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Potential Energy Surfaces in Transition States for Associative Reactions of Metal Carbonyl Clusters: Reactions of $Rh_4(CO)_{12}$ with P-Donor Nucleophiles

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The metal carbonyl cluster $Rh_4(CO)_{12}$ reacts with a wide variety of P-donor nucleophiles solely by an associative mechanism, and the rate constants can be analyzed quantitatively according to the electronic and steric properties of the nucleophiles by the QALE method. An unexpected outcome of this analysis is that inclusion of what has become known as the "aryl effect" is clearly necessary, together with positive contributions to the rates of effects due to the π-acidity of the phosphite nucleophiles. A simple way of representing the individual contributions of the various effects to the overall rates is described, and the general σ-basicity and steric effects can be represented graphically by a three-dimensional "log k_2 surface" upon which the aryl and π-acidity effects can separately be superimposed as additional peaks. A free energy surface can be obtained by a simple scale change.

Introduction

Quantitative studies of the influence of electronic and steric properties of P-donor and other nucleophiles on the rates of associative reactions of metal carbonyls have a long history.[1] They have shown increasing success in the precise fitting of data to equations that include a variety of parameters that quantify the detailed nature of the nucleophiles.[2,3] A typical equation[4] that has been used successfully by Poë et al.[2−5] for associative reactions is shown below (eq 1), where α is the standard

$$\log k_2 = \alpha + \beta(\mathrm{p}K_a{}' + 4) + \gamma(\theta - \theta_{\mathrm{th}})\lambda \qquad (1)$$

reactivity referenced to a weakly basic nucleophile ($\mathrm{p}K_a{}' = -4$) that is sufficiently small for steric effects to be unimportant. The sensitivity (β) to the σ-basicity of the nucleophile is measured relative to $\mathrm{p}K_a{}'$ (a parameter closely related to $\mathrm{p}K_a$[2,3a]), and the coefficient γ describes the dependence of rate on ligand size as measured by Tolman's cone angles (θ).[1d,6] The steric threshold, θ_{th}, is the largest cone angle for which steric effects no longer exist, and λ is a switching function[5] ($\lambda = 1$ for $\theta > \theta_{\mathrm{th}}$ and $\lambda = 0$ for $\theta < \theta_{\mathrm{th}}$).

An integral part of these developments has been the parallel application of the same approach to physical processes far beyond those involved in associative reactions of the sort mentioned here. A general equation has been applied[7] to many properties such as carbonyl stretching frequencies, metal−P bond lengths, equilibrium constants, rate constants for quite different reactions, enthalpies of activation, and reduction potentials.[7] Recent publications[8] have dealt successfully with the problematic separation of σ-donor and π-acidity effects,[1f,9] and added credence has been given to the validity of potentially contentious effects such as the "aryl effect"[7,10] (a property related to the number of phenyl groups on the nucleophiles) and others related to the presence on the P-donor atom of specific pendant groups or atoms such as OR or OAr, and halogens.[7,11]

We report here a kinetic study of the associative reactions of a wide range of P-donor nucleophiles with the simple metal carbonyl cluster $Rh_4(CO)_{12}$. Earlier work[12] had shown that it reacts with PPh_3 by a purely

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[1] (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. (b) Poë A. J.; Twigg, M. V. *J. Organomet. Chem.* **1973**, *50*, C39. (c) Poë, A. J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1860. (d) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (e) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771. (f) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981. (g) Dahlinger, K.; Falcone, F.; Poë, A. J. *Inorg. Chem.* **1986**, *25*, 2654.

[2] Farrar, D. H.; Poë, A. J.; Zheng, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5146.

[3] (a) Chen, L.; Poë, A. J. *Coord. Chem. Rev.* **1995**, *143*, 265, and references therein. (b) Brodie, N. M. J.; Poë, A. J. *J. Organomet. Chem.* **1971**, *383*, 531. (c) Brodie, N. M. J. Ph.D. Thesis, University of Toronto, 1989. (d) Chen, L.; Poë, A. J. *Can. J. Chem.* **1989**, *67*, 1924. (e) Hudson, R. H. E.; Poë, A. J. *Organometallics* **1995**, *14*, 3238. (f) Poë, A. J.; Zheng, Y. *Inorg. Chim. Acta* **1996**, *252*, 311.

[4] This equation was derived (see ref 2) following the closely similar one derived by Giering, Prock, et al., ref 5.

[5] Liu, H.-Y.; Eriks, K.; Prock, A..; Giering, W. P. *Organometallics* **1990**, *9*, 1758.

[6] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

[7] (a) Fernandez, Prock and Giering have a web page (ref 7b) describing their QALE methodology (QALE = quantitative analysis of ligand effects) and giving examples of recent analyses of a wide variety of data together with a listing of all relevant literature. (b) www.bu.edu/qale/.

[8] (a) Chen, L. Ph.D. Thesis, University of Toronto, 1991. (b) Fernandez, A. L.; Reyes, C.; Prock, A.; Giering, W. P. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1033. (c) Woska, D.; Prock, A.; Giering, W. P. *Organometallics* **2000**, *19*, 4629. (d) Bunten, K. A.; Chen, L.; Fernandez, A. L.; Poë, A. J. *Coord. Chem. Rev.* **2002**, *233*, 41.

[9] (a) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315. (b) Stewart, R. P.; Treichel, P. M. *Inorg. Chem.* **1968**, *7*, 1942. (c) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1. (d) Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391. (e) Alyea, E. C.; Song, S. *Comments Inorg. Chem.* **1996**, *18*, 189.

[10] (a) Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 1742. (b) Farrar, D. H.; Hao, J. H.; Poë, A. J.; Stromnova, T. A. *Organometallics* **1997**, *16*, 2827.

[11] Poë, A. J.; Babij, C. Unpublished calculations.

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associative path, and our studies show that this is quite general and that the rate constants fit well to eq 2. This

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

equation is very unusual for associative reactions of P-donor nucleophiles in that it includes two additional terms, in E_{ar} and $pK_a'\pi$, that reveal contributions to the rates that are assignable to the aryl effect[10] and the P-donors' abilities to act as π-electron acceptors,[8d] respectively. The contributions of the various terms are simply quantified, and a novel way of representing the data in terms of a three-dimensional "potential energy surface" is presented.

Experimental Section

General Procedures. Tetrarhodiumdodecacarbonyl (Strem) was used as received. Dichloromethane (Anachemia) and chlorobenzene (Caledon) were predried over $CaCl_2$ and distilled over CaH_2 and P_2O_5, respectively. Solid phosphorus ligands, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane ($P(OCH_2CH_2)_3CEt$, etpb) (Lancaster), triphenylphosphine, tri(*p*-chlorophenyl)phosphine, tri(*p*-fluorophenyl)phosphine, tri(*p*-methoxyphenyl)phosphine, tri(*p*-tolyl)phosphine, tricyclohexylphosphine (Strem), and tri(*p*-dimethylaminophenyl)phosphine (Organometallics Inc.), were checked for purity by $^{31}P\ \{^1H\}$ NMR and recrystallized from hexanes if necessary. Liquid P-donors, tributylphosphine (Aldrich), triphenyl phosphite, triisopropyl phosphite, triethyl phosphite, and triisopropylphosphine (Strem), were checked for purity by $^{31}P\{^1H\}$ NMR and distilled under reduced pressure if necessary. Trimethylphosphine (1.0 M solution in Toluene) (Aldrich) was used as received. Nitrogen (Matheson Pre-purified) was passed through a Dririte column before use.

Instruments. Infrared spectra were recorded on a Nicolet Magna-IR 550 FTIR optical bench in absorbance mode using 1.0 mm path length solution cells with NaCl windows. ^{31}Phosphorus $\{^1H\}$ NMR spectra were recorded on a Varian 300 MHz spectrometer, and chemical shifts were referenced to H_3PO_4 as standard. Kinetic studies were made with a Hi-Tech SF-51 UV−vis stopped-flow apparatus equipped with an SU-40 spectrophotometer interfaced with a Hewlett-Packard Series 300 computer and connected with a Hewlett-Packard printer.

Kinetic Studies. Stopped-flow kinetic techniques were required for monitoring the substitution reactions. Measurements at 10 °C in chlorobenzene were conducted exactly as reported elsewhere.[2] All runs were performed using pseudo-first-order ratios of phosphine over rhodium complex. Pseudo-first-order rate constants (k_{obs}) were obtained by using software provided with the stopped-flow apparatus and were generally an average of five repetitions obtained at three wavelengths between 380 and 450 nm.

Results

Course of the Reactions. The addition of 1 equiv of any P-donor to a solution of $Rh_4(CO)_{12}$ in CH_2Cl_2 results in immediate color change from light brown to red, and the FTIR spectrum of this solution in the carbonyl stretching region shows a typical pattern for $Rh_4(CO)_{11}L$ clusters (Table S1 in Supporting Information).[13] The complex reacts with a large excess of nucleophile to give an initial red solution as above, followed by much slower conversion to other species.[13] It was impossible to monitor the rate of decay of $Rh_4(CO)_{12}$, and therefore only product growth was followed. Typical UV−vis absorption spectra between 300 and 600 nm for the reaction of $Rh_4(CO)_{12}$ with a 10-fold excess PPh_3 are shown in Figure S1, and a typical trace of the absorbance with time is shown in Figure S2. Although multisubstitution or cluster fragmentation reactions were evident from the FTIR spectra after the initial rapid reaction, the data could usually be fitted to a single-exponential equation because the rates of the subsequent reaction were much slower than the first substitution step. The only exception was reaction with etpb, which exhibited double-exponential behavior resulting from mono- and disubstitution reactions of comparable rates.

Table 1. Kinetic and Stereoelectronic Parameters for Reaction of P-Donor Nucleophiles with $Rh_4(CO)_{12}$ at 10 °C in Chlorobenzene

no.	phosphine	pK_a'[a]	θ[b]	E_{ar}[c]	$pK_a'\pi$[d]	π_p[e]	$\log k_2$ (expt)	$\log k_2$ (calc)[f]
1	etpb	−0.30	101	0	8.50	5	5.50	5.57
2	$P(OEt)_3$	1.64	109	0	3.97	2.9	5.53	5.48
3	PMe_3	6.45	118	0	0	0	5.95	5.89
4	$P(OPh)_3$	−2.79	128	0	5.33	4.1	4.41	4.38
5	$P(O\text{-}i\text{-}Pr)_3$	3.38	130	0	4.00	2.9	5.29	5.23
6	$P(n\text{-}Bu)_3$	8.67	132	0	0	0	5.57	5.67
7	$P(p\text{-}ClC_6H_4)_3$	0.87	145	2.7	0	0	4.21	4.29
8	$P(p\text{-}FC_6H_4)_3$	1.63	145	2.7	0	0	4.40	4.42
9	PPh_3	3.28	145	2.7	0	0	4.75	4.70
10	$P(p\text{-}tol)_3$	4.46	145	2.7	0	0	4.95	4.90
11	$P(p\text{-}MeOC_6H_4)_3$	5.13	145	2.7	0	0	5.01	5.02
12	$P(i\text{-}Pr)_3$	9.88	160	0	0	0	4.50	4.69
13	$P(Cy_3)$	11.26	170	0	0	0	4.67	4.51
14	$P(p\text{-}Me_2NC_6H_4)_3$	8.67	145	2.7	0	0	5.18[g]	5.80[g]

[a] From ref 3a.. [b] From ref 1d. [c] From ref 10a. [d] From refs 8a,d. [e] W. P. Giering's π_p parameter from ref 8b. [f] See text. [g] Note the deviant nature of the data for this nucleophile, which we have therefore treated as an "outlier".

Kinetics. Values of k_{obs} are given in Table S2. Plots of k_{obs} versus [L] (Figure S3) are linear with intercepts generally indistinguishable from zero, and the data follow the rate equation typical of a second-order associative reaction. Second-order rate constants (k_2) (Table S2) were determined from a linear least-squares analysis using proportional weighting. Values of $\log k_2$ and relevant ligand parameters are reported in Table 1, and the dependence of $\log k_2$ on pK_a' is shown in Figure 1.

Discussion

The selective formation of $Rh_4(CO)_{11}L$ from 1:1 mixtures of Rh cluster and phosphine and the clearly distinguishable kinetics of the appropriate color changes in the presence of pseudo-first-order excesses of phosphine provide convincing evidence that the first stage of reaction observed in the UV did indeed form the monosubstituted product. This supplements and extends the evidence provided by the low-temperature IR studies performed by Basolo et al.[12]

Graphical Data Analysis. Giering, Prock, et al.[14] described how graphical analysis of ligand effects should

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(12) Kennedy, J. R.; Basolo, F.; Trogler, W. C. *Inorg. Chim. Acta* **1988**, *146*, 75.

(13) Whyman, R. J. *Chem. Soc., Dalton Trans.* **1972**, 1375.

(14) Bartholomew, J.; Fernandez, A. L.; Lorsbach, B. A.; Wilson, M. R.; Prock, A.; Giering, W. P. *Organometallics* **1996**, *15*, 295.

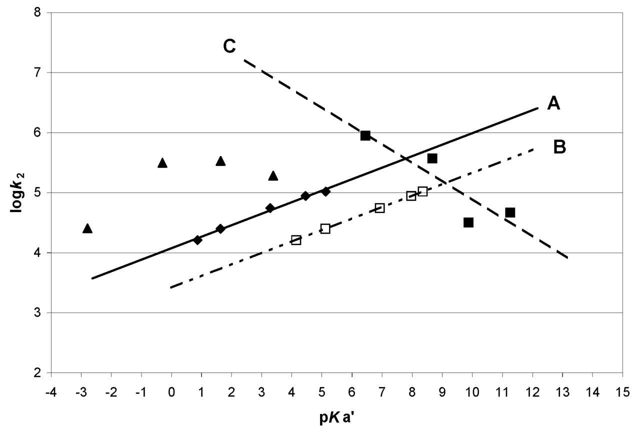

Figure 1. Electronic profile for associative reactions of P-donor nucleophiles with $Rh_4(CO)_{12}$ in chlorobenzene at 10 °C. (A) Isosteric triaryl ($P(p\text{-}XC_6H_4)_3$) nucleophiles (diamonds). (B) Theoretical values for $P(p\text{-}XC_6H_4)_3$ nucleophiles if forced to pass through $pK_a' = 9.1$ (open squares). (C) Trialkylphosphine (PR_3) nucleophiles (solid squares). Phosphite nucleophiles (solid triangles).

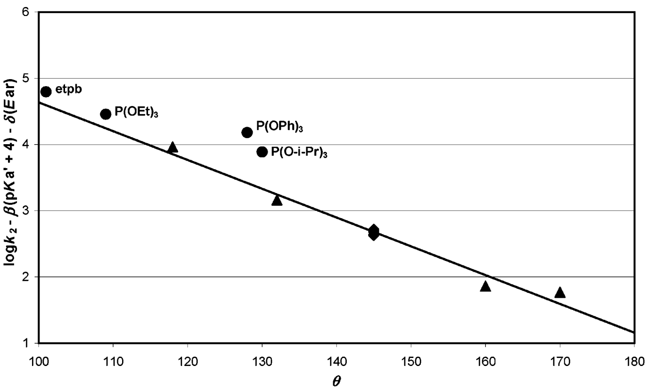

Figure 2. Steric profile for the reactions of P-donor nucleophiles (PR_3 (solid triangles) and PAr_3 (solid diamonds), phosphites (solid circles)) with $Rh_4(CO)_{12}$ in chlorobenzene at 10 °C. The profile was obtained using graphically estimated parameters, ($\beta = 0.19$ and $\delta = 0.24$), and the line is drawn through the PR_3 and PAr_3 nucleophiles only.

be used in conjunction with regression analysis to gain a consistent interpretation of regression results, and we have generally followed their protocols.

The data shown in Figure 1 provide initial qualitative or semiquantitative indications of the importance of the various terms in eq 2.

(i) Effect of σ-Basicity. The excellent linearity of the plot of log k_2 against pK_a' for the strictly isosteric (p-$XC_6H_4)_3P$ nucleophiles shows that the gradient (0.19) should provide a precise value of the coefficient β. The data for the nucleophile (p-$Me_2NC_6H_4)_3P$ (Table 1) are clearly deviant for reasons that are not obvious to us, and they are disregarded here and in the following analysis.

(ii) Existence of a Steric Effect. The data for the trialkylphosphines also lie on a reasonably straight line, but obviously not on the same line as the triarylphosphines. This shows that there must be a significant steric effect because otherwise the two sets of data would lie on the same line. The linearity of this plot is a result of the good correlation between the pK_a' and θ values for these nucleophiles (Figure S4), but this means that this straight line does not allow the derivation of the steric effects separately from the electronic ones. However, the fact that the point for PMe_3 lies on the same line as the other trialkylphosphines does suggest that the steric threshold, if any, must lie below 118°, the cone angle for PMe_3.

(iii) Aryl Effect. The correlation mentioned above, between pK_a' and θ values for trialkylphosphines, is useful in showing whether there is an aryl effect or not. From the correlation of a large number of trialkylphosphines it is possible to predict that a trialkyl ligand with a cone angle of 145°, the same as those of the triarylphosphines, would have a pK_a' value of 9.1 (Figure S5). However, the intersection in Figure 1 of the lines for those two sets of ligands is close to a $pK_a'$of 7.8. The line, parallel to that for the triarylphosphines, but intersecting the trialkylphosphine line at $pK_a' = 9.1$, lies an average of 0.66 below that for the triarylphosphines, which suggests that the aryl effect leads to a pronounced enhancement of the rates. Giering, Prock, et al. have proposed that $E_{ar} = 2.7$ for triarylphospines[10a] so that a value of $\delta = 0.66/2.7 = 0.24$ results.

(iv) Quantification of the Steric Effect. This is provided by the steric profile shown in Figure 2, where values of $0.19(pK_a' + 4)$ for the σ-donor effect and 0.66 for the aryl effect have been subtracted from the values of log k_2. The gradient of the line provides a value of $\gamma = 0.044\ \text{deg}^{-1}$. The existence of a steric threshold, but one below 118°, will be demonstrated below in conjunction with consideration of π-acidity effects.

(v) Effects of π-Acidity and the Steric Threshold. The nucleophiles $P(OPh)_3$ and P(O-i-Pr)$_3$ have almost equal cone angles (Table 1), but a line going through their data points in Figure 1, and drawn parallel to the line for the triarylphosphines, lies significantly above the latter. This cannot be due simply to a steric effect, because the point for P-n-Bu$_3$ ($\theta = 132°$) does not lie as high, and this suggests that there is also an accelerating effect of ~0.6−0.8 in log k_2 due to the π-acidity of these phosphites. This is confirmed by the steric profile in Figure 2, which was drawn without consideration of the data for the phosphites. Clearly the points for $P(OPh)_3$ and P(O-i-Pr)$_3$ lie significantly above the steric profile, the deviations leading to an average value of $\phi = 0.15$ when divided by the appropriate values of $pK_a'\pi^{8d}$ from Table 1. Since these two phosphites appear to lead to an acceleration of the rates due to their π-acidity, a similar acceleration would be expected for the etpb and $P(OEt)_3$ nucleophiles. When the appropriate values of $\phi pK_a'\pi^{8d}$ are subtracted from their points, they both fall below the steric profile in a way that suggests that there is a steric threshold at ~117° and that provides a value of ~3.7 for α.

There is, therefore, excellent justification for a regression analysis of the data in terms of eq 2, the results of which are given in Table 2 using data for various combinations of nucleophiles.

Regression Analysis of Data. Statistical analysis of the kinetic data was used to confirm the initial values obtained from the graphical data analysis and to provide a more accurate measure of the contributions of each stereoelectronic parameter to log k_2. The rate data were fitted according to eq 2, taken in several stages to show the internal consistency of the contributions made by

Table 2. Kinetic Parameters from Regression Analyses Performed on Data for Associative Reactions of P-Donor Nucleophiles with $Rh_4(CO)_{12}$

no.	θ_{th} (deg^{-1})	α (deg^{-1})	β (deg^{-1})	γ (deg^{-1})	δ (deg^{-1})	ϕ (deg^{-1})	r^2 (deg^{-1})	σ(log k_2)	$\sigma(\theta)^a$
1^b	∼117	∼3.7	0.19	−0.044	0.24	0.15			
2^c		NA	0.19(1)				0.991	0.04	
3^d		NA	0.19(3)	−0.044(4)	0.24(8)		0.968	0.13	2.4
$4^{e,f}$	≤118	NA	0.19(3)	−0.043(3)	0.23(6)	0.14(5)	0.972	0.12	2.2
$5^{f,g}$	117	4.15(20)	0.17(2)	−0.042(3)	0.18(5)	0.09(3)	0.972	0.11	2.4
$6^{g,h}$	117	3.92(23)	0.19(2)	−0.044(2)	0.23(5)	$0.18(4)^i$	0.977	0.10	2.2

[a] See ref 15. [b] Estimates from graphical analysis. [c] Isosteric triaryl ($P(p\text{-}XC_6H_4)_3$) nucleophiles. [d] Trialkyl (PR_3) and isosteric $P(p\text{-}X\ C_6H_4)_3$ nucleophiles. [e] PR_3, $P(p\text{-}X\ C_6H_4)_3$, and phosphite nucleophiles ($\theta \geq 118$). [f] Using π parameters ($pK_a'\pi$) derived by Poë et al.[8d] [g] All nucleophiles included. [h] Using the π_p values derived by Giering et al.[8b] [i] This coefficient is different because of the use of the different π-acidity parameter.

different sets of nucleophiles. The resulting regression analyses are presented in Table 2, together with those from the graphical analyses for comparison.

First, data for the triarylphosphine nucleophiles alone were fitted and provide a value of β identical to that obtained graphically. Inclusion of the trialkylphosphines leads to values of γ and δ that are again identical to the graphically obtained ones, and inclusion of all ligands with $\theta \geq 118°$ leads to unchanged values of β, γ, and δ and a value for ϕ equal to that obtained graphically. Finally, inclusion of all the ligands, and allowance for the existence of a steric threshold, leads to essentially unchanged parameters. This treatment of the data was undertaken by using either the values of $pK_a'\pi$[8a,d] given in Table 1 or the π_p values (Table 1) estimated for ligand π-acidities by Giering, Prock, et al.[8b] and derived in an entirely different way. The fits are not significantly different, as would be expected from the good correlation between the two sets of π-acidity parameters,[8d] although the fit is very slightly better in the latter case with this particular collection of phosphite ligands.

The values of log k_2, calculated using coefficients obtained from our analysis no. 5 in Table 2, are included in Table 1. It is apparent that the values for the triaryl nucleophiles do not deviate in a systematic way according to their pK_a' values as might have been expected if the aryl effect were dependent on the nature of the para substituent X.

The steric profile obtained from our analysis is shown in Figure 3, and the value of $\sigma(\theta)$,[15] obtained by assuming that *all* the deviations are due to uncertainties in the cone angles, is only 2.4°. This is another measure of the excellence of the fit of the data to eq 2. However, the data for the two smallest ligands, which lie below the steric threshold and cannot have deviations due to uncertainties in their cone angles, do show deviations not untypical of those for the larger ligands, so uncertainties in the cone angles cannot be a major factor. This is additional evidence supporting the validity of Tolman's cone angles.[8d]

Nature of the Transition State. It has been suggested that the high susceptibility of metal carbonyl clusters to nucleophilic attack may be a result of a cluster's ability to undergo M−M bond breaking concurrently with M−L bond making, and so avoid breaking the "18-electron rule".[3,16] Examples analogous to this process have been detected,[17a] and it is consistent with the predictions of the more general PSEP theory[17b] according to which addition of a pair of electrons to the cluster will cause a change from a closed *nido* structure to an open *arachno* one. This explanation can be applied to this rhodium cluster, as indicated by the structure shown in Figure 4. The carbonyl ligands in $Rh_4(CO)_{12}$ are highly fluctional and indistinguishable from each other in solution.[18] Therefore, rearrangement of the bridging carbonyls on forming the intermediate shown in Figure 4 will not require much energy. Loss of CO and re-formation of the Rh−Rh bond will lead to the substituted product.

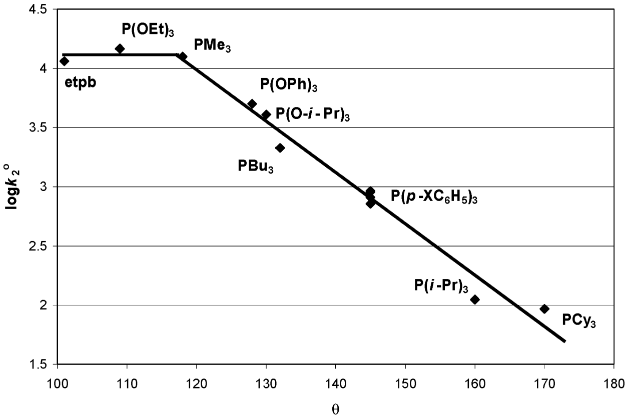

Figure 3. Steric profile from analysis of data for all P-donor nucleophiles (see Table 2, analysis 5) (log $k_2° =$ log $k_2 - \beta(pK_a' + 4) - \delta(E_{ar}) - \phi(pK_a'\pi)$).

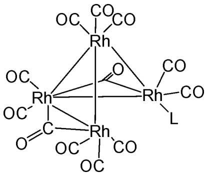

Figure 4. Schematic depicting a proposed *arachno* intermediate in which each Rh atom has maintained its 18-electron configuration.

Contribution of Each Parameter to log k_2. Assessment of the relative contribution of each effect in the QALE equation[7] is of great importance. Giering, Prock, et al.[19] now obtain the relative contributions of each effect by taking the product of the coefficient and the maximum range that the associated parameter is

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[15] Values of $\sigma(\theta)$ are obtained from an inverse steric profile (i.e., a plot of θ vs log $k_2 - α - \beta(pK_a' + 4) - \delta E_{ar} - \phi pK_a'\pi$).

[16] Poë, A. J.; Sekhar, V. *Inorg. Chem.* **1985**, *24*, 4376.

[17] (a) Adams, R. D.; Chi, Y.; DesMarteau, D. D.; Lentz, D.; Marschall, R.; Scherrmann, A. *J. Am. Chem. Soc.* **1992**, *114*, 10822. (b) Mingos, D. M. P.: Johnson, R. L. *Str. Bond.* **1987**, *68*, 29.

[18] (a) Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1083. (b) Johnson, B. F. G.; Benfield, R. E. *J. Chem. Soc., Dalton Trans.* **1978**, 1554.

[19] Wilson, M. R.; Prock, A.; Giering, W. P.; Fernandez, A. L.; Haar, C. M.; Nolan, S. P.; Foxman, B. M. *Organometallics* **2002**, *21*, 2758.

Table 3. Absolute Contribution (in kcal mol^{-1}) of the Terms in Eq 2[a] to $\Delta G^‡$

ligand	$\beta(\mathrm{p}K_a' + 4)$	$\gamma(\theta - 117)$	$\delta(E_{ar})$	$\phi(\mathrm{p}K_a'\pi)$
etpb	−0.81	0.00	0.00	−1.01
$P(OEt)_3$	−1.24	0.00	0.00	−0.47
PMe_3	−2.30	0.05	0.00	0.00
$P(OPh)_3$	−0.27	0.60	0.00	−0.63
$P(O\text{-}i\text{-}Pr)_3$	−1.62	0.71	0.00	−0.47
$P(n\text{-}Bu)_3$	−2.78	0.82	0.00	0.00
$P(p\text{-}ClC_6H_4)_3$	−1.07	1.53	−0.64	0.00
$P(p\text{-}FC_6H_4)_3$	−1.24	1.53	−0.64	0.00
PPh_3	−1.60	1.53	−0.64	0.00
$P(p\text{-}MeC_6H_4)_3$	−1.86	1.53	−0.64	0.00
$P(p\text{-}MeOC_6H_4)_3$	−2.01	1.53	−0.64	0.00
$P(i\text{-}Pr)_3$	−3.05	2.36	0.00	0.00
$P(Cy)_3$	−3.35	2.90	0.00	0.00
$P(p\text{-}Me_2NC_6H_4)_3$	−2.78	1.53	−0.64	0.00
maximum[b]	−3.35	2.90	−0.64	−1.01
minimum[b]	−0.27	0.00	0.00	0.00

[a] $\alpha = 11.16$ for all nucleophiles. [b] Ignoring signs.

judged to have. Each of these products is then divided by the total sum of all such products. This method has the drawback of involving rather arbitrary choices of the "maximum ranges". Moreover, it does not seem to account for the standard reactivity (the term *e* in their equation,[19] corresponding to our α in eq 2), which is an important contributor to log k_2 albeit one that depends on the chosen standard reference value of pK_a'.[3]

In our view, a less ambiguous way of describing the contributions is to calculate them for each nucleophile independently. This can be done in terms of the absolute contributions of each term in eq 2 to the Gibbs free energy of activation ($\Delta G^‡$), and these are listed in Table 3 and shown graphically in Figure 5. The latter clearly demonstrates the ability of the terms involving β, δ, and ϕ to decrease the free energy barriers and enhance the rates of reaction, whereas the steric parameter, γ, adds to the barriers and decreases the rates. The maximum and minimum contributions of each term are given in Table 3, and the maximum contributions, not each by the same nucleophile of course, are −3.4, 2.9, −0.6, and −1.0 kcal mol^{-1} for the terms in β, γ, δ, and ϕ, respectively, while the barrier representing the standard reactivity is 11.2 kcal mol^{-1} for all nucleophiles.

An alternative representation of the contributions of each term can be obtained as follows. Equation 2 implies that each value of k_2 is made up of a standard rate constant, k_α (which is the antilog of α), that is multiplied by a series of modifying factors, $f(\sigma)$, $f(\mathrm{st})$, etc., that are equal, respectively, to the antilogs of each term $\beta(\mathrm{p}K_a' + 4)$, $\gamma(\theta - \theta_{th})\lambda$, etc. Thus the modifying factors provide a quantitative measure of how much the various contributions increase or decrease the standard rate constant. Values of k_α/k_2 are given in Table 4 together with the values of the various modifying factors.

Both methods of representing the data show the dominant contributions of the σ-donor and steric effects, but the π-acid and aryl effects can be seen to be quite significant. The results in Table 4 also show that the standard reactivity, as defined,[3] is always less than any observed value of k_2.

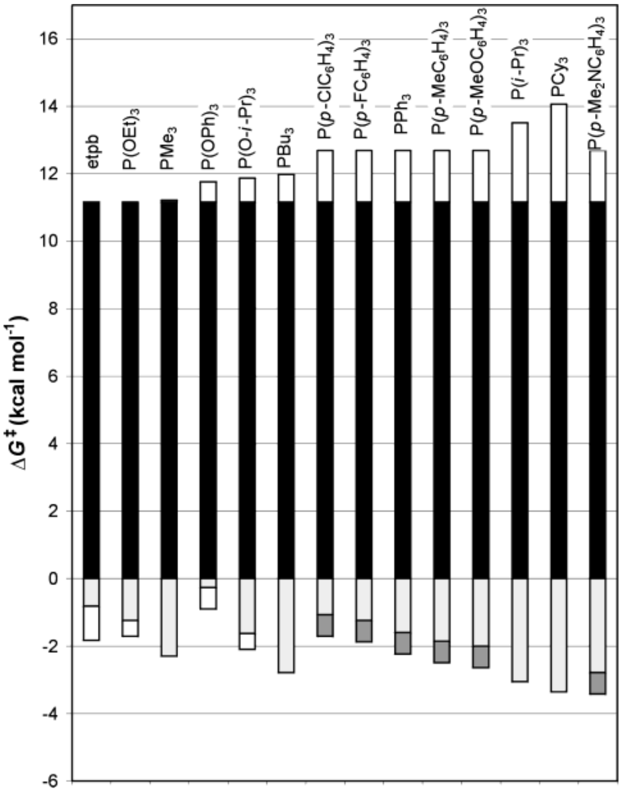

Figure 5. Bar graph showing absolute contribution of each term in eq 2 to $\Delta G^‡$ ($\theta_{th} = 117°$; $T = 10$ °C). Standard reactivity (black); σ-donicity contributions (lighter gray); steric contributions (no fill, top); aryl effect contributions (darker gray); π-acidity contributions (no fill, bottom).

Table 4. Contributions of k_α to k_2 and the Electronic and Steric Factors[a] that Modify k_α

ligand	k_α/k_2[b] (%)	$f(\sigma)$	$f(\mathrm{st})$	$f(\mathrm{ar})$	$f(\pi)$
etpb	4	4	1	1	6
$P(OEt)_3$	5	9	1	1	2
PMe_3	2	60	1/1.1	1	1
$P(OPh)_3$	58	2	1/2.9	1	3
$P(O\text{-}i\text{-}Pr)_3$	8.2	20	1/3.5	1	2
$P(n\text{-}Bu)_3$	3.0	140	1/4.3	1	1
$P(p\text{-}ClC_6H_4)_3$	74	7	1/15	3.1	1
$P(p\text{-}FC_6H_4)_3$	54	9	1/15	3.1	1
PPh_3	28	17	1/15	3.1	1
$P(p\text{-}MeC_6H_4)_3$	18	27	1/15	3.1	1
$P(p\text{-}MeOC_6H_4)_3$	13	36	1/15	3.1	1
$P(i\text{-}Pr)_3$	29	230	1/64	1	1
$P(Cy_3)$	44	390	1/170	1	1
$P(p\text{-}Me_2NC_6H_4)_3$	2	140	1/15	3.1	1
maximum	74	390	1/170	3.1	6
minimum	2	2	1	1	1

[a] $k_2 = k_\alpha f(\sigma) f(\mathrm{st}) f(\mathrm{ar}) f(\pi)$. A factor of 1 means the term has no effect on k_α. [b] k_α is constant at 1.4×10^4 M^{-1} s^{-1}. The values of k_2 are the antilogs of the log k_2(calc) values in Table 1.

General Representation. A new method of graphically describing simultaneously the behavior of all possible P-donor nucleophiles (real or hypothetical) is proposed. Using the determined coefficients from the analysis, a "log k_2 surface" was constructed (Figure 6). This type of plot gives us an instant picture of how any nucleophile should behave in the absence of aryl or π-acidity effects. Aryl or π-acidity contributions to log k_2 are shown by adding their respective contributions to the profile. An equivalent surface in terms of free energies is easily constructed by a scale change to the *y*-axis.

Comparison with Reactions of Other Metal Carbonyl Clusters. The kinetics of reactions of $M_4(CO)_{12}$ (M = Co, Rh, and Ir) have been studied, and reactions of $Co_4(CO)_{12}$ with PPh_3 showed that it did not follow simple associative or dissociative mechanisms.[12] Data

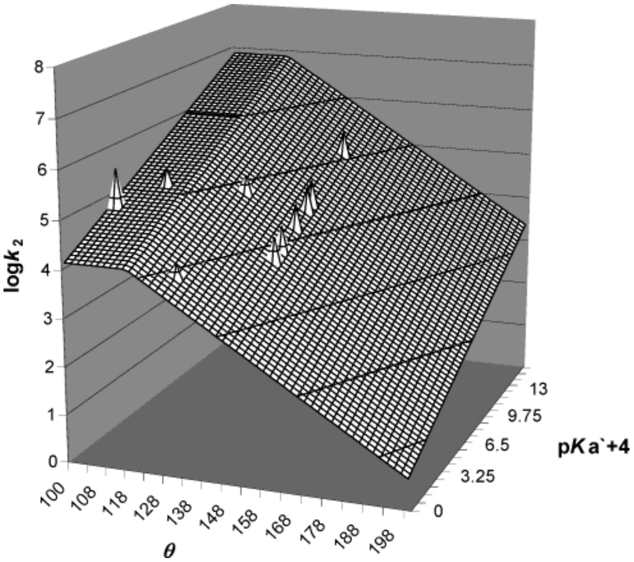

Figure 6. "log k_2 surface" constructed for all possible combinations and θ and pK_a'. The spikes account for the contributions from E_{ar} and $pK_a'\pi$ terms for the $P(p\text{-}XC_6H_4)_3$ and phosphite nucleophiles, respectively. The log k_2 values used in this figure are calculated, not observed.

in Table S3 show that the rhodium cluster exhibits the highest standard reactivity yet observed (4.1) for reactions of metal carbonyl clusters (or of any metal carbonyls), being nearly 2 orders of magnitude more reactive than the other second-row clusters $Ru_5C(CO)_{15}$ (2.86 for ligands smaller than 130°)[20] and $Ru_6C(CO)_{17}$ (2.13),[2] both at 25 °C. Standard reactivities for substituted Rh_4 carbonyl clusters are also quite high,[3b,c] viz., $Rh_4(CO)_{10}(PCy_3)_2$ (1.60), $Rh_4(CO)_9\{(HC(PPh_2)_3\}$ (2.44), and $Rh_4(CO)_9(etpb)_3$ (0.15) at 25 °C. By comparison, the third-row cluster $Ir_4(CO)_{12}$ has a standard reactivity that could be ~6 orders of magnitude less than for associative reactions of $Rh_4(CO)_{12}$ at 10 °C.[1g,21] Analysis of M−M stretching force constants by Raman spectroscopic methods provides a relevant measure of the ease of cluster deformation, and solution[22] and solid state spectra of the clusters $Rh_4(CO)_{12}$[23] and $Ir_4(CO)_{12}$[24] have been reported. The derived force constants are 89 and 169 N m^{-1} for $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$, respectively, and these are entirely consistent with the proposed importance of M−M bond breaking as a major factor in determining the reactivities of these clusters.

The electronic parameter, β, for the $Rh_4(CO)_{12}$ cluster has an intermediate value of 0.17, while the substituted Rh_4 clusters cover a wide range from 0.02 for the sterically strained $Rh_4(CO)_{10}(PCy_3)_2$, which seems to require almost no Rh−P bond making in the transition state, to 0.36 for the sterically rigid $Rh_4(CO)_9\{HC(PPh_2)_3\}$, both at ~25 °C. These values compare with the rather high value of ~0.33 for $Ir_4(CO)_{12}$[1g,3a] extrapolated to 10 °C, which suggests that rather extensive bond making is required for reactions of this intrinsically unreactive cluster. The iridium cluster exhibits the need for substantially lower amounts of Ir−P bond making in the transition state at higher temperatures, with β decreasing to 0.18 at 100 °C. This observation is consistent with P−Ir bond making being less important at higher temperatures where Ir−Ir bond breaking is easier, as indicated by the higher standard reactivity.

Steric effects in $Rh_4(CO)_{12}$ are very different from the iridium analogue. The Rh cluster has quite a well-defined steric threshold at 117°, while $Rh_4(CO)_9(etpb)_3$ and $Rh_4(CO)_{10}(PCy_3)_2$ have substantially higher thresholds.[3b] By contrast, the Ir cluster seems to have no steric threshold above 101°. However, when steric factors do come into play, these rhodium clusters are clearly more flexible than the iridium clusters, as evidenced by the much less negative γ values, and in accordance with the relative force constants mentioned above. However, the cluster $Rh_4(CO)_9\{(HC(PPh_2)_3)\}$, with the rigid bridging ligand and $\gamma = -0.112$, is the most inflexible of the series. This, and its high need for Rh−P bond making, seems to be characteristic of the unique nature of this bridged Rh cluster.

Finally, the existence of detectable, if small, aryl and π-acidity effects in the reactions of $Rh_4(CO)_{12}$ distinguish it from all the other M_4 clusters, although the smaller number of nucleophiles involved in these other studies might make detection of these effects difficult.

Summary and Conclusions

The metal carbonyl cluster $Rh_4(CO)_{12}$ undergoes nucleophilic substitution reactions via a purely associative path. The data give an excellent fit to the QALE equation (eq 2) with significant and very unusual contributions to log k_2 from aryl and π-acidity effects. This cluster has an exceptionally high standard reactivity toward nucleophilic attack. It has only a moderate need for metal−nucleophile bond making in the transition state, which is also quite highly flexible. The development of new methods of presenting data provides a simple approach to graphical representation of ligand effects.

The systematic kinetic study of associative reactions of metal carbonyls is a useful way of providing a quantitative description of the dynamic nature of a complex, and it can predict how the complex will behave in the presence of specific P-donor nucleophiles. The data can be analyzed successfully by the QALE method, and the contribution of each parameter can be quantified. The coefficients α, β, γ, δ, and ϕ provide a unique "kinetic fingerprint", each compound responding to the various effects in different ways. Steric effects are usually important in determining rates of reactions along with the effects of σ-basicity of the P-donor nucleophile. The recent addition of new parameters, E_{ar} and $pK_a'\pi$ (or π_p), adds two new dimensions to the analysis of kinetic data. Although the physical cause of the aryl effect remains obscure, its existence is clearly established,[7b,10] as is that of π-acidity effects. It was originally thought that the effects of π-acceptor ligands would be minimal for associative reactions.[2,3a] This is clearly not always the case, as is made evident by the analysis of data for $Rh_4(CO)_{12}$ in this study, and by

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(20) Farrar, D. H.; Poë, A. J.; Zheng, Y. *J. Am. Chem. Soc.* **1994**, *116*, 6252.

(21) The cluster $Ir_4(CO)_{12}$ shows no steric threshold above 101° (see refs 1g and 8d, and Table S3) and therefore has a standard reactivity greater than ~−2 at 10 °C.

(22) Creighton, A. J.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1981**, 1498.

(23) Oxton, I. A. *Inorg. Chem.* **1980**, *19*, 2825.

(24) Quicksall, C. O.; Spiro, T. G. *Inorg. Chem.* **1969**, *8*, 2011.

reanalysis of data for $Ru_3(CO)_{12}$,[8a,11] which have clear contributions from aryl and π-effects.

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Supporting Information Available: Additional tables and figures include spectroscopic and kinetic data and a summary of QALE analyses for a number of metal carbonyl clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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