

Kinetics

Pseudo-first-order rate constants were obtained by fitting single or, occasionally, double exponential curves to absorbance decreases at 2060 and 2027 cm^{-1}, and/or UV-vis absorbance decreases at 385 or 394 nm, or increases at 505 nm. Values of k_{obs} increased with increasing concentration, [L], of the P-donor nucleophiles, and were fitted by proportionally weighted linear least squares analysis to the rate equation $k_{obs} = k_1 + k_2[L]$, where k_1 is the rate constant for the CO-dissociative pathway,[2] which is always evident, and k_2 is the rate constant for the associative pathway. The rate constants and their precisions are shown in Tables S2, S3, and S4. † There was generally agreement between the values obtained by different methods of monitoring the reactions, and excellent closeness of fit to the rate equation as shown by standard errors of measurement of only a few percent. The values of k_1 were only approximately constant, but the concentration of nucleophile was chosen to provide maximum contribution to k_{obs} by the second-order reaction. A problem was encountered with the rate constants for reactions with $P(O\text{-}i\text{-}Pr)_3$ in chlorobenzene which increased linearly with [$P(O\text{-}i\text{-}Pr)_3$] only up to ca. 100 mM, after which they became less reproducible and the spectral changes were no longer characteristic of a substitution reaction. The values listed for k_2 for this nucleophile were obtained from the initial slopes.

The values of the various electronic and steric parameters for the P-donor nucleophiles, and the corresponding values of logk_2, are given in Table 1. E_{ar} values of 1, 2, and 3[18] were used when there were 1, 2, and 3 aryl groups, respectively, in the nucleophile. The electronic parameters χ_d and π_p for $PPhCl_2$,

No.	L	$\chi_d{}^a$/cm^{-1}	$pK_a'{}^b$	θ^c/°	$E_{ar}{}^d$	$\pi_p{}^a$	$pK_a'(\pi)^e$	$\log k_2$
	In chlorobenzene							
1	P(p-F$_3$CPh)$_3$	20.5	−1.39	145	3 (2.7)	0	0	−4.377
2	P(p-ClPh)$_3$	16.8	0.87	145	3 (2.7)	0	0	−3.623
3	P(p-FPh)$_3$	15.7	1.63	145	3 (2.7)	0	0	−3.465
4	P(p-MePh)$_3$	11.5	4.46	145	3 (2.7)	0	0	−2.320
5	P(p-MeOPh)$_3$	12.3	5.13	145	3 (2.7)	0	0	−2.215
6	P(p-Me$_2$NPh)$_3$	10.6	8.67	145	3 (2.7)	0	0	−1.474
7	PPh$_3$	13.25	3.28	145	3 (2.7)	0	0	−2.812
8	PPh$_2$Me	12.6	4.06	136	2 (2.2)	0	0	−1.656
9	PPh$_2$Et	11.1	4.6	140	2 (2.3)	0	0	−1.827
10	PPh$_2$Cl	22.8	−3.15^f	137	2 (3.4)	1.8	2.10^g	−2.870
11	PPhMe$_2$	10.5	5.07	122	1 (1)	0	0	−0.903
12	PPhEt$_2$	8.6	5.94	136	1 (1.1)	0	0	−1.423
13	PPhCl$_2$	32.4	−9.6^f	131	1 (3.7)	3.5	5.13^g	−4.101
14	PMe$_3$	8.55	6.4	118	0	0	0	−0.666
15	P(n-Bu)$_3$	5.25	8.67	132 (136^h)	0	0	0	−1.288
16	P(OMe)$_3$	17.9	0.83	107	0 (1)	2.8	4.85	−1.983
17	P(OEt)$_3$	15.8	1.64	109	0 (1.1)	2.9	3.98	−1.780
18	P(OPh)$_3$	23.6	−2.79	128	0 (1.3)	4	5.33	−3.015
19	P(O-i-Pr)$_3$	13.4	3.38	130	0 (1.3)	2.9	4.00	−2.132
20	etpb	20.2	−0.30	101	0 (0.2)	5	8.50	−1.674
21	P(NC$_4$H$_4$)$_3$	31.9	−9.27^f	145	(3.3)	1.9	1.32^g	−3.567
22	P(NC$_4$H$_8$)$_3$	−1.2	13.0^f	146	(−0.6)	0.9	0.50^g	—
23	P(i-Pr)$_3$	3.45	9.88	160	0	0	0	—
	In decalin							
20	etpb	20.2	−0.30	101	0 (0.2)	5	8.50	−1.755
16	P(OMe)$_3$	17.9	0.83	107	0 (1)	2.8	4.85	−1.963
11	PPhMe$_2$	10.5	5.07	122	1 (1)	0	0	−0.991
18	P(OPh)$_3$	23.6	−2.79	128	0 (1.3)	4	5.33	−2.816
19	P(O-i-Pr)$_3$	13.4	3.38	130	0 (1.3)	2.9	4.00	−1.963
8	PPh$_2$Me	12.6	4.06	136	2 (2.2)	0	0	−1.677
12	PPhEt$_2$	8.6	5.94	136	1 (1.1)	0	0	−1.531
7	PPh$_3$	13.25	3.28	145	3 (2.7)	0	0	−2.907
	In toluene							
2	P(p-ClPh)$_3$	16.8	0.87	145	3 (2.7)	0	0	−3.796
4	P(p-MePh)$_3$	11.5	4.46	145	3 (2.7)	0	0	−2.268

^{a} From ref. 9d. ^{b} From ref. 10c. ^{c} From ref. 8. ^{d} G & P's values in parentheses. ^{e} From refs. 15 and 13. ^{f} Calculated from G & P's χ_d values. ^{g} 'p$K_a'(\pi)$ equivalents' calculated using $pK_a'(\pi) = 1.78 \pm 0.13(\pi_p) - 1.10 \pm 0.37$, see text. ^{h} Value preferred by G & P et al.

PPh$_2$Cl, P(NC$_4$H$_4$)$_3$, and P(NC$_4$H$_8$)$_3$ were determined by G & P et al.[9c] Since experimental pK_a values are not available for these ligands, pK_a' values had to be calculated [10c] from pK_a' = 18.93 − (0.0464 × 145) − 0.673χ_d, using G & P's χ_d values. Values of the π-acidity parameter are given by π_p, as obtained by G & P et al.,[9b] and also as p$K_a'(\pi)$ values, obtained originally by Chen [15] and explained and tabulated more recently by Bunten et al.[13] The set of π_p and p$K_a'(\pi)$ values correlate quite well ($r^2 = 0.947$ [13]) according to eqn. (4)

$$pK_a'(\pi) = -1.10(37) + 1.78(13)\pi_p \qquad (4)$$

and this allows direct conversion of the π_p values to the same dimensionless form as the pK_a' values. Derivation of values of p$K_a'(\pi)$ requires values of pK_a to be known,[13] but when pK_a values are not available p$K_a'(\pi)$ values can be interpolated from this correlation. The major difference between π_p and p$K_a'(\pi)$ values is that the former were derived by a linear regression analysis of a set of simultaneous QALE equations (eqn. (1)) that were appropriate for different physical properties.[9b] This was done in such a way that values of π_p, and quite unexpected values of 'E_{ar}' for these π-acid but non-aryl ligands, were obtained at the same time. The derivation [13,15] of the values of p$K_a'(\pi)$ ignored the existence of any E_{ar} parameter for these non-aryl π-acid ligands, and any effect of doing this should become apparent when both sets of parameters are used and the results compared.

The value of k_{obs} for the bulky P(i-Pr)$_3$ ligand ($\theta = 160°$), did not vary with ligand concentration ($k_{obs} = k_1$) and this ligand could therefore not be used in the QALE analysis. Although the formation of Ru$_3$(CO)$_{11}$P(NC$_4$H$_8$)$_3$ was detected by IR spectroscopy, the absorbance vs. time data could not be fitted using single or double exponential curves and it was not possible to obtain k_{obs} values or, therefore, a value of k_2.

The dependence of $\log k_2$ on (pK_a' + 4) is shown in Fig. 1, where least squares lines are drawn through the data for the $\theta \approx 130°$ and $\theta = 145°$ P-donor nucleophiles. Good fits are observed, but values of β for the 130° and 145° ligands are evidently very different ($\beta = 0.13(1)$ and $\beta = 0.30(2)$, respectively) and analysis of all the data according to eqn. (3) is inevitably unsuccessful. Something more sophisticated is therefore clearly required.

Discussion

'Graphical' analysis of the chlorobenzene data

G & P's [19] protocol for combining a graphical analysis of ligand effect data with a regression analysis in order to gain a self-consistent interpretation of the regression results was adopted, with some modifications.

Dependence on σ-basicity

A good estimate of $\beta = 0.30(2)$ can be obtained from a plot of $\log k_2$ vs. (pK_a' + 4) for the P(p-XC$_6$H$_4$)$_3$ nucleophiles as shown in Fig. 1. Since the parameters $\theta = 145°$ and $E_{ar} = 3$ are both constant for this ligand set and there is no evidence for any π-acidity, the variation in $\log k_2$ values should reflect the
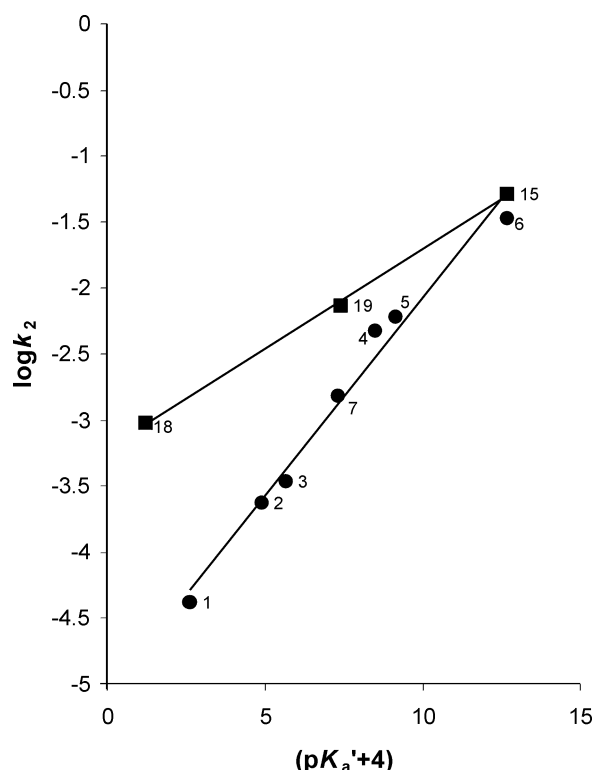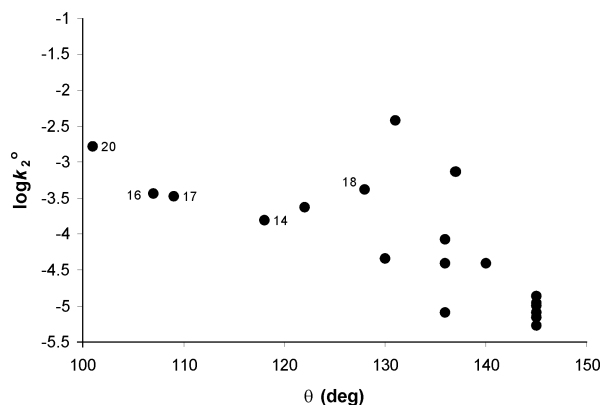
Fig. 1 Electronic profile for associative reactions of P-donor nucleophiles with $Ru_3(CO)_{12}$ in chlorobenzene at 51.2 °C. Nearly isosteric nucleophiles ($\theta \approx 130°$) (■); precisely isosteric nucleophiles ($\theta = 145°$) (●).

sensitivity of the system to ligand σ-basicity only. As such the gradient provides a precise ($r^2 = 0.979$, $\sigma(\log k_2) = 0.156$) value for β which should be applicable to the σ-basicity effects of all the nucleophiles.

Effects of π-acidity

With β at 0.30, it is now possible to construct a steric profile by subtracting the σ-basicity effect from $\log k_2$ ($\log k_2° = \log k_2 - (0.30)(pK_a' + 4)$) and plotting $\log k_2°$ against θ as in Fig. 2. This plot bears no resemblance to the rather orderly steric profiles usually obtained in this way but it is apparent that $\log k_2°$ does not vary greatly with θ for $\theta \leq ca.$ 128°. The average $\log k_2°$ value for etpb, $P(OPh)_3$, $P(OEt)_3$, $P(OMe)_3$, and PMe_3 is $-3.37(37)$, suggesting that these ligands probably fall below a steric threshold. However, the phosphites are π-acids and values for $pK_a'(\pi)$ vary from zero (for PMe_3) to 8.5 for etpb (Table 1). The possibility of a π-effect must therefore be considered. A plot of $\log k_2°$ vs. $pK_a'(\pi)$ for the phosphites and PMe_3 is reasonably linear, as shown in Fig. 3, and the gradient provides an estimate

Fig. 2 Initial steric profile for associative reactions of P-donor nucleophiles with $Ru_3(CO)_{12}$ in chlorobenzene at 51.2 °C, where $\log k_2° = \log k_2 - (0.30)(pK_a' + 4)$.
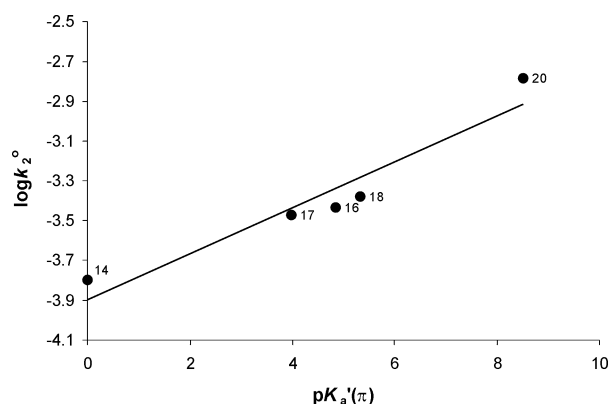
Fig. 3 A plot of $\log k_2°$ vs. $pK_a'(\pi)$ for the phosphites and PMe_3 ($\theta \leq ca.$ 128°) is linear and the gradient provides an estimate of the π-effect with $\phi = 0.115(20)$.

of the π-effect with $\phi = 0.115(20)$. If this π-effect is subtracted from $\log k_2°$, then the average $\log k_2° - (0.12)pK_a'(\pi)$ value is -3.92 and the standard deviation drops to 0.11. This value can be taken as a good estimate of the standard reactivity, a, and it should be noted that no additional parameter, such as G & P's E_{ar} parameter, is required to describe the behaviour of the phosphites in this system.

Steric and aryl effects

Although the data in Fig. 2 for $\theta \leq ca.$ 128° can be rationalized satisfactorily in terms of simple contributions from the σ-basicity and π-acidity of the nucleophiles, treated separately, the data for $\theta \geq ca.$ 130° are badly scattered, but a tendency for $\log k_2°$ to decrease can be detected. Significantly, almost all the nucleophiles involved contain at least one aryl group. There is only one trialkyl nucleophile ($P(n\text{-Bu})_3$) and a reliable separation of steric and aryl effects cannot be obtained graphically. For this to be possible one would need trialkyl nucleophiles with cone angles greater than that of $P(n\text{-Bu})_3$,[19] but it turns out that these are all so large that no k_2 values are observable. As a result these data have to be analyzed by deriving values for both aryl and steric effects simultaneously. This is done by taking the value already derived graphically for β, and by solving for γ and δ in eqn. (2) with $\phi = 0$. For reasons that will be discussed below, the data for $P(NC_4H_4)_3$, $P(O\text{-}i\text{-Pr})_3$, and the chloro nucleophiles PPh_2Cl and $PPhCl_2$ were omitted from this analysis, and the data for the nucleophile $P(n\text{-Bu})_3$ present a special problem. Although $P(n\text{-Bu})_3$ has a Tolman cone angle of 132°,[8] G & P et al. have decided that a value of 136° is preferable on the basis of an improved fit to a particular set of data.[20] This adjustment is not always needed and, in line with the procedures recommended recently,[13] we believe that such changes should not be undertaken lightly. However, in the data being considered here, the value taken for the cone angle of $P(n\text{-Bu})_3$ turns out to be of considerable importance. Normally, when a reasonably large number of rate constants for trialkylphosphine nucleophiles have been collected, an uncertainty in the value of one of their cone angles would have little effect on the overall success of the QALE analysis. In this group of reactions $P(n\text{-Bu})_3$ is the only trialkyl nucleophile whose cone angle has any importance. It turns out that the results of the analysis are very dependent on the precise cone angle assigned to it, and the analysis with the cone angle 136° gives superior results: $\gamma = -0.18(3)$, $\delta = 0.52(12)$, $r^2 = 0.853$ and $\sigma(\log k_2°) = 0.167$, compared with $\gamma = -0.20(6)$, $\delta = 0.78(29)$, $r^2 = 0.637$ and $\sigma(\log k_2°) = 0.261$. Although the first r^2 value is not particularly satisfactory, using the cone angle 132° makes the results much worse. A plot of $\log k_2° + 0.18\theta$ vs. E_{ar} is given in Fig. 4 and confirms the significance of the aryl effect in these reactions. A plot of $\log k_2° - 0.52E_{ar} - (0.12)pK_a'(\pi)$ vs. θ is given in Fig. 5 for all the nucleophiles, and the contrast with Fig. 2 is dramatic. The point of

| No.	θ_{th}	α	β	γ/deg^{-1}	δ	ϕ	r^2	$\sigma(\log k_2)$
1[a]	130	−3.92	0.299(19)	−0.18(3)	0.52(12)	0.115(20)	–	–
2	130	−4.0(2)	0.30(2)	−0.17(2)	0.47(10)	0.13(3)	0.982	0.157
3[b]	130	−4.1(2)	0.31(1)	−0.16(1)	0.43(8)	0.14(2)	0.980	0.145
4[c]	130	−4.1(2)	0.31(2)	−0.17(2)	0.48(11)	0.21(5)	0.980	0.173
5[d]	127	0.84(20)	−0.20(2)	−0.11(2)	0.35(11)	0.18(7)	0.955	0.255

[a] Graphical estimates, see text. [b] Including decalin and toluene data. [c] Using π_p. [d] Regression analysis according to eqn. (1) and including data for nucleophiles **10** and **13**.
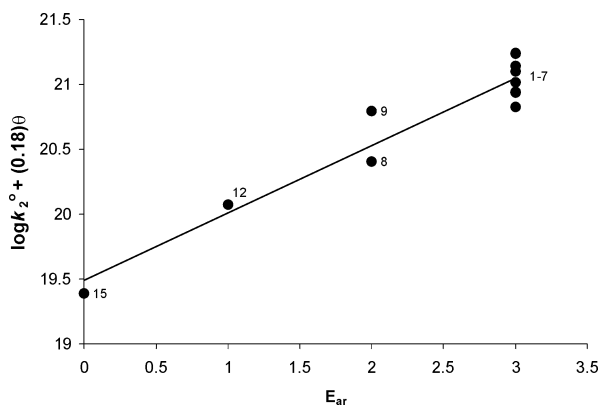
Fig. 4 A plot of $\log k_2° + 0.18\theta$ vs. E_{ar} for $PR_{3-n}Ar_n$ ($\theta \geq ca.$ 130°).
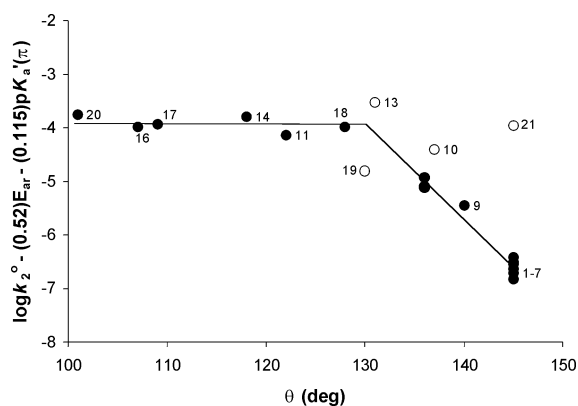
Fig. 5 A plot of $\log k_2° − 0.52E_{ar} − 0.12pK_a'(\pi)$ vs. θ for all nucleophiles. Outliers are shown as open circles.

intersection of the gradient in Fig. 5 with the horizontal line defined by $a = −3.90(11) = \log k_2° − 0.115\ pK_a'(\pi)$ gives the steric threshold $\theta_{th} = 130°$.

The data point for P(O-i-Pr)$_3$ falls well off this profile, and the problems of obtaining a reliable value for k_2 for this nucleophile were described above. We therefore regard P(O-i-Pr)$_3$ as being an "outlier" in this context. The data for the nucleophiles PPh$_2$Cl and PPhCl$_2$ also deviate considerably from the steric profile in Fig. 5. For these nucleophiles, G & P attribute an extra "aryl effect" to the pendant chloro groups.[9a] If we were to follow this concept we would expect the deviations to be Δ(PPhCl$_2$) = 2Δ(PPh$_2$Cl) but this is not the case. The behavior of these nucleophiles clearly requires further exploration, as does the behaviour of the relatively new ligand P(NC$_4$H$_4$)$_3$, which also appears to be very deviant. Although there is nothing to suggest that the substitution reaction for P(NC$_4$H$_4$)$_3$ is unusual in any way, and the corresponding $\log k_2$ value is considered to be reliable, the E_{ar} and π_p values assigned to this ligand have not been widely tested and this may explain the difficulty in fitting this ligand. Additionally, in the light of recent doubts about crystallographically determined cone angles,[13] the reliability of using $\theta = 145°$ for P(NC$_4$H$_4$)$_3$ is not certain as well. There is therefore no basis for including the data for this nucleophile in the analysis. The coefficients

obtained by the essentially graphical analysis of data for the 17 other nucleophiles, as described above, are listed in Table 2.

Regression analysis

The results of fitting the data to eqn. (2) using a linear regression analysis are listed in Table 2. The optimum fit (r^2 is at a maximum; analysis no. 2) is achieved using $\theta_{th} = 130°$, excluding the data for the nucleophiles already discussed, and taking the cone angle for P(n-Bu)$_3$ as 136°. The agreement between the values for the coefficients that were estimated by the almost completely graphical method and the final values obtained from the regression analysis is excellent. As expected, using π_p instead of $pK_a'(\pi)$ values to fit the data lead to essentially the same results (Table 2, no. 4), with the change in ϕ corresponding to the change in the π-acidity parameter. The consistency of the β coefficient across all analyses confirms the original assumption that E_{ar} is constant for all P(p-XC$_6$H$_4$)$_3$ ligands regardless of X is justified.

If we assume, with G & P et al.,[9a] that there is an accelerating effect due to pendant chloro groups that is proportional to their number, then the analysis leads to essentially the same results but with a very slight decrease in r^2 to 0.976 ($\sigma(\log k_2)$ = 0.195). For comparison, the data (excluding those for P(NC$_4$H$_4$)$_3$ and P(O-i-Pr)$_3$) were fitted to eqn. (1) using all of Giering's values for the χ, θ, E_{ar}, and π_p parameters. This leads to quite a poor fit with $r^2 = 0.955$ and $\sigma(\log k_2) = 0.255$ (Table 2, no. 5).

The nature of the aryl 'parameter'

A comment on the distinct nature of the so-called aryl "parameter" is appropriate. The values described by the parameters pK_a', θ, and $pK_a'(\pi)$ are obtained by physical or chemical measurements of essentially absolute properties. In contrast, E_{ar} values are proportional to the *number* of pendant phenyl groups on the P atom in the P-donor molecules, and as such are strictly relative, *i.e.* E_{ar} values of 1, 2, and 3 (or 2.7 as G & P et al. would have it [18,20]) for 1, 2, and 3 pendant phenyl groups, respectively, are equivalent to values of 2, 4, and 6 or, for that matter, values of 15.6, 31.2, and 48.6. All that is affected is the corresponding coefficient. If the number and selection of PR$_n$Ar$_{3-n}$ nucleophiles in the data set are sufficient, the absence or presence of an aryl effect can be established graphically as has been done above. Evidence for an aryl effect is represented by deviations from expected behaviour – that observed for the PR$_3$ nucleophiles in the system – that are closely related only to the number of aryl groups on the P-atom and not (as yet) to any known and measurable physical property. Information about the nature and magnitude of the aryl effect can only be obtained by examination of each individual system. Hence, it is not really necessary to use G & P's method of simultaneous equations to obtain E_{ar} values for new ligands. The graphical approach described here can be extended to other pendant groups, if an E_X value of 1 is assigned per X pendant group and as long as the data set includes the PX$_3$, PX$_2$Ph, and PXPh$_2$ analogues. We have successfully applied this approach elsewhere in a quite different context.[21]

Solvent effects

The use of the different solvents chlorobenzene, toluene, and decalin shows that there are no detectable systematic solvent effects due to these rather closely related solvents. The ratios of the values of $\log k_2$ in decalin and toluene to the corresponding ones in chlorobenzene have an average value of 1.10(6). Not only does this show that the values of $\log k_2$ in these other solvents can be included in the regression analyses for these reactions (Table 2, no. 3), but it also emphasizes the excellent internal consistency of the kinetic data. The absence of a solvent effect is graphically represented in Fig. 6, where the decalin and toluene data have been added to the steric profile originally constructed using the chlorobenzene data.
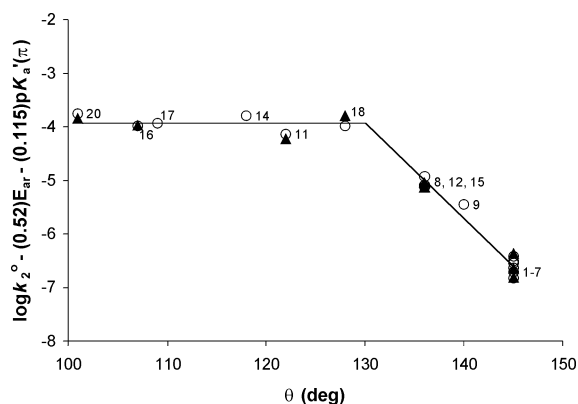
Fig. 6 A plot of $\log k_2^\circ - 0.52E_{ar} - 0.12pK_a'(\pi)$ *vs.* θ for 17 nucleophiles, where the data in decalin and toluene (▲) have been added to the steric profile originally constructed using the data for chlorobenzene (○).

Contributions of the various parameters to the rates

Contributions were calculated using the results from regression analysis no. 2, Table 2. Absolute contributions, in kcal mol^{-1}, of each parameter to $\Delta G^\ddagger$ for each nucleophile are shown in Fig. 7 and are tabulated in Table 3. The standard reactivity (a) and steric effects ($\gamma(\theta - \theta_{th})$) both add to the total activation energy barrier, and increasing σ-basicity ($\beta(pK_a'+4)$), π-acidity ($\phi pK_a'(\pi)$), and the aryl effect (δE_{ar}) contribute to lowering the barrier. The contribution from a is constant at 25.4 kcal mol^{-1} and the maximum contributions in kcal mol^{-1} from the other terms are -5.83 from $\beta(pK_a'+4)$ for $P(n\text{-Bu})_3$ and $P(p\text{-Me}_2\text{-NC}_6\text{H}_5)_3$, $+3.75$ from $\gamma(\theta - 130)$ for PAr$_3$, -2.13 from δE_{ar} for PAr$_3$, and -1.02 kcal mol^{-1} from $\phi pK_a'(\pi)$ for etpb. However, the a and $\beta(pK_a'+4)$ contributions are closely related and depend on the selection of $pK_a' = -4$ as a standard basicity. The
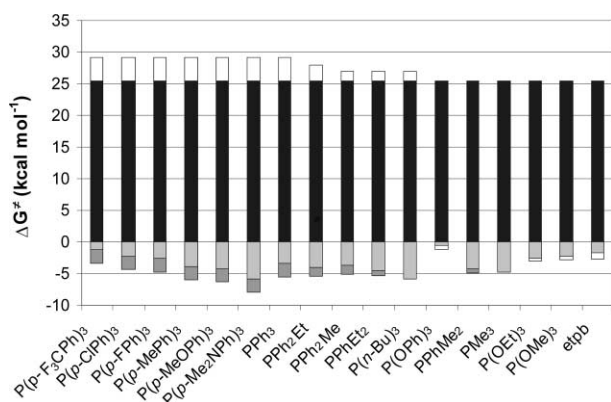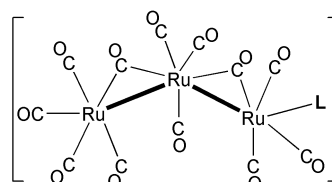
contribution of the aryl and π-acidity effects are quite small absolutely, compared with the overall values of $\Delta G^\ddagger$, but they are nevertheless quite significant in determining the relative rates. This is more evident when a different method is used to compare the various contributions.

This method involves comparing the effects of each nucleophile on the *rate constants*. This can be done because the antilog of the term, a, corresponds to a standard rate constant, while the antilogs of all the other terms, $\beta(pK_a' + 4)$ *etc.*, correspond to the modifying effect that each term has on the standard rate constant. Thus a value of $+1.41$ for δE_{ar} corresponds to an enhancement of the standard rate constant by a factor of 26, whereas a value of -2.55 for $\gamma(\theta - 130)$ corresponds to a *decrease* in the rate constant by a factor of ≈ 350. The factors are given in Table 3.

Comparison of the different effects for particular nucleophiles is of interest. Thus, the π-acidity of P(OPh)$_3$ contributes more to lowering $\Delta G^\ddagger$ than does its σ-basicity. The favourable aryl contribution of PPh$_2$Me is only marginally smaller than its unfavourable steric contribution, and the unfavourable steric contribution of PPh$_3$ is greater than its favourable σ-basicity contribution.

The significant contributions of π-acidity and aryl effects to the rates of associative reactions of Ru$_3$(CO)$_{12}$ are very unusual, only the corresponding reactions of Rh$_4$(CO)$_{12}$ having been shown also to exhibit contributions of both these sorts.[10i] For the latter, the contributions are somewhat smaller so that, for example, the π-acidity of etpb reduces $\Delta G^\ddagger$ by only 1.01 kcal mol^{-1} (*i.e.* an increase by a factor of *ca.* 6 compared with the standard rate constant) for reaction with Rh$_4$(CO)$_{12}$ at 10 °C, as compared with a reduction of 1.40 kcal mol^{-1} (an increase by a factor of *ca.* 13 compared with the standard rate constant) for reaction with Ru$_3$(CO)$_{12}$ at 51 °C. The aryl effect associated with PPh$_3$ reduces $\Delta G^\ddagger$ by 0.64 kcal mol^{-1} (an increase by a factor of *ca.* 3.5) for reaction with Rh$_4$(CO)$_{12}$, while the reduction in $\Delta G^\ddagger$ for reaction with Ru$_3$(CO)$_{12}$ is 2.13 kcal mol^{-1} (an increase by a factor of *ca.* 26). It may be that the different temperatures used to study the reactions of these two clusters contribute to these differences, but too little is known, unfortunately, about the temperature dependence of coefficients in equations such as 1 and 2 for this factor to be allowed for. In general, the coefficients of the various parameters are significantly smaller in the associative reactions of Rh$_4$(CO)$_{12}$ than in those of Ru$_3$(CO)$_{12}$, showing that the latter is more discriminating in its susceptibility to nucleophilic attack. This may be due to its lower intrinsic reactivity, so that the larger modifying contribution has to be seen against the larger intrinsic barrier to reaction, or to the smaller standard reactivity.

All these comparisons have to be seen in the light of the proposed transition states for reactions of this sort. These associative reactions are believed to proceed through intermediates in which the 18-electron count for each metal in the cluster is maintained by breaking one metal–metal bond at the same time as two electrons are added from the incoming nucleophile, and by conversion of terminal carbonyls to bridging ones. Clear evidence for formation of such intermediate adducts has been obtained for reactions of several other carbonyl clusters.[10] The proposed intermediate for associative substitution reactions of Ru$_3$(CO)$_{12}$ is shown in Fig. 8.

Fig. 7 Bar graph showing absolute contribution of each term in eqn. (2) to $\Delta G^\ddagger$ (θ_{th} = 130°; T = 51.2 °C). Standard reactivity (black); σ-donicity contribution (lighter gray); steric contribution (no fill, top); aryl contribution (darker gray); π-acidity contribution (no fill, bottom). ("Ph" in p-XPh = C$_6$H$_4$.)

**Fig. 8** The proposed intermediate for associative substitution reactions of Ru$_3$(CO)$_{12}$.

Table 3 Contributions of each parameter expressed as absolute Gibbs free energies of activation (in kcal mol^{-1})^a or as factors, f,^{b} that modify the standard rate constant, $k(a)$

L	$\beta(pK_a' + 4)$		$\gamma(\theta - 130)$		δE_{ar}		$\phi pK_a'(\pi)$	
	$\Delta G^{\ddagger}$	$f(\sigma)$	$\Delta G^{\ddagger}$	$f(st)$	$\Delta G^{\ddagger}$	$f(ar)$	$\Delta G^{\ddagger}$	$f(\pi)$
P(p-F$_3$CPh)$_3$	−1.20	6	3.75	1/350	−2.13	26	0	1
P(p-ClPh)$_3$	−2.24	29	3.75	1/350	−2.13	26	0	1
P(p-FPh)$_3$	−2.59	49	3.75	1/350	−2.13	26	0	1
P(p-MePh)$_3$	−3.89	350	3.75	1/350	−2.13	26	0	1
P(p-MeOPh)$_3$	−4.20	550	3.75	1/350	−2.13	26	0	1
P(p-Me$_2$NPh)$_3$	−5.83	6300	3.75	1/350	−2.13	26	0	1
PPh$_3$	−3.35	150	3.75	1/350	−2.13	26	0	1
PPh$_2$Me	−3.71	260	1.5	1/10	−1.42	9	0	1
PPh$_2$Et	−3.96	380	2.5	1/50	−1.42	9	0	1
PPhMe$_2$	−4.17	530	0	1	−0.71	3	0	1
PPhEt$_2$	−4.57	960	1.5	1/10	−0.71	3	0	1
PMe$_3$	−4.81	1400	0	1	0	1	0	1
P(n-Bu)$_3$	−5.83	6300	1.5	1/10	0	1	0	1
P(OMe)$_3$	−2.22	28	0	1	0	1	−0.58	4
P(OEt)$_3$	−2.59	49	0	1	0	1	−0.48	3
P(OPh)$_3$	−0.56	2	0	1	0	1	−0.64	5
etpb	−1.70	13	0	1	0	1	−1.02	13

^{a} a = 25.4 kcal mol^{-1} for all nucleophiles. ^{b} Standard rate constant $k(a)$ = antilog(a) = 9.7×10^{-5} M^{-1} s^{-1} and $k_2 = k(a)f(\sigma)f(st)f(ar)f(\pi)$. An f value of unity means there is no effect on k_2.

Potential energy surface

A 'logk_2 surface' can be constructed using the results from regression analysis no.2, Table 2 and is shown in Fig. 9. The smooth surface represents the effects of all possible nucleophiles, each with its own values of pK_a' and θ and in the absence of aryl or π-acidity effects, on the transition state. The spikes denote additional contributions due to π-acidity and aryl effects for certain nucleophiles. This logk_2 surface can be converted into a free energy or potential energy surface by a simple scale change for the y-axis. However, a free energy surface would be difficult to represent, unless *minus* $\Delta G^{\ddagger}$ was plotted on the y-axis, because 'negative spikes' would represent a graphical problem.
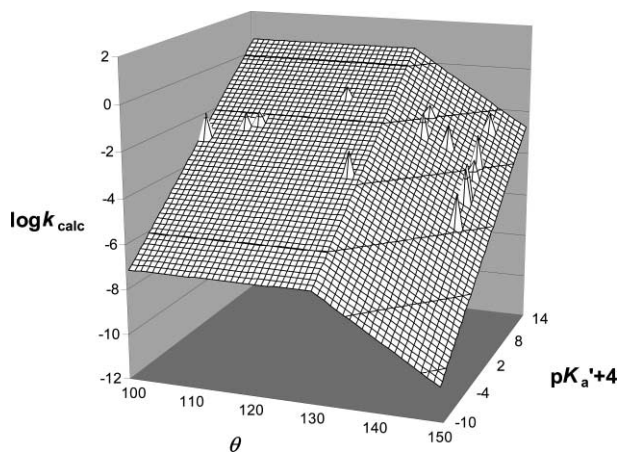
Fig. 9 The "logk_2 surface" from calculated values of k_2 according to the effects of the σ donor (pK_a' + 4) and steric (θ) parameters alone. The 'spikes' represent the increased values of logk_2 due to π-acidity (horizontal surface) and aryl (sloping surface) effects.

Conclusions

The application of the quantitative analysis of ligand effects (QALE) to the rates of associative reactions of metal carbonyls with P-donor nucleophiles provides a series of unique coefficients that define the kinetic natures of particular metal carbonyls. It provides a picture of the dynamic properties of a complex and allows prediction of the response of a complex to attack by hypothetical P-donor nucleophiles with known electronic and steric properties. This dynamic characterization of each complex complements those provided by various spectroscopic techniques and crystallographically obtained structural parameters. Thus, relationships between rates and lengths or stretching frequencies (or force constants) of metal–metal bonds can be illuminating in understanding the kinetic results in terms of proposed mechanisms for reactions of M–M bonded carbonyls.

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