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Mechanism of the Disubstitution Reaction Between Monosubstituted Complexes of $Fe(CO)_2(NO)_2$ and Phosphine Ligands

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Disubstitution reactions of the $Fe(CO)(NO)_2L$ complexes with $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (diphos), other phosphinic ligands and $As(C_6H_5)_3$ were investigated.

A kinetic associative mechanism was deduced for most of the ligands. For $P(C_6H_5)_3$ and $P(n-C_4H_9)_3$ the following kinetic law was found:

$$v = (k_1 + k_2[L])[complex]$$

The first order path was dissociative and the second order one was associative with the ligand.

For the reaction with diphos, the following reactivity order, depending on the substrate ligand, was found:

$$CO > As(C_6H_5 \gg P(O-C_6H_5)_3 > P(O-n-C_4H_9) >$$
$$> P(C_6H_5)_3 > P(n-C_9H_4)_3$$

This order was discussed and tentatively explained on the basis of the effect of the basicity of the ligands.

Introduction

It is known that in the isoelectronic series $Ni(CO)_4$[1,2] $Co(CO)_3NO$,[3] $Fe(CO)_2(NO)_2$[4] the presence of NO groups in the complex shifts the mechanism of substitution from a dissociative to an associative one.[5] Thus for the $Ni(CO)_4$ complex a dissociative, for $Co(CO)_3NO$ a mixed associative and dissociative, and for $Fe(CO)_2(NO)_2$ an associative mechanism were observed. It has also been observed that the presence of a phosphine ligand in the complex markedly changes the mechanism of the disubstitution of $Co(CO)_2NOL$ complexes.[6]

The objects of this study were (i) to ascertain whether this happens also in the disubstitution reaction of $Fe(CO)(NO)_2L$ complexes, even though the associative mechanism only was found for monosubstitution of $Fe(CO)_2(NO)_2$ and (ii) to observe the reactivity order in the ligand exchange reactions. To these ends the following reactions are been studied:

$$Fe(CO)(NO)_2L + diphos \rightarrow Fe(NO)_2diphos + L + CO \qquad (1)$$

with $L = P(C_6H_5)_3$, $P(n-C_4H_9)_3$, $P(O-n-C_4H_9)_3$, $P(O-C_6H_5)_3$, $As(C_6H_5)_3$,

and

$$Fe(CO)(NO)_2L + L \rightarrow Fe(NO)_2L_2 + CO \qquad (2)$$

with $L = P(C_6H_5)_3$, $P(n-C_4H_9)_3$, $P(O-n-C_4H_9)_3$.

Experimental

(a) *Materials.* The monosubstituted complexes were prepared by methods described in refs. 7 and 8. Solids were purified by recrystallization from methanol and liquids by chromatography on Al_2O_3 with a 1/2 CH_2Cl_2-n-pentane mixture as eluent. The monosubstituted complexes must be purified immediately before the kinetic runs, because they decompose with evolution of NO even if kept under nitrogen at $-15°C$. On spite of the precautions taken, the $Fe(CO)(NO)_2Sb(C_6H_5)_3$ complex was impure and kinetic runs were not reproducible. The disubstituted complexes were prepared according to refs. 9 and 10.

All the complexes used were identified by melting points, CO and NO stretching frequencies and analysis of C, H, and N.

The phosphinic, arsinic and stibinic ligands were commercial products, except for diphos that was prepared according to ref. 11.

(b) *Kinetic Measurements.* Runs were performed in toluene solution. The solvent was dried by distillation over sodium metal and deaerated by nitrogen flushing.

Slow runs were carried out in dark ampoules sealed under flushing nitrogen and fast runs in a nitrogen filled flask, from which aliquots were withdrawn through a serum cap. For the reaction between $Fe(CO)(NO)_2As(C_6H_5)_3$ and diphos a two-lobe flask was used; the ligand and complex solutions were prethermostated to measure the zero-point of the runs.

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(9) E. Morris and F. Basolo, *J. Am. Chem. Soc.*, *90*, 2536 (1968).

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Table I. Pseudo first-order ($k_{I\,obs}$) and second-order ($k_{II\,obs}$) rate constants in toluene, at various temperatures, for the reaction: $Fe(CO)(NO)_2L + diphos \rightarrow Fe(NO)_2diphos + CO + L$ $L = P(C_6H_5)_3$, $P(O{-}n{-}C_4H_9)_3$, $P(O{-}C_6H_5)_3$. $As(C_6H_5)_3$, CO Complex concentration $[C] = \sim 5.10^{-3}$ mole/liter.

L	T °C	$10^2 \times [L]$ mole/l	$k_{I\,obs}$ sec^{-1}	$k_{II\,obs}$ $l.mole^{-1}sec^{-1}$
$P(C_6H_5)_3$	50	5.03	0.91×10^{-6}	1.81×10^{-5}
	50	5.73	1.03×10^{-6}	1.80×10^{-5}
	50	7.17	1.12×10^{-6}	1.56×10^{-5}
	50	10.04	1.42×10^{-6}	1.42×10^{-5}
	50	15.22	1.77×10^{-6}	1.16×10^{-5}
	60	3.04	2.93×10^{-6}	9.60×10^{-5}
	60	6.26	3.33×10^{-6}	5.03×10^{-5}
	60	8.98	4.19×10^{-6}	4.65×10^{-5}
$P(n{-}C_4H_9)_3$	50	2.99	3.81×10^{-7}	1.27×10^{-5}
	50	5.00	3.78×10^{-7}	7.56×10^{-6}
	50	8.18	4.37×10^{-7}	5.34×10^{-6}
	50	10.20	4.46×10^{-7}	4.37×10^{-6}
$P(O{-}n{-}C_4H_9)_3$	50	3.03	4.26×10^{-7}	1.40×10^{-5}
	50	7.88	1.15×10^{-6}	1.46×10^{-5}
	50	10.18	1.51×10^{-6}	1.49×10^{-5}
$P(O{-}C_6H_5)_3$	50	3.09	1.70×10^{-6}	5.51×10^{-5}
	50	5.16	2.73×10^{-6}	5.38×10^{-5}
	50	8.08	4.31×10^{-6}	5.34×10^{-5}
	50	9.72	5.48×10^{-6}	5.64×10^{-5}
$As(C_6H_5)_3$	50	3.00		1.60×10^{-2}
	50	9.08		1.35×10^{-2}
CO [a]	50	2.52		4.46×10^{-2}
	50	1.65		4.44×10^{-2}

[a] The $k_{II\,obs}$ values refer to the rate constants of the first step of monosubstitution of $Fe(CO)_2(NO)_2$ with diphos.

The concentration of the complex was measured with a Perkin-Elmer mod. 337 infrared spectrophotometer using 0,5 mm. NaCl cells by observing the disappearance of CO stretching band and, sometimes, the appearance of the NO stretching band of lower frequency. The reference cell contained a ligand solution of the same concentration as that in the sample cell. The temperature was either 50°C or 60°C. The stability of the monosubstituted complex in the absence of oxygen was sufficient for the runs, which were followed to 40-70% completion, depending upon the ligand and temperature.

The absorbance of the solution, after complete reaction, was obtained experimentally only for some fast reactions; in the other cases it was calculated by application of Beer's law to the disubstituted complex. All the rate studies were carried out using at least an eightfold excess of ligand concentration. The concentration of the substrate was $\sim 5.10^{-3}$ mole/liter. The experimental results follow the equation of ref. 3. For the reaction between $Fe(CO)(NO)_2As(C_6H_5)_3$ and diphos, equation (3) was employed for the first order consecutive steps.[12]

$$c = a\left[1 + \frac{1}{k_1 - k'_{22}}\left(k'_{22}e^{-k_1t} - k_1e^{-k'_{22}t}\right)\right] \qquad (3)$$

In the equation *a* is the initial concentration of the monosubstituted complex, *c* is the concentration of the chelate complex at the *t* time, k'_{22} the rate constant for the second step of the reaction and $k_1 = k'_2$ [diphos] is the pseudo-first-order rate constant of the first step.

The k''_{22} rate constant of the chelation step was estimated independently from the reaction between $Fe(CO)_2(NO)_2$ and diphos.[13]

Equation (3) was solved using an IBM 1620 computer to give the values of k_1 and thus of k'_2.

The symbols used refer to the mechanism presented in Figure 2, path 2.

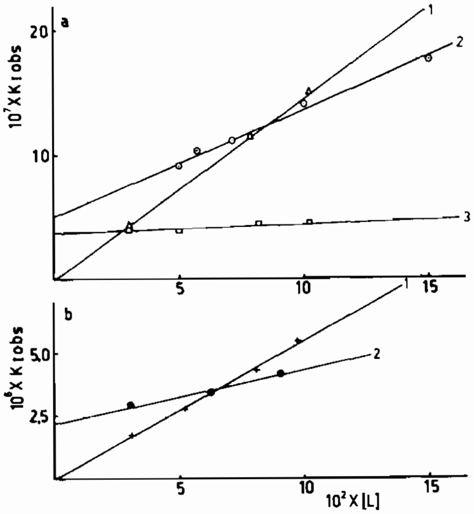

Figure 1. $k_{I\,obs}/[L]$ plots for the reaction $Fe(CO)(NO)_2L + diphos \rightarrow Fe(NO)_2\ diphos + L + CO$ in toluene. a) 50°C, $L = P(O{-}n{-}C_4H_9)_3$ (line 1), $L = P(C_6H_5)_3$ (line 2), $L = P(n{-}C_4H_9)_3$ (line 3); b) $L = P(O{-}C_6H_5)_3$ at 50°C (line 1), $L = P(C_6H_5)_3$ at 60°C (line 2). [L] = ligand conc. in mole/liter.

Results

The kinetic results are collected in Tables I, II, III. Table I reports the experimental first order ($k_{I\,obs}$) and second order ($k_{II\,obs}$) rate constants for the type

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(13) R.J. Hawby, D. Morris, E.M. Thorsteinson, and F. Basolo, *Inorg. Chem.*, *5*, 27 (1966).

Table II. Pseudo-first order ($k_{I\ obs}$) and second order ($k_{II\ obs}$) rate constants in toluene, at various temperatures, for the reaction: $Fe(CO)(NO)_2L + L \rightarrow Fe(NO)_2L_2 + CO$ $L = P(C_6H_5)_3$, $P(n{-}C_4H_9)_3$, $P(O{-}n{-}C_4H_9)_3$, diphos Complex concentration $[C] = \sim 5.10^{-3}$ mole/liter.

L	T °C	10×[L] mole/l.	$k_{I\ obs}$ sec^{-1}	$k_{II\ obs}$ l.mole^{-1}sec^{-1}
$P(C_6H_5)_3$	50	2.02	5.69×10^{-7}	2.82×10^{-6}
	50	5.34	6.38×10^{-7}	1.20×10^{-6}
	50	6.14	6.99×10^{-7}	1.14×10^{-6}
	50	7.98	7.72×10^{-7}	0.97×10^{-6}
	60	1.10	1.98×10^{-6}	1.80×10^{-5}
	60	3.97	2.36×10^{-6}	5.97×10^{-5}
	60	7.12	2.69×10^{-6}	3.78×10^{-6}
$P(n{-}C_4H_9)_3$	50	1.04	5.77×10^{-7}	5.57×10^{-6}
	50	1.98	6.98×10^{-7}	3.02×10^{-6}
	50	3.96	9.58×10^{-7}	2.42×10^{-6}
	50	5.92	12.20×10^{-7}	2.06×10^{-6}
$P(O{-}n{-}C_4H_9)_3$	50	0.98	2.83×10^{-7}	2.90×10^{-6}
	50	2.94	7.98×10^{-7}	2.71×10^{-6}
	50	3.02	8.09×10^{-7}	2.68×10^{-6}
	50	5.29	12.65×10^{-7}	2.39×10^{-6}
	50	6.03	14.90×10^{-7}	2.46×10^{-6}
[diphos] [a]	50	0.245	1.18×10^{-4}	
	50	0.252	1.33×10^{-4}	
	50	0.165	1.34×10^{-4}	

[a] The $k_{I\ obs}$ values refer to the chelation step for the reaction between $Fe(CO)_2(NO)_2$ and diphos.

Table III. First order rate constant (k_1) of dissociative step and second order rate constant (k_2) of associative step for the chelation and disustitution reactions

L	T °C	Chelation k_1 sec^{-1}	Chelation k_2 l.mole^{-1}sec^{-1}	Disubstitution k_1 sec^{-1}	Disubstitution k_2 l.mole^{-1}sec^{-1}
$P(C_6H_5)_3$ [a]	50	5.0×10^{-7}	8.7×10^{-6}	5.0×10^{-7}	3.3×10^{-7}
	60	2.2×10^{-6}	2.2×10^{-5}	2.0×10^{-6}	9.0×10^{-7}
$P(n{-}C_4H_9)_3$	50	3.7×10^{-7}	8.0×10^{-7} [b]	4.0×10^{-7}	1.4×10^{-6}
$P(O{-}n{-}C_4H_9)_3$	50	—	1.4×10^{-5}		2.3×10^{-6}
$P(O{-}C_6H_5)_3$	50	—	5.5×10^{-5}	not observed	
$As(C_6H_5)_3$ [c]	50	—	1.5×10^{-5}	not observed	

[a] Thermal paramethers or $Fe(CO)(NO)_2P(C_6H_5)_3$ complex; chelation reaction: first order $\Delta E^* = 30 \pm 1$Kcal/mole, $\Delta S^* = +4 \pm 3$ e.u.; second order, $\Delta E^* = 19.0 \pm 1$ Kcal/mole, $\Delta S^* = -25 \pm 3$ e.u.; Disubstitution reaction: first order, $\Delta E^* = 28 \pm 1$ Kcal/mole, $\Delta S^* = -2 \pm 3$ e.u.; second order $\Delta E^* = 21 \pm 1$ Kcal/mole, $\Delta S^* = -26 \pm 3$ e.u. [b] Inaccurate value owing to slight slope of fig. 1. [c] Inaccurate valuc owing to the calculation method (eqn. 3).

(1) reaction with $P(C_6H_5)_3$, $P(n{-}C_4H_9)_3$, $P(O{-}n{-}C_4H_9)_3$, $P(O{-}C_6H_5)_3$, $As(C_6H_5)_3$ and CO ligands.

Table II reports the experimental first order ($k_{I\ obs}$) and second order ($k_{II\ bbs}$) rate constants for the disubstitution reaction of the type (2) with $P(C_6H_5)_3$, $P(n{-}C_4H_9)_3$ and $P(o{-}n{-}C_4H_9)_3$ ligands.

Table III gives the first order (k_1) and the second order (k_2) path rate constants both for the type (1) and for the type (2) reactions.

Discussion

(a) *Ligand Exchange and Chelation Reactions with Diphos.* For the $P(O{-}n{-}C_4H_9)_3$, $P(O{-}C_6H_5)_3$, $As(C_6H_5)_3$ and CO ligands the kinetics are first order in the substrate and in the ligand concentration.

For the $P(C_6H_5)_3$ and $P(n{-}C_5H_9)_3$ ligands, the $k_{I\ obs}$ values follow the equations (4) (Figure 1).

$$k_{I\ obs} = k_1 + k_2[L] \qquad (4)$$

This requires that the kinetics follow a two term mechanism: one of first order with rate constant k_1, the other of second order with rate constant k_2.

The activation energy and entropy data give useful information about the reaction mechanism. In fact the values for the first-order path with $P(C_6H_5)_3$ ligand are $\Delta E^* = 30 \pm 1$ Kcal/mole; $\Delta S^* = +4 \pm 3$ e.u. which support a dissociative mechanism.[3,14] For the second order path $\Delta E^* = 19 \pm 1$ Kcal/mole, $\Delta S^* = -25 \pm 3$ e.u.; these values support an associative mechanism.[3,5]

All the experimental results suggest the following mechanism (Figure 2):

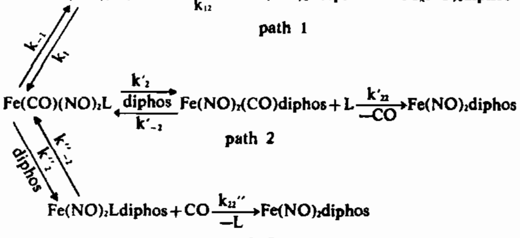

Figure 2 Mechanism of the disubstitution reaction of $Fe(CO)(NO)_2L$ with diphos.

Supposing the three paths occur simultaneously, using the stationary state approximation for path 1, and assuming that the first step be always much slower than the following ones, the kinetic law (4) is obtained with $k_2=k'_2+k''_2$.

Only for the $P(C_6H_5)_3$ and $P(n-C_4H_9)_3$ ligand the path 1 of the Figure 2 is kinetically observable. For all other ligand the paths 2 and 3 are prevailing.

Unlike the $Co(CO)_2NOL$ complexes,[14] the $Fe(CO)(NO)_2L$ ones show an appreciable first order dissociative path to the reaction with $P(C_6H_5)_3$ e $P(n-C_4H_9)_3$, although two NO groups are present.[5]

The associative reaction mechanism can proceed by a preliminary ligand exchange (path 2, Figure 2) or disubstitution reaction (path 3, Figure 2) followed by chelation.

The complexes with $As(C_6H_5)_3$ and $P(O-C_6H_5)_3$, owing to the large basicity difference with respect to diphos,[15] react by ligand exchange (path 2, Figure 2).[12]

For $As(C_6H_5)_3)$ this mechanism was also supported by the slow initial decrease of the CO stretching intensity. If the disubstitution was the first step of the reaction the CO stretching intensity should decrease also at the beginning; this was not observed because, being the first step an exchange process (path 2, Fig. 2), a monosubstituted complex $Fe(NO)_2CO$ diphos was obtained and its CO stretching overlaps that of monosubstituted $Fe(NO)_2(CO)As(C_6H_5)_3$. Therefore the exchange could not be followed directly, but the rate constant was calculated using the equation (3) and the rate constant (k'_{22}) for the chelation was measured independently.[12,13]

For the $P(C_6H_5)_3$ ligand the large difference between the disubstitution rate constant ($k_2 = 3 \cdot 3.10^{-7}$ $l.mole^{-1}$ sec^{-1} at 50° C) and the chelation one ($k_2 = 87 \cdot 0.10^{-7}$ $l.mole^{-1}$ sec^{-1} at 50° C) (tab. 3) cannot be explained by the small ligand effect on the rate of disubstitution (see Table III). The exchange mechanism followed by chelation (path 2, Figure 2) is probably the reason of this large difference.

From the data for the complex $Fe(CO)(NO)_2P(O-n-C_4H_9)_3$, we cannot decide about the 2 and 3 paths of Fig. 2, being nearly equal the basicities of $P(O-n-C_4H_9)_3$, we cannot decide about the 2 and 3 paths of Fig. 2, being nearly equal the basicities of $P(O-n-C_4H_9)_3$ and diphos ligands. It is possible that both mechanisms occur contemporarily, as observed for the same reaction with the $Co(CO)_2NOP(O-CH_3)_3$ complex.[12]

The reaction between $Fe(CO)(NO)_2P(n-C_4H_9)_3$ and diphos shows a particular behaviour: the rate constant values, calculated following the disappearance of the CO stretching band of the monosubstituted complex, do not agree with the values calculated following the lower frequency NO stretching band; the IR spectrum shows a band which cannot be assigned to chelate complex (Figure 3); while the reaction proceeds, this band disappears. This may be explained assuming the formation of the intermediate $Fe(NO)_2P(n-C_4H_9)_3$ diphos, that gives, by subsequent chelation, the $Fe(NO)_2$ diphos complex. This mechanism is possible if the reaction proceeds following path 3 of Figure 2; nevertheless, the contemporary reaction by path 2 of Fig. 2 cannot be excluded.

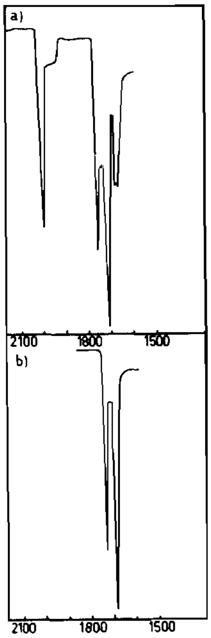

Figure 3. IR spectrum of $Fe(NO)_2$ diphos (b) and during the kinetic runs for the reaction between $Fe(CO)(NO)_2P(n-C_4H_9)_3$ and diphos (a).

The $Fe(CO)(NO)_2Sb(C_6H_5)_3$, also freshly crystallized, reacted by a mechanism different from the corresponding reaction of $Co(CO)_2NO\ Sb(C_5H_5)_3$.[12] The reaction was not consecutive, but it gave the chelate complex directly. Because the kinetics were not reproducible, it is not possible to clarify the mechanism.

The reactivity order of the dissociative path is $P(C_6H_5)_3 > P(n-C_4H_9)_3$ which agrees with the reactivity order for the $Co(CO)_2NOL$[12] and $Mn(NO)(CO)_3L$[16] complexes. It can be due to the basicity or steric effect of the ligands[12,15]. The reactivity order of the associative path is the following:

$$CO > As(C_6H_5)_3 \gg P(O-C_6H_5)_3 > P(O-n-C_4H_9)_3 > \\ > P(C_6H_5)_3 > P(n-C_4H_9)_3$$

It is the same as that found for $Co(CO)_2NOL$.[12] The Figure 4 reports the plots – log k_2 *Vs.* ΔHNP[17] for the reaction of $Fe(CO)(NO)_2L$ and $Co(CO)_2NOL$ with diphos. The trends are linear for both complexes. This means the basicity is the main factor affecting the reactivity.

(b) *Disubstitution Reaction.* The kinetic runs were performed for the $P(C_5H_5)_3$, $P(n-C_4H_9)_3$ and $P(O-n-C_4H_9)_3$ ligands. The $As(C_6H_5)_3$ and $P(O-C_6H_5)_3$ ligands react very slowly, making so difficult to follow

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[14] (a) R.J. Angelici and J.R. Graham, *J. Am. Chem. Soc.*, *87*, 5586 (1965). (b) E.E. Siefert and R.J. Angelici, *J. Organometal. Chem.*, *8*, 374 (1967).

[15] C.A. Streuli, *Anal. Chem.*, *32*, 985 (1960).

[16] H. Waversik and F. Basolo, *J. Am. Chem. Soc.*, *89*, 4626 (1967).

[17] Difference in half-neutralization potentials from that of N,N'-diphenilguanidine taken as a standard, using nitromethane as a solvent[15].

the disubstitution reaction for decomposition of the substrate.

The reaction is first order in the ligand and in the substrate for the $P(O{-}n{-}C_4H_9)_3$ lingand. For the $P(C_6H_5)_3$ and $P(n{-}C_4H_9)_3$ lingands the $k_{I\,obs}$ values follow the equation (4) (Figure 5). The values of rate constants for the first order path (k_1) (Tab. III) and the values of thermal paramether (Table III) for $P(C_6H_5)_3$ are the same of those found for the similar reaction with diphos. This suggests a dissociative mechanism also for the first order path of the disubstitution. The thermal parameters of the second-order path suggest an associative mechanism.[3]

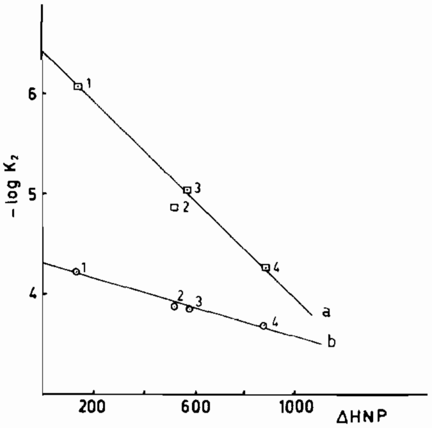

Figure 4. Free energy relationship between $-\log k_2$ and ΔHNP for the reaction of $Fe(CO)(NO)_2L$ (line a) and $Co(CO)_2NOL$ (line b) with diphos; $L=P(n{-}C_4H_9)_3$ (point 1), $P(O{-}n{-}C_4H_9)_3$ (point 2), $P(C_6H_5)_3$ (point 3), $P(O{-}C_6H_5)_3$ (point 4). Data for $Co(CO)_2NOL$ are taken from ref. 12.

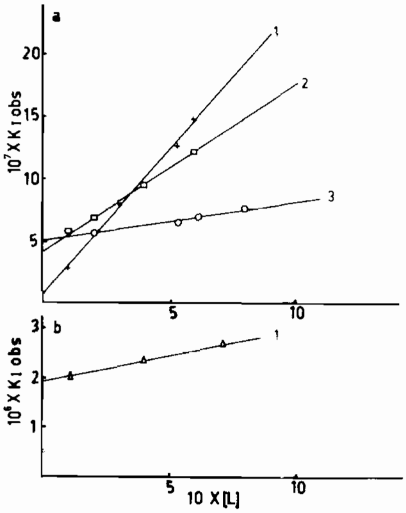

Figure 5. $k_{I\,obs}/[L]$ plots for the reaction $Fe(CO)(NO)_2L+L \rightarrow Fe(NO)_2L_2+CO$ in toluene. a) 50°C, $L=P(O{-}n{-}C_4H_9)_3$ (line 1), $L=P(n{-}C_4H_9)_3$ (line 2), $L=P(C_6H_5)_3$ (line 3); b) 60°C, $L=P(C_6H_5)_3$ (line 1).

The results are explained by the following scheme

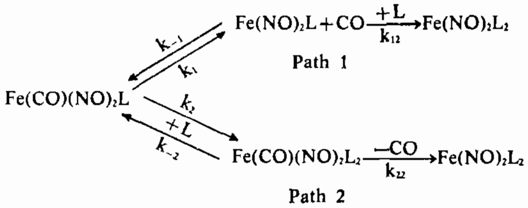

Figure 6. Mechanism of the disubstitution reaction of $Fe(CO)(NO)_2L$.

The reactivity order of dissociative path is equal to the chelation process; also in this instance the same considerations are effective.

The reactivity for the associative path is the following:

$$P(O{-}n{-}C_4H_9)_3 > P(n{-}C_4H_9)_3 > P(C_6H_5)_3$$

This order is difficult to interpret, because the ligand properties act both in the substrate and in the nucleophile, leading often to a superimposition of competive effects. Anyway, it agrees with that found for the corresponding reaction of $Co(CO)_2NOL$[12] and $Mn(CO)_3NOL$.[16]

As for the series $Ni(CO)_4$[1,2] $Co(CO)_3NO$[3,5], $Fe(CO)_2(NO)_2$[4,9] also for the $Ni(CO)_3L$[18], $Co(CO)_2NOL$[14] and the present $Fe(CO)(NO)_2L$ complexes the reaction mechanism of substitution changes fom dissociative for the $Ni(CO)_3L$ complex to prevailingly associative for $Co(CO)_2NOL$ and $Fe(CO)(NO)_2L$. For the last two complexes the dissociative contribution to the reaction mechanism changes with the ligand characteristics. Whereas the monosubstitution reaction of $Fe(CO)_2(NO)_2$ proceeds by an associative mechanism only, the disubstitution proceeds by associative and dissociative mechanism at the same time. This difference is due to the nature of the ligand L; the ligand L, more basic than a CO group, increases the negative charge on the metal. This is supported by the fact that the infrared spectra of monosubstitution compounds show a C–O and N–O stretching frequency lower than the non-substituted complex.[19] It follows that the ligand approach is hindered; moreover the increase of negative charge on the metal strengthens the M–C bond. Therefore both the associative and dissociative way of reaction are hindered, but the dissociative way is hindered less than the associative one.

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