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RATES OF SUBSTITUTION REACTIONS OF SOME DERIVATIVES OF HEXACARBONYLMOLYBDENUM(0)

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INTRODUCTION

During the last few years there has been an increasing number of investigations on the kinetics and mechanism of substitution reactions of metal carbonyls and some of their derivatives[1]. Hexacarbonylmolybdenum(0) has been the subject of some of these studies carried out in several different laboratories. In most cases its reactions are more rapid and less complicated than are corresponding reactions of the analogous hexacarbonyls of chromium(0) and tungsten(0).

The rate of ^{14}CO exchange with $Mo(CO)_6$ was found[2] to be first order, being zero order in concentration of CO and first order in concentration of $Mo(CO)_6$. On this basis the exchange was assigned a dissociation (S_N1) mechanism. Kinetic studies have likewise been made on the replacement of CO in $Mo(CO)_6$ with arenes[3-5] olefins[5], phosphines[6] and amines[6]. The results of these investigations were also explained on the basis of a dissociation mechanism. However, Angelici and Graham[7] have recently observed that at high concentration of reagent the rate of reaction of $Mo(CO)_6$ increases with increasing reagent concentration. The rate of reaction follows the two-term rate law

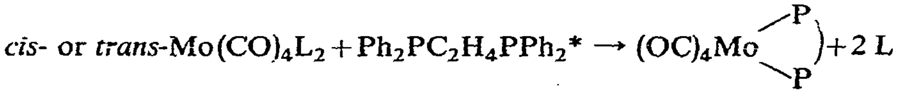
$$\text{Rate} = (k_D + k_L[L])[Mo(CO)_6] \qquad (1)$$

where k_D is believed to be the S_N1 dissociation rate constant and k_L the S_N2 displacement rate constant.

Three systems have been studied where derivatives of $Mo(CO)_6$ react at rates which depend on the nature and concentration of the entering reagent. One of these[8] dealt with the exchange of ^{14}C-arene with (arene)$Mo(CO)_3$. It was suggested that exchange takes place by two paths, both involving bimolecular displacement processes. Another system investigated[9] was that of the reaction of $Mo(CO)_4$bipy with different phosphites L to form *cis*-$Mo(CO)_3$(bipy)L and *trans*-$Mo(CO)_4L_2$. The rate of reaction followed rate law (1) and its interpretation was the same as that given for the reaction of $Mo(CO)_6$.

The third system investigated[10] was that of the reaction of different (arene)-$Mo(CO)_3$'s with various reagents to form *cis*-$Mo(CO)_3L_3$. The rates of these reactions are first order in the concentration of both substrate and nucleophile, and they were designated as S_N2 reactions. The bimolecular displacement reactions in these systems were attributed to the nature of the arene–Mo bond which can readily adjust to accommodate a pair of electrons from the attacking nucleophile. Similar observations have been made on metal carbonyl substrates containing either cyclopentadienyl[11] or nitrosyl[12] ligands, presumably because of a M–L behavior analogous to that of M–arene.

This paper reports kinetic data on some reactions of type (2):



$$cis\text{- or } trans\text{-}Mo(CO)_4L_2 + Ph_2PC_2H_4PPh_2^* \rightarrow (OC)_4Mo\langle P\text{–}P\rangle + 2\,L \qquad (2)$$

and some reactions of type (3):

(3)

The results obtained show that for both types of reactions the rates are first order in substrate concentrations, but at the experimental conditions used the rates of (2) do not depend on the concentration of $Ph_2PC_2H_4PPh_2$, whereas the rates of (3) do depend on L. These results are discussed in terms of possible mechanism of ligand substitution reactions.

EXPERIMENTAL

Compounds and solvents

The $Mo(CO)_6$ was obtained from the Climax Molybdenum Co. The reagents PCl_3 and $P(OC_6H_5)_3$ (British Drug Houses), $PCl_2C_6H_5$ (Eastman Kodak Co.) and $P(n\text{-}C_4H_9)_3$ (purum Fluka) were used as obtained. The pyridine, 4-picoline (British Drug Houses), 3-picoline (RP Erba), 3-chloropyridine and 3,4-lutidine (purum Fluka) were distilled before use.

Thiophene-free benzene was refluxed over sodium wire and then fractionally distilled. The sym-tetrachloroethane was shaken with conc. H_2SO_4, washed with water, dried over $CaCl_2$ and distilled. Chloroform was purified according to Fieser[13].

The 1,2-bis(diphenylphosphino)ethane was prepared by the method of Chatt and Hart[14], $Mo(CO)_4C_8H_{12}$ was prepared according to Fischer and Fröhlich[15]. The method of Hieber and Peterhans[16] was used to prepare $Mo(CO)_4(PPh_3)_2$ and, after separation of the two isomers, the *trans* compound was further purified by chromatography on silica gel using benzene as eluent.

The compound *trans*-$Mo(CO)_4[P(OPh)_3]_2$ was prepared in good yield following the recipe of Poilblanc and Bigorgne[17]. $Mo(CO)_4C_2H_4(PPh_2)_2$ was prepared according to Zingales and Canziani[18]. The compounds *cis*-$Mo(CO)_4(PCl_3)_2$, *cis*-$Mo(CO)_4(PCl_2C_6H_5)_2$, *cis*-$Mo(CO)_4$(3-picoline)$_2$ and *cis*-$Mo(CO)_4(py)_2$ were prepared by adding, under nitrogen, an excess of ligand to a n-heptane solution of $Mo(CO)_4C_8H_{12}$. The identity and purity of all these compounds were confirmed by their nitrogen, carbon and hydrogen analyses. The analyses and IR spectra of these compounds in the C–O stretching region are given in Table 1.

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* $Ph_2PC_2H_4PPh_2 = (C_6H_5)_2PC_2H_4P(C_6H_5)_2$ = diphos and C_8H_{12} = 1,5-cyclooctadiene.

Kinetic studies

The rates of the substitution reactions were followed by observing changes in the IR spectra of the reaction mixtures. All the kinetic studies were carried out under pseudo-first order conditions, using at least a tenfold excess of reagent. Light and air were always excluded. All reactions proceeded to completion and the infinite spectra were in good agreement with those of the known products prepared independently. Usually about twenty measurements were made during a period of three half-lives. A Perkin–Elmer spectrophotometer Model 621, or a Beckman spectrophotometer model I.R. 9 were used to follow the reaction. An aluminum foil-wrapped flask containing the solution of metal carbonyl and one containing a solution of the reagent, both under nitrogen, were brought to constant ($\pm 0.1°$) temperature. At zero time the ligand solution was poured into the foil-wrapped flask and mixed well. Samples of the reaction mixture were removed at various times with an eye-dropper, under nitrogen, and placed in a 1 mm IR cell and the spectrum was quickly measured. A 1 mm IR cell containing the solvent or the same concentration of ligand was used as a reference.

From the transmittance, linear plots of $\ln(A-A_\infty)$ *vs.* time were obtained, and the values of k_{obsd} were calculated from the slopes of these lines. In these calculations A is the absorbance at time t ($A=\log(1/T)$ where T is the transmittance) and A_∞ is the absorbance at $t=\infty$ calculated for every spectra. The rates for reaction (2) were determined by following the appearance of the highest frequency carbonyl absorption of $Mo(CO)_4$(diphos), or by following the disappearance of the highest frequency carbonyl absorption of *cis*-$Mo(CO)_4L_2$.

The rates of reaction (3) were followed by monitoring the disappearance of the highest frequency carbonyl absorption of $Mo(CO)_4C_8H_{12}$ as it reacts with the various reagents. A 10% or better precision is obtained for the values of the rate constants. It was also determined that in the solvents used the variations of the absorption intensities with changes in concentration of $Mo(CO)_4C_8H_{12}$, *cis*-$Mo(CO)_4$(diphos), *cis*-$Mo(CO)_4(PCl_3)_2$ and *cis*-$Mo(CO)_4(PCl_2C_6H_5)_2$ follow the Lambert–Beer law.

RESULTS

Several derivatives of $Mo(CO)_6$ were prepared and their analyses and IR spectra are given in Table 1. Reaction mixtures for which the product was not isolated gave IR spectra analogous to the disubstituted derivatives.

The rates of the reaction (2) at 60° in benzene solution are recorded in Table 2. Because of the low solubility of diphos in benzene, it was not possible to use diphos concentrations in excess of 0.07 M. Attempts were made to use some other substrates, but without success. The chief difficulty was that the IR spectra in the C–O stretching region of the starting materials, $Mo(CO)_4L_2$, overlap with those of the product, $Mo(CO)_4$(diphos), and it was not possible to obtain quantitative data on the rates of reaction.

The rates of reaction (3) at 25° and 40° in the solvents chloroform, benzene and sym-tetrachloroethane are given in Table 3. Plots of some of the experimental rate constants, k_{obsd} *versus* reagent concentrations, are shown in Fig. 1. The activation parameters for reaction (3) are given in Table 5. The values of $\Delta H^{\neq}$ are estimated to

TABLE 1

INFRARED AND ANALYTICAL DATA

	CO stretching frequencies (cm^{-1})				*Solvent*	*Ref.*
cis-$Mo(CO)_4(PCl_3)_2$	2072	2004	1994	1986	Hydrocarbon	17
cis-$Mo(CO)_4(PCl_2C_6H_5)_2$	2051	1980	1958		n-heptane	
trans-$Mo(CO)_4[P(OC_6H_5)_3]_2$	1940				hydrocarbon	17
trans-$Mo(CO)_4[P(C_6H_5)_3]_2$	1952	1903			hydrocarbon	17
cis-$Mo(CO)_4\ C_2H_4[P(C_6H_5)_2]_2$	2020	1919	1907	1881	$CHCl_3$	25
cis-$Mo(CO)_4[P(n\text{-}C_4H_9)_3]_2$	2011	1912	1898	1885	n-heptane	
cis-$Mo(CO)_4(py)_2$	2025	1907	1881	1839	CH_3CN	26
cis-$Mo(CO)_4(3\text{-pic})_2$	2012	1898	1872	1835	$CHCl_3$	
cis-$Mo(CO)_4(4\text{-pic})_2$	2012	1895	1873	1826	$CHCl_3$	
cis-$Mo(CO)_4(3,4\text{-lut})_2$	2009	1891	1872	1827	$CHCl_3$	
cis-$Mo(CO)_4(3\text{-Clpy})_2$	2013	1892	1850	1833	$CHCl_3$	
cis-$Mo(CO)_4C_8H_{12}$	2036	1950	1930	1883	$CHCl_3$	

	Analyses					
	C		*H*		*N*	
	Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
$Mo(CO)_4(PCl_3)_2$	9.95	9.2				
$Mo(CO)_4(PCl_2C_6H_5)_2$	33.95	34.2	1.78	1.6		
$Mo(CO)_4(py)_2$	45.92	46.2	2.75	2.4	7.65	7.4
$Mo(CO)_4(3\text{-pic})_2$	48.74	48.2	3.58	3.8	7.11	7.0

be ±1 kcal/mole and $\Delta S^{\neq}$ ±2 e.u. Attempts to use some other solvents failed. For example in acetone, nitromethane and nitrobenzene solution, $Mo(CO)_4C_8H_{12}$ decomposes even under nitrogen. Solid reagents such as $P(C_6H_5)_3$, $As(C_6H_5)_3$ and diphos were not used, because they were not sufficiently soluble to give solutions of high enough concentration to drive the reactions to completion.

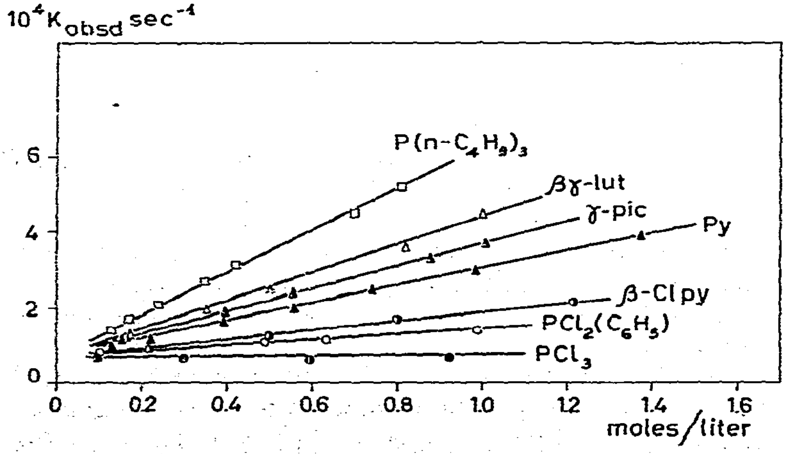
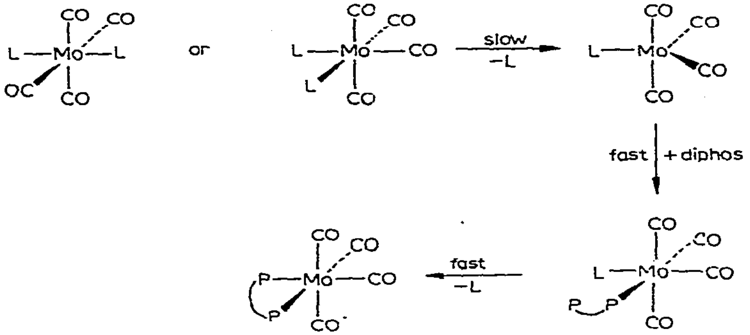


Fig. 1. Plot of k_{obsd} for the reaction of $Mo(CO)_4C_8H_{12}$ with different ligands at 25° in chloroform.

DISCUSSION

The rates of reaction of *cis*-$Mo(CO)_4[(PCl_2C_6H_5)]_2$ and of *trans*-$Mo(CO)_4$-$[P(C_6H_5)]_2$ with diphos to yield $Mo(CO)_4$(diphos) do not depend on the concentration of diphos (Table 2). These results are similar to those reported by Werner[6] for the reactions between $Mo(CO)_6$ and various phosphine and amine reagents. The simplest interpretation of such a first-order process is that substitution takes place by a dissociation (S_N1) mechanism. A possible reaction sequence, in accord with the experimental observations, may be represented as follows:



The slow and rate-determining step is that of the loss of L from either *cis*- or *trans*-$Mo(CO)_4L_2$ to perhaps form the same five-coordinated species. Attack on Mo by the entering diphos is then rapid to give the final product. This attack may take place in the equatorial plane *cis* to L (as shown) or *trans* to L. In either case the same product is readily formed when the remaining L is lost and the Mo–diphos chelate ring is closed.

The data in Table 2 also show that the rates of reaction of *cis* and *trans*-$Mo(CO)_4L_2$ with diphos increase with changes in L in the order:

$$P(OC_6H_5)_3 \ll P(C_6H_5)_3 < PCl_2C_6H_5 \ll PCl_3$$

These results are similar to those found by Meriwether and Fiene[19] for the rates of

TABLE 2

RATES OF REACTION OF $Mo(CO)_4L_2$ WITH $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ IN BENZENE SOLUTION AT 60° AND 0.004 M CARBONYL

$Mo(CO)_4L_2$	*Ligand conc.*	10^5k (*sec*$^{-1}$)
cis-$Mo(CO)_4(PCl_3)_2$		very fast (at 25°)
cis-$Mo(CO)_4(PCl_2C_6H_5)_2$	0.0305 M	21
	0.0422	23
	0.0695	21
trans-$Mo(CO)_4[P(C_6H_5)_3]_2$	0.0292	2.9
	0.0493	2.9
	0.0588	2.9
	0.0687	2.9
trans-$Mo(CO)_4[P(OC_6H_5)_3]_2$		very slow

TABLE 3

RATES OF REACTION OF $Mo(CO)_4C_8H_{12}$ WITH DIFFERENT LIGANDS IN DIFFERENT SOLVENTS AT 25° AND 0.0045 M CARBONYL

Ligand	*Ligand conc.*	$10^4 k_{obsd}$
Chloroform solution		
$P(n\text{-}C_4H_9)_3$	0.121 M	1.47
	0.171	1.78
	0.235	2.15
	0.343	2.59
	0.415	3.08
	0.550	3.82
	0.688	4.52
	0.805	5.23
$PCl_2C_6H_5$	0.102 M	0.80
	0.488	1.10
	0.645	1.21
	0.980	1.36
	0.126[a]	5.30
	0.415[a]	6.20
	0.650[a]	7.11
	0.835[a]	7.68
PCl_3	0.094 M	0.72
	0.301	0.75
	0.589	0.70
	0.940	0.82
Pyridine	0.127 M	1.06
	0.215	1.08
	0.391	1.64
	0.558	2.00
	0.728	2.44
	0.979	2.99
	1.38	3.84
	0.172[a]	6.70
	0.310[a]	8.10
	0.631[a]	11.5
	0.851[a]	13.8
3-Picoline	0.114 M	1.03
	0.174	1.17
	0.201	1.27
	0.455	1.90
	0.675	2.49
	0.983	3.15
4-Picoline	0.105 M	1.04
	0.157	1.21
	0.384	2.00
	0.558	2.40
	0.867	3.33
	1.03	3.80
3-Chloropyridine	0.223 M	0.95
	0.494	1.24
	0.797	1.73
	1.21	2.10
3,4-Lutidine	0.168 M	1.19
	0.345	2.02
	0.513	2.58
	0.822	3.64
	1.01	4.48
Benzene solution		
$P(n\text{-}C_4H_9)_3$	0.123 M	4.04
	0.259	7.26
	0.355	9.81
	0.473	12.9
Pyridine	0.102 M	1.59
	0.148	1.93
	0.345	3.33
	0.603	4.68
	0.793	5.83
3-Picoline	0.101 M	1.77
	0.241	2.83
	0.348	3.74
	0.453	4.74
	0.704	6.54
	1.05	8.97
sym-Tetrachloroethane solution		
3-Picoline	0.081 M	0.68
	0.378	1.71
	0.574	2.46
	0.734	3.03
	1.04	4.11

[a] At 40°.

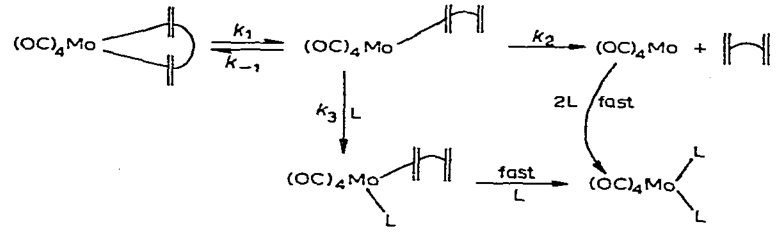
replacement of L in $Ni(CO)_2L_2$. Here too the rates of reaction were first-order. It was concluded that the bond strengths of Ni–P in these systems are due primarily to σ bonding and thus the ease of Ni–P bond cleavage will increase with decreasing basicity of the ligand. In terms of this explanation $P(OC_6H_5)_3$ presents an unexplained anomaly, and it continues to be anomalous in the Mo systems described here. These results also suggest that the Mo–P bond strengths in *cis*- and *trans*-$Mo(CO)_4L_2$ is largely due to σ bonding and that the most important factor in the replacement of L is the rupture of the Mo–P bond. This agrees with the observation that six-coordinated metal complexes usually undergo substitution reactions by a dissociation process[20]. However had it been possible to use higher concentrations of diphos or to use instead a better nucleophile, then the second term, $k_L[L]$ in equation (1) may have contributed to the overall rate of reaction. The extent of such a contribution would perhaps be less than that found in reactions of $Mo(CO)_6$ because of the steric retardation of bimolecular attack due to the bulky L ligands in $Mo(CO)_4L_2$.

For the compound $Mo(CO)_4(C_8H_{12})$, the data in Table 3 show that its rates of reaction with various reagents, (3), depend on the nature and the concentration of the reagents. A plot (Fig. 1) of some of these data show that the rates of reaction observed increase linearly with increasing concentration of nucleophile. Furthermore in each case the plots extrapolate to approximately the same value of k_{obsd} at zero concentrations of different reagents. This means that k_{obsd} can be represented by the two-term equation

$$k_{obsd} = k_D + k_L[L] \tag{4}$$

which is the same as the experimental results found for the reaction of $Mo(CO)_6$ and corresponds to rate law (1).

Although the interpretation of the reaction paths corresponding to k_D and k_L for the reaction of $Mo(CO)_6$ appears to be straightforward, the same is not true for the reaction of $Mo(CO)_4(C_8H_{12})$. This system is complicated because a bidentate ligand is being replaced and at least two possible mechanisms must be considered. One of these that is in agreement with the experimental results is shown by the following scheme:



The two species shown above as being less than six-coordinated may instead be solvated. According to this reaction scheme and applying the steady-state approximation the observed rate constant, k_{obsd}, is given by the eqn. (5).

$$k_{obsd} = k_1 \frac{k_2 + k_3[L]}{k_{-1} + k_2 + k_3[L]} \tag{5}$$

This rate expression and proposed mechanism is similar to that suggested[21] for the acid hydrolysis of $[Fe(bipy)_3]^{2+}$.

On the basis of this mechanism the results obtained (Fig. 1) can be explained providing that $k_{-1} \simeq k_3[L]$ at the concentrations of L that were used in these experiments. At low concentrations of L, it follows that $k_{-1} \gg k_3[L]$ and eqn. (5) reduces to eqn. (6):

$$k_{obsd} = k_1 \left(\frac{k_2}{k_{-1} + k_2} \right) \tag{6}$$

This then accounts for the nonzero intercept in Fig. 1 at the extrapolated limit of $L = 0$. Eqn. (5) also requires that at some sufficiently high concentration of L, where $k_{-1} \ll k_3[L]$, a limiting rate be reached. At this point $k_{obsd} = k_1$ and the reaction will no longer depend on the concentration of L. However, this condition is not reached at 1.5 M L which suggests that $k_{-1} \simeq k_3[L]$ at even the highest experimentally practical concentration of L.

There is a second mechanism which provides an alternative or additional explanation for the dependence of the rate of reaction of $Mo(CO)_4(C_8H_{12})$ on the concentration and nature of L. This is the direct S_N2 displacement by L to yield the product *cis*-$Mo(CO)_4L_2$. Such a path must be considered possible because it seems to be involved in reactions of $Mo(CO)_6$[7].

The experimental results do not permit a choice between the reaction path corresponding to k_3 in the above scheme and an S_N2 displacement for that portion of the reaction which depends on L. In fact both may make a contribution and this would account for the failure to observe a limiting rate corresponding to k_1 at high concentrations of L. Alternatively this limiting rate may have been reached even at the lowest concentrations of L used providing that the active intermediate in the above scheme reacts rapidly compared to chelate ring closure, k_2 and/or $k_3 \gg k_{-1}$.

TABLE 4

RATE CONSTANTS FOR THE REACTION $Mo(CO)_4C_8H_{12} + 2\,L \rightarrow Mo(CO)_4L_2$ AT 25° WITH CHANGES IN THE NATURE OF L

L	*Solvent*	$10^4 k^0_{obsd}$ *(sec^{-1})*[a]	$10^4 k$ *M^{-1} sec^{-1}*[b]	*ΔHNP*[c]
$P(n\text{-}C_4H_9)_3$	$CHCl_3$	0.7	5.4	131
	Benzene	0.9	25	
3,4-Lutidine	$CHCl_3$	0.7	3.8	181
4-Picoline	$CHCl_3$	0.7	3.0	220
3-Picoline	$CHCl_3$	0.7	2.5	246
	Benzene	0.9	7.6	
	sym-$C_2H_2Cl_4$	0.4	3.6	
Pyridine	$CHCl_3$	0.7	2.3	286
	$CHCl_3$[d]	4.9	10.5	
	Benzene	0.9	6.0	
3-Cl-pyridine	$CHCl_3$	0.7	1.2	466
$PCl_2C_6H_5$	$CHCl_3$	0.7	0.64	unknown
	$CHCl_3$[d]	4.9	3.3	
PCl_3	$CHCl_3$	0.7		unknown

[a] Values of k_{obsd} for L equal to zero. [b] Values of k calculated from the slope of the line. [c] Difference half-neutralization potential between L and N,N'-diphenylguanidine in nitromethane. The smaller ΔHNP, the more basic is L[22]. [d] At 40°.

Thus it is not known whether the extrapolated values of k_{obsd} at zero concentration of L listed in Table 4 correspond to k_1 or to the combination of rate constants given by eqn. (6).

Table 4 also contains the values of kM^{-1} sec^{-1} calculated from the slope of the lines in Fig. 1 and the values of ΔHNP[22]. These values (footnote [c], Table 4) are a measure of the basicities of the reagents towards a proton in nitromethane solution. A linear free energy plot of log k *versus* ΔHNP is shown in Fig. 2.

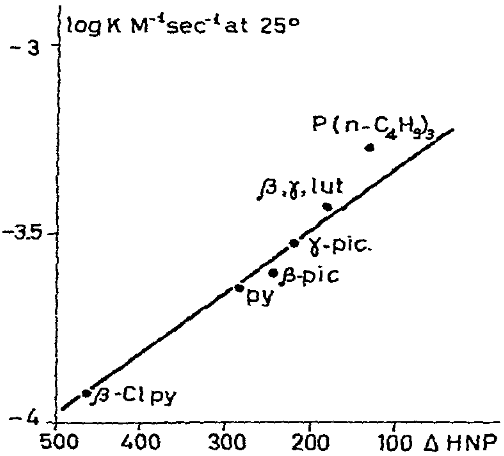


Fig. 2. The linear free energy relationship of the rate of reaction with the basicity of the nucleophile for the reaction of $Mo(CO)_4C_8H_{12}$ with different reagents at 25° in chloroform. See footnote[c], Table 4 for definition of ΔHNP.

Although the values of kM^{-1} sec^{-1} for the reactions of $Mo(CO)_4(C_8H_{12})$ depend on the nature of the reagent, the maximum difference in rates is only about one order of magnitude. It is apparent that the rates increase for changes in L in the order:

$$P(n\text{-}C_4H_9)_3 > \text{3,4-lutidine} > \text{4-picoline} \simeq \text{3-picoline} \simeq \text{pyridine} > \text{3-chloropyridine} > PCl_2C_6H_5 > PCl_3$$

The linear free energy plot shows that for pyridine and its derivatives, the rates of reaction increase with an increase in the basicity of the nucleophile. Also shown is that $P(n\text{-}C_4H_9)_3$ appears to be a better nucleophile than would be expected in terms of its basicity. This is similar to the results obtained previously which show that P-atom ligands are better reagents than are N-atom ligands of the same basicity. The results are explained in terms of the polarizability of the ligand atom making an appreciable contribution to its nucleophilic strength towards these substrates. The metals in these systems are of the class (b)[23] or soft acid[24] type and show a ligand atom preference of N < P > As > Sb.

Finally the activation parameters for the reactions of $Mo(CO)_4(C_8H_{12})$ are given in Table 5 and these values show differences that resemble those for the reactions of $Mo(CO)_6$. Thus the first-order path has a high enthalpy and a positive entropy compared with the second-order path which has a lower enthalpy and negative entro-

TABLE 5

ACTIVATION PARAMETERS FOR THE REACTION $Mo(CO)_4C_8H_{12} + 2\,L \rightarrow Mo(CO)_4L_2$ IN $CHCl_3$ SOLUTION[a]

L	$\Delta H_1^{\neq}$ (*Kcal/mole*)	$\Delta S_1^{\neq}$ (*e.u.*)	$\Delta H_2^{\neq}$ (*Kcal/mole*)	$\Delta S_2^{\neq}$ (*e.u.*)
Pyridine	24	3	18	−12
$PCl_2C_6H_5$	24	3	20	−10

[a] Values of $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ are calculated from values of k_{obsd}^{0} at 25° and 40°. Values of $\Delta H_2^{\neq}$ and $\Delta S_2^{\neq}$ are calculated from values of kM^{-1} sec^{-1} at 25° and 40°.

py of activation. These results are consistent with dissociation and displacement processes for the two paths, respectively.

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SUMMARY

The rates of the reaction of *cis*-$Mo(CO)_4L_2$ and *trans*-$Mo(CO)_4L_2$ with 1,2-bis(diphenylphosphino)ethane (diphos), to yield $Mo(CO)_4$(diphos) do not depend on the concentration of diphos. The rates of reaction increase with changes in L in the order: $P(OC_6H_5)_3 \ll P(C_6H_5)_3 < PCl_2C_6H_5 \ll PCl_3$. The complex $Mo(CO)_4(C_8H_{12})$ undergoes substitution reactions with neutral monodentate ligands having nitrogen or phosphorus as donor atoms to give $Mo(CO)_4L_2$. The reactions proceed according to the two-term rate law:

$$\text{Rate} = k_1[Mo(CO)_4(C_8H_{12})] + k_2[Mo(CO)_4(C_8H_{12})][L]$$

The rates decrease for changes in L in the order: $P(n\text{-}C_4H_9)_3 >$ 3,4-lutidine > 4-picoline ≃ 3-picoline ≃ pyridine > 3-chloropyridine $> PCl_2C_6H_5 > PCl_3$. The results are discussed in terms of the possible reaction mechanism.

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