Reaction Mechanisms of Metal–Metal-bonded Carbonyls. Part 13.[1] Substitution Reactions of μ-Diphenylacetylene-bis(tricarbonylcobalt)-(*Co–Co*)

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The kinetics have been studied of substitution (in decalin at 55 °C) of one carbonyl ligand in the complex $[Co_2(C_2Ph_2)(CO)_6]$ by several phosphorus-donor ligands covering a wide range of nucleophilic character $\{L = PBu^n_3$, PPh_3, PEt_2Ph, $PEtPh_2$, $P(OEt)_3$, $P(OPh)_3$, and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (etpb)$\}$. Reactions under an atmosphere of argon follow the rate equation $k_{obs.} = k_1 + k_2[L]$, and the dependence of log k_2 on the basicity of L shows that bond making (probably to the metal) plays an important part in the transition state for the bimolecular path. The effect of carbon monoxide on the path governed by the limiting first-order rate constant k_1 has been studied and found to be consistent with, but not to prove, a simple CO-dissociative mechanism for substitution by this path. If this is the mechanism, the data for reactions under carbon monoxide provide relative rate constants for bimolecular attack by the various ligands at the vacant co-ordination site. This would be the first example where relative nucleophilicities have been determined towards a fully co-ordinated complex and a co-ordinatively unsaturated form of the same complex.

THE complex μ-diphenylacetylene-bis(tricarbonylcobalt)-(*Co–Co*) has been shown [2] to undergo a substitution reaction with tri-n-butylphosphine according to the rate equation $k_{obs.} = k_1 + k_2[PBu_3]$, where $k_{obs.}$ is the observed pseudo-first-order rate constant for the reaction. The rate constant k_2 was ascribed to nucleophilic attack at a cobalt atom in the complex. We have extended this study to include a series of other phosphorus-donor nucleophiles, and the dependence of the values of k_2 on the nature of the nucleophiles is found to be consistent with attack at a cobalt atom. We have also studied the effect of carbon monoxide on the substitution for which k_1 is the limiting rate constant.

EXPERIMENTAL

The complex $[Co_2(C_2Ph_2)(CO)_6]$ was prepared as before.[2] The i.r. spectrum in decalin (2 090m, 2 056s, 2 028s, 2 025s, and 2 010 cm^{-1}) was in very close agreement with those obtained previously. Tri-n-butylphosphine (Baker Chemicals) and diethylphenyl- and ethyldiphenyl-phosphine (Strem Chemicals) were distilled under reduced pressure [110 (10), 65 (2), and 130 °C (1 mmHg), respectively],† the last two compounds being sealed in vials under argon before use. Triethyl and triphenyl phosphites (B.D.H.) were either distilled under reduced pressure [21—22 (0.9) and 172—174 °C (9.4 mmHg), respectively], or used as received. Triphenylphosphine and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane $\{P[(OCH_2)_3CEt]$ (etpb)$\}$ (Strem Chemicals) were recrystallised from methanol and hexane, respectively. Carbon monoxide (C.P. grade, 99.5%) and argon (99.998%) were supplied by Union Carbide of Canada Ltd. Decalin (J. T. Baker, analysed reagent) was dried over molecular sieves.

Procedures.—Solutions for kinetic runs were prepared individually by weighing appropriate quantities of ligand and complex into Schlenk reaction tubes and adding decalin (10 cm^3) by pipette. The reaction tubes were then sealed with rubber septum caps, the solutions degassed by two or three freeze–pump–thaw cycles, and the tubes filled with argon or carbon monoxide under atmospheric pressure, wrapped in aluminium foil, and immersed in an oil-bath maintained at 55.0 ± 0.1 °C. Samples were removed from the reaction vessel periodically through stainless-steel tubing, inserted through the caps, by applying a suitable pressure of gas. The spectra of the samples were recorded immediately with a Perkin-Elmer 257 spectrophotometer. Decalin in a matched cell was used as a reference. In the case of runs under argon the build-up of carbon monoxide in the solution was prevented by periodically shaking the reaction tube and flushing the space above the solution with argon. Band maxima were calibrated against polystyrene and are accurate to ±3 cm^{-1}.

RESULTS

As found previously [2] with tri-n-butylphosphine, the complex $[Co_2(C_2Ph_2)(CO)_6]$ reacts with phosphorus ligands in two successive, although not always clearly separated, stages and it was possible to follow the growth and decay of the spectra characteristic of the various species present in the solution. The band wavenumbers observed for the initial and final products all show a very similar pattern to those of $[Co_2(C_2Ph_2)(CO)_5(PBu_3)]$ and $[Co_2(C_2Ph_2)(CO)_4(PBu_3)_2]$, respectively, and no side products were observed. The i.r. spectra assigned in this way are shown in Table 1.

The course of the first stage of the reaction was followed by monitoring the decrease in absorbance of the bands at 2 090 and either 2 056 or 2 028 cm^{-1}. Even under an atmosphere of carbon monoxide, the reactions involved complete loss of the hexacarbonyl complex and all the pseudo-first-order rate plots obtained were linear to at least 80% completion of reaction, the values of A_∞ being taken as zero. Rate constants were quite independent of the wavelength of the band used to follow the reaction and are reported in Table 2. The excellent linearity of the rate plots for reactions under argon, and the relatively quite small effect of 1 atm of carbon monoxide, showed that the runs under argon were not affected by any small periodic accumulation of carbon monoxide that might have occurred during the reaction.

DISCUSSION

All the reactions under argon followed the general rate equation $k_{obs.} = k_1 + k_2[L]$. The data were analysed by a weighted least-squares treatment, in which all the values of $k_{obs.}$ for a particular nucleophile were assumed to have the same percentage uncertainty. The values of k_1 and k_2, together with the uncertainty of an individual measurement of $k_{obs.}$, are given in Table 3. All the uncertainties are standard deviations corrected for the

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† 1 mmHg ≈ 13.6 × 9.8 Pa, 1 atm = 101 325 Pa.

[1] Part 12, J. P. Fawcett and A. J. Poë, *J.C.S. Dalton*, 1976, 2039.

[2] M. Basato and A. J. Poë, *J.C.S. Dalton*, 1974, 456.

number of degrees of freedom, so that 95% confidence levels can be obtained by doubling the standard deviations. The rate constant k_2 can be assigned to a bimolecular process with a degree of bond making that can be inferred from the extent of the dependence of k_2 on the nature of the nucleophilic ligand. The values of k_1 for all the nucleophiles apart from PBu^n_3 are in good agreement with the weighted mean of $(2.54 \pm 0.02) \times 10^{-4}$ s^{-1}. Previous experience with PBu^n_3 in such reactions [3,4] has shown that low or even negative values of k_1 are frequently observed. It is assumed that, whatever the cause of this may be, it does not seriously affect the value of k_2. This seems reasonable since the value of k_2 obtained in this work is in excellent agreement with that obtained previously [2] over a quite different range of values of $[PBu_3]$. A plot of values of log k_2 against the corresponding half-neutralisation potentials (h.n.p.s) [5] (for titration of the nucleophiles against perchloric acid in nitromethane) is shown in the Figure. The qualitative significance of such plots, and the quantitative significance of the gradients and of the deviations of some points from the plots, have been discussed in some detail.[6] Although the various contributing factors are not all clearly separable, the gradients are a measure

TABLE 1

C–O Stretching bands (cm^{-1}) observed [a] during the reaction of $[Co_2(C_2Ph_2)(CO)_6]$ with several phosphorus-donor ligands in decalin

			$[Co_2(C_2Ph_2)(CO)_5L]$ [b]			
L = $P(OPh)_3$	etpb	PPh_3	$P(OEt)_3$	$PEtPh_2$	PEt_2Ph	PBu_3
2 072	2 070	2 063	2 067	2 059	2 060	2 060
2 023	2 030	2 028	2 018	2 006	2 014	2 010
2 015	2 015	2 004	2 008	1 998	2 009	2 001
		1 969	1 995 (sh)	1 960		
			$[Co_2(C_2Ph_2)(CO)_4L_2]$ [c]			
2 045	2 046	2 023	2 030	2 011	2 015	2 015
2 004 (sh)	1 995	1 968	1 985 (sh)	1 967 (sh)	1 962 (sh)	1 968 (sh)
1 993			1 975	1 957	1 956	

[a] Owing to the large number of bands observed during the reaction, it is by no means certain that the list includes all the bands characteristic of the complexes shown. [b] Assigned by observing the growth of intensity followed by a decrease. [c] Assigned by observing growth coincident with the decay of bands assigned to $[Co_2(C_2Ph_2)(CO)_5L]$.

TABLE 2

Pseudo-first-order rate constants for reaction of $[Co_2(C_2Ph_2)(CO)_6]$ with some phosphorus-donor ligands [a] in decalin at 55.0 °C. [Complex] = 5×10^{-4}—1.5×10^{-3} mol dm^{-3}

	Under argon									Under carbon monoxide						
$10^2[P(OPh)_3]$	3.67	6.45	10.0	20.2	30.0	39.8				0.75	1.54	1.78	2.16	2.90	4.05	10.20
$10^4k_{obs.}/s^{-1}$	2.67	2.67	2.69	2.78	2.91	2.92				0.48	0.75	0.90	0.90	1.16	1.37	2.07
$10^2[etpb]$	5.92	8.28	15.6	20.1	24.2	33.1				0.634	0.847	1.07	1.27	3.12		
$10^4k_{obs.}/s^{-1}$	2.74	2.77	2.96	3.18	3.17	3.48				0.96	1.25	1.28	1.44	2.10		
$10^2[PPh_3]$	5.90	10.4	20.0	30.2	40.4					0.630	0.780	1.13	2.44			
$10^4k_{obs.}/s^{-1}$	2.61	2.69	2.76	2.85	3.00					0.457	0.582	0.736	1.40			
$10^2[P(OEt)_3]$	0.66	0.97	1.16	10.0	15.7	20.4	25.7	30.4	40.2	0.351	0.663	0.972	1.16	2.16	3.32	
$10^4k_{obs.}/s^{-1}$	2.50	2.60	2.61	3.56	4.24	4.49	5.57	6.30	7.06	0.427	0.741	0.938	1.03	1.84	2.13	
										0.434	0.774	0.978				
$10^2[PEtPh_2]$	1.09	1.87	3.74	4.67	7.86	10.80				1.05	1.98	3.81	5.05	6.95	9.53	
$10^4k_{obs.}/s^{-1}$	2.38	2.50	2.86	2.93	3.10	3.39				1.19	1.56	2.15	2.38	2.80	3.39	
$10^2[PEt_2Ph]$	2.19	3.39	6.03	7.87	9.92					0.676	1.21	2.02	3.65	6.24		
$10^4k_{obs.}/s^{-1}$	3.27	3.82	4.66	5.28	5.95					1.12	1.84	2.54	3.28	4.62		
$10^2[PBu_3]$	0.37	0.65	0.85	1.11	4.85	14.4	29.1	4.97		0.567	1.27	1.60	2.55	3.14		
$10^4k_{obs.}/s^{-1}$	2.42	2.75	3.36	3.72 [b]	8.30 [b]	21.4 [b]	39.6 [b]	69.0 [b]		0.92	2.24	2.40	3.77	4.67		

[a] All the concentrations are in mol dm^{-3}. [b] From ref. 2.

TABLE 3

Kinetic parameters [a] obtained from the rate equation $k_{obs.} = k_2[L] + \{k_1(k_3/k_{-1})([L]/[CO])/1 + (k_3/k_{-1})([L]/[CO])\}$

L	Δ(h.n.p.)[b] / mV	10^4k_1 / s^{-1}	10^4k_2 / dm^3 mol^{-1} s^{-1}	$\sigma(k_{obs.})$ / %	k_3/k_{-1}
$P(OPh)_3$	875	2.63 ± 0.03	0.80 ± 0.12	1.4	0.15 ± 0.01
etpb	650	2.56 ± 0.06	2.74 ± 0.30	2.2	0.54 ± 0.02
PPh_3	573	2.56 ± 0.03	1.05 ± 0.13	1.4	0.20 ± 0.01
$P(OEt)_3$	520	2.46 ± 0.06	11.5 ± 0.5	4.2	0.30 ± 0.01
$PEtPh_2$	400	2.34 ± 0.10	10.2 ± 1.9	5.2	0.44 ± 0.04
PEt_2Ph	300	2.57 ± 0.10	34.5 ± 1.9	2.6	0.55 ± 0.03
PBu_3	131	2.02 ± 0.09	133 ± 5	5.8	0.11 ± 0.02

[a] The quantities k_1,k_2, and $\sigma(k_{obs.})$ were obtained only from data for reactions under argon, k_3/k_{-1} from data for reactions under carbon monoxide. All the uncertainties are standard deviations (see text). [b] Ref. 5.

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[3] A. J. Poe and M. V. Twigg, *Inorg. Chem.*, 1974, **13**, 2982.

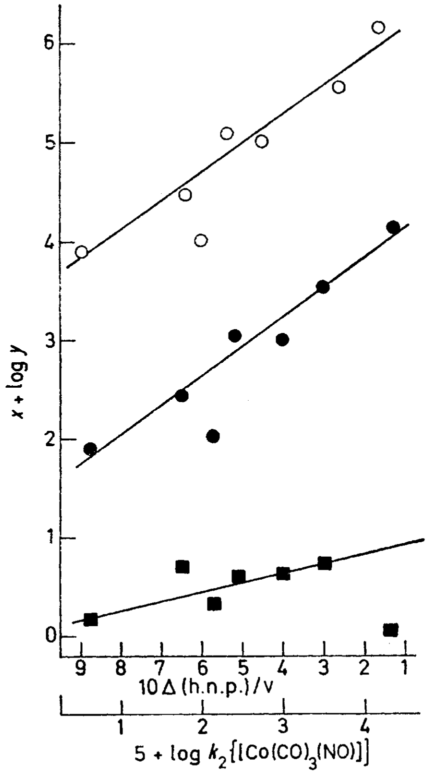
[4] F. Faraone, F. Zingales, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, 1968, **7**, 2362.

[5] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, pp. 571—578.

[6] A. J. Poë and M. V. Twigg, *J.C.S. Dalton*, 1974, 1860.

of the discriminating ability of the electrophile and, therefore, a rough measure of the amount of bond making in the transition state. The deviation of the larger ligands from the linear plots is a measure of unfavourable steric effects and these too will be larger the greater the bond making. Comparison between complexes of different co-ordination number, or even only of different stereochemistry, will involve some obvious difficulties.

According to the plot in the Figure, $-(\log k_2)/\Delta$(h.n.p.) = 2.92 ± 0.26 V^{-1} when the point for L = PPh_3 is ignored. This is comparable with 3.4 V^{-1} for $[(OC)_3\overline{Fe(\mu\text{-}S_2C_6H_3Me)Fe}(CO)_3]$ (in toluene at 35 °C) [7] and *ca.* 2.5 V^{-1} for $[Ru_3(CO)_{12}]$ in decalin at 50 °C.[6] Both these complexes are quasi-octahedral. The present value is much greater than the 0.7 V^{-1} for the simple octahedral $[Cr(CO)_6]$, less than the 3.7 V^{-1} for the trigonal-bipyramidal $[Mn(CO)_4(NO)]$, and much less than the 4.8 and 6.0 V^{-1} for the tetrahedral complexes $[Co(CO)_3(NO)]$ and $[Fe(CO)_2(NO)_2]$, respectively.[6] Thus the discrimination shown by the complexes is a clear function of both the co-ordination number and the lack of definition of the oxidation state of the metal, the latter resulting in a flexibility in the electronic distribution that allows relatively easy approach to the metal by a nucleophile.[5]



Plots of log k_2 against values of log k_2 for reaction of corresponding nucleophiles with $[Co(CO)_3(NO)]$ [(○), $x = 8$, $y = k_2$], of log k_2 against Δ(h.n.p.) [(●), $x = 6$, $y = k_2$], and of log k_3/k_{-1} against Δ(h.n.p.) [(■), $x = 1$, $y = k_3/k_{-1}$]. The nucleophiles are, from left to right, $P(OPh)_3$, etpb, PPh_3, $P(OEt)_3$, $PEtPh_2$, PEt_2Ph, and PBu_3

The deviation, from the straight line, of log k_2 for triphenylphosphine as nucleophile, $\Delta(PPh_3)$, is *ca.* -0.7_0 which is about three times larger than that for the next most deviating nucleophile which is, significantly, the quite bulky $PEtPh_2$. The value of $\Delta(PPh_3)$ is slightly less than the value −1 for $[Ru_3(CO)_{12}]$, but is much greater than the values for $[M(CO)_6]$ (M = Cr, Mo, and W), where bond making is much less pronounced, and the negligible value for $[(OC)_3\overline{Fe(\mu\text{-}S_2C_6H_3Me)Fe}(CO)_3]$ where bond making is pronounced [6] but where the metal is sterically quite accessible.[7] The similarities in behaviour of $[Co_2(C_2Ph_2)(CO)_6]$ and $[Ru_3(CO)_{12}]$ extend also to the activation parameters for reaction with tributylphosphine.[2,3]

The use of Δ(h.n.p.) values in plots such as those in the Figure raises the question of their reliability and physical relevance. However, it follows from the excellent linearity of the plot of log k_2 against Δ(h.n.p.) for $[Co(CO)_3(NO)]$,[5] for which the largest number of data is available, that the Δ(h.n.p.) values quoted do provide an empirically satisfactory way of representing the data. An alternative is to use $[Co(CO)_3(NO)]$ as a standard complex and plot log k_2 for any complex under study against log k_2 for the reaction of corresponding nucleophiles with $[Co(CO)_3(NO)]$. Such a plot for this system is also shown in the Figure and is very close in its form to that involving Δ(h.n.p.). The gradient of 0.70 is virtually identical with the appropriate values of $(\log k_2)/\Delta$(h.n.p.), *viz.* 2.92/4.8, and $\Delta(PPh_3)$ is 0.6_8, so there seems to be no particular advantage in this type of plot. Even though the relation between Δ(h.n.p.) values and nucleophilic character towards transition metals in metal carbonyls would not by any means have been predicted to be so close, the fact that empirically it is makes plots of log k_2 against Δ(h.n.p.) useful for comparative purposes.

The path governed by the limiting rate constant k_1 can most simply be assigned a CO-dissociative mechanism, although it has been pointed out [8] that other mechanisms, possible for metal–metal bonded carbonyls, would lead to identical kinetic behaviour. In the absence of any evidence for such mechanisms, we analysed the data on the assumption that a CO-dissociative mechanism is operating. Thus the competition constants k_3/k_{-1} in Table 3 were estimated as follows. The general rate equation for substitution by both dissociative and associative paths is shown in (1), where k_3/k_{-1} is the quotient of the rate constants for

$$k_{obs.} = k_2[L] + \{(k_1k_3[L]/k_{-1}[CO])/(1 + k_3[L]/k_{-1}[CO])\} \quad (1)$$

nucleophilic attack by L and carbon monoxide at the vacant co-ordination site created by CO dissociation. When [CO] = 0, equation (1) simplifies to the form $k_{obs.} = k_1 + k_2[L]$ found for reactions under argon. Equation (1) can be rearranged to (2) where $k_{obs.}^{CO}$ is

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[7] P. C. Ellgen and J. N. Gerlach, *Inorg. Chem.*, 1973, **12**, 2526.

[8] D. G. DeWit, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1976, 528.

$$k_3/k_{-1} = ([\mathrm{CO}]/[\mathrm{L}])(k_{\mathrm{obs.}}{}^{\mathrm{CO}} - k_2[\mathrm{L}])/(k_{\mathrm{est.}}{}^{\mathrm{Ar}} - k_{\mathrm{obs.}}{}^{\mathrm{CO}}) \quad (2)$$

the observed rate constant for reaction at a particular value of [L] under carbon monoxide; [CO] was taken to be 5.7×10^{-3} mol dm^{-3},[9] and $k_{\mathrm{est.}}{}^{\mathrm{Ar}}$ is the value of the rate constant for reaction with the same value of [L] estimated from the rate parameters k_1 and k_2 in Table 3. This estimation, and its uncertainty, was made by taking into account the covariance of k_1 and k_2. The uncertainty in $k_{\mathrm{obs.}}{}^{\mathrm{CO}}$ was assumed to be the same as that derived for $k_{\mathrm{obs.}}{}^{\mathrm{Ar}}$ for reaction with the same nucleophile, and the uncertainty in k_2 was taken from Table 3. In this way a set of values of k_3/k_{-1} for each nucleophile was obtained together with a standard deviation for each value. The weighted mean of each set was calculated. The individual standard deviations provided a suitable means of weighting the individual values of k_3/k_{-1} because they took account, for instance, of the low precision of quotients obtained from values of [L] where $(k_{\mathrm{est.}}{}^{\mathrm{Ar}} - k_{\mathrm{obs.}}{}^{\mathrm{CO}})$ was small. In some cases the individual standard deviations in k_3/k_{-1} were quite compatible with the appropriately calculated uncertainty in the weighted mean, but in others the individual standard deviations were evidently too small. Thus the individual quotients for L = $\mathrm{P(OEt)_3}$ were 0.300 ± 0.016, 0.296 ± 0.018, 0.280 ± 0.018, 0.307 ± 0.020, 0.386 ± 0.040, and 0.435 ± 0.070. These are all compatible with the weighted mean and weighted standard deviation of 0.301 ± 0.006. For L = $\mathrm{P(OPh)_3}$, however, the individual values were 0.169 ± 0.003, 0.147 ± 0.003, 0.161 ± 0.003, 0.135 ± 0.003, 0.150 ± 0.004, 0.148 ± 0.004, and 0.170 ± 0.009 with a weighted mean and uncertainty of 0.153 ± 0.001. Since each value is subject to small systematic uncertainties (due to variation in the atmospheric pressure), in addition to more random experimental errors, we ' rounded up ' all the standard deviations so as to provide conservative estimates for the relative uncertainties. Doubling the standard deviations for the values of k_3/k_{-1} in Table 3 provides, therefore, at least 95% confidence limits as far as the relative values are concerned. Since the value taken for [CO] may have an error of up to 5%,[9] all the values of k_3/k_{-1} in Table 3 could have this additional systematic error.

The value of k_3/k_{-1} for L = $\mathrm{PBu_3}$ has to be considered separately. Making use of the value of k_1 obtained for this nucleophile leads to the reasonably compatible values of 0.075 ± 0.023, 0.159 ± 0.040, 0.050 ± 0.025, 0.047 ± 0.025, and 0.053 ± 0.030 with a weighted mean and standard deviation of 0.108 ± 0.017. The percentage uncertainties here are much larger than in the other cases because of the greater relative importance of the bimolecular path. In addition, however, the value of k_3/k_{-1} must be considered suspect because of the low value of k_1 found from the reactions under argon. It does not seem possible to dismiss the results with L = $\mathrm{PBu_3}$ as being simply due to difficulties in handling tributylphosphine, since the data obtained quite independently by Basato and Poë [2] are in excellent agreement with ours. It may be that the process governed by k_1 is not simply CO dissociative. Reversible formation of a different reactive intermediate, followed by reversible addition of L and subsequent reversible loss of carbon monoxide before final formation of the product, would lead to exactly the same rate law.[8] The source of the variation in k_1 may be associated with the occurrence of some such mechanism, possibly in addition to a simple CO-dissociative process, and this would not be unexpected in such a relatively complicated molecule. The quotient k_3/k_{-1} would, in this case, represent a combination of rate constants for a larger number of reactions and the dependence of this quantity on the nature of L would not have any simple significance. Nevertheless, it seems worthwhile to plot log k_3/k_{-1} against Δ(h.n.p.) to see what features such a plot has, and this has been done in the Figure. For a simple CO-dissociative mechanism this plot describes the relative nucleophilicity of the various phosphines towards a co-ordination site which has been vacated by a carbonyl ligand. The straight line drawn (ignoring the value for L = $\mathrm{PBu^n{}_3}$, for the reasons given above) has a gradient of *ca.* 1 V^{-1}. This is probably a maximum gradient since a nearly horizontal line could be drawn if the point for L = $\mathrm{P(OPh)_3}$ were considered to be low rather than that for L = etpb being high. Although this implies, as expected for a reactive electrophile, a lower discrimination than that exerted by the fully co-ordinated complex, it could be almost as high as that shown by the fully co-ordinated complexes $[\mathrm{M(CO)_6}]$ (M = Mo and W).[3] Since there is some ambiguity as to exactly what process or processes the values of k_3/k_{-1} relate to, and since no other comparable competition parameters covering such a range of ligand nucleophilicity are available, further discussion of these results would not seem to be justified at present.

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[6/400 *Received, 27th February,* 1976]

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[9] M. Basato, J. P. Fawcett, and A. J. Poë *J.C.S. Dalton*, 1974, 1350.