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Kinetics of Disubstitution Reactions of 1,2-bis(diphenylphosphino) Ethane with Monosubstituted Derivatives of Co(CO)$_3$NO[1]

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The kinetics of reaction between a series of monosubstituted cobalt carbonyls Co(CO)$_2$NOL (with L= Sb(C$_6$H$_5$)$_3$, As(C$_6$H$_5$)$_3$, P(C$_6$H$_5$)$_3$, P(OC$_6$H$_5$)$_3$, P(OCH$_3$)$_3$, and P(n–C$_4$H$_9$)$_3$) and the same bidentate ligand 1,2-bis(diphenylphosphino)ethane, have been studied. In all cases the end product is the disubstituted chelate complex Co(CO)NOP(C$_6$H$_5$)$_2$CH$_2$CH$_2$P(C$_6$H$_5$)$_2$. For L=P(C$_6$H$_5$)$_3$ and P(OCH$_3$)$_3$ there are formed to an appreciable extent, at relatively low ligand-to-complex conc. ratios, also the disubstituted complexes Co(CO)NOL$_2$. There is good evidence that the associative reaction mechanism goes through a path involving a primary step of substrates ligand displacement, followed by chelation. Only for Co(CO)$_2$NOP(OCH$_3$)$_3$, a primary step of substrate ligand displacement, follow-ligand, again followed by chelation, is competitive with the above one. The order of reactivity for primary ligand displacement is the following: Sb(C$_6$H$_5$)$_3$>CO> As(C$_6$H$_5$)$_3$>P(OC$_6$H$_5$)$_3$>P(C$_6$H$_5$)$_3$>P(n–C$_4$H$_9$)$_3$. It is interpreted on the basis of the varied basicity and polarizability of the substrate ligands, and in specific cases of their additional π-bonding ability. Steric factors do not seem to play a relevant role.

Introduction

The influence of substrate ligands in neutral carbonilic complexes of zerovalent metals on the rate constant for the reaction of these substrates with different ligands, has been recently emphasized, particularly for dissociative kinetic mechanisms in tetrahedral[2] and octahedral[3,4] complexes. For associative-type processes the effect of the entering ligand is not easily experimentally separated from that of the substrate one. A reaction suitable for this end is that[5] between Co(CO)$_2$NOL (with L having a phosphorus, arsenic or carbon donor atom) and phosphorus ligands. Here, when the entering ligand is different from the substrate one, the reaction goes through ligand displacement with no appreciable disubstitution.

We have extended some previous work[6] to the reaction between Co(CO)$_2$NOL (with L having a phosphorus, arsenic or antimony donor atom) and the bidentate ligand (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$ (diphos). The relatively low basicity of this ligand, reducing the rate of the primary path of ligand displacement, has allowed to localize situations where a primary path of CO disusbstitution becomes competitive. The type of reaction studied has two additional experimental advantages (a) the primary step is always followed by chelation, so that the final product is a disubstituted complex with CO and NO stretching bands clearly separated from those of the starting complex, (b) the process of chelation is much faster than the primary step of ligand displacement or CO disubstitution, so that the product of the first attack is subtracted from the equilibrium and it is possible to get substitution of ligands of relatively high basicity.

Experimental Section

(a) *Disubstituted Complexes Obtained During the Kinetic Runs.* The final product of the kinetic runs in toluene solution, in the reactions between the monosubstituted complexes Co(CO)$_2$NOSb(C$_6$H$_5$)$_3$, Co(CO)$_2$NOAs(C$_6$H$_5$)$_3$, Co(CO)$_2$NOP(n–C$_4$H$_9$)$_3$, Co(CO)$_2$NOP(OC$_6$H$_5$)$_3$ and the above bidentate ligand diphos was for complex/ligand ratios ranging from 1/10 to 2/1, only the disubstituted chelate compound Co(CO)NOP(C$_6$H$_5$)$_2$CH$_2$CH$_2$P(C$_6$H$_5$)$_2$; it was identified through m.p. (164-165°C), analysis and IR spectrum.[6] By reaction between Co(CO)$_2$NOP(C$_6$H$_5$)$_3$ or Co(CO)$_2$NOP(OCH$_3$)$_3$ and the diphos, were instead obtained two compounds of different nature.

In the case of Co(CO)$_2$NOP(C$_6$H$_5$)$_3$ a dark compound with a definite melting point, but ranging for different runs between 185° and 197°C, was obtained in addition to the chelate complex (which was the only product on working in excess of ligand); from IR evidence it turned out to be a disubstituted complex, with CO and NO stretching frequencies (νCO=1959, νNO=1714 cm^{-1}) almost coincident with those of the triphenylphosphinic disubstituted complex[5] and of the chelate.[6] This compound could be separated from the chelate and the excess monosubstituted complexes,

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[4] F. Zingales, F. Canziani, and F. Basolo, *J. Organometal. Chem.*, 7, 461 (1967).

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[6] G. Cardaci, A. Foffani, G. Distefano, and G. Innorta, *Inorg. Chim. Acta*, *1*, 340 (1967).

taking advantage of its slightly lower solubility in a CH_2Cl_2-*n*-hexane 1/1 mixture. The dark crystals so obtained, well distinct from the red ones of the chelate, gave to analysis C=69.17, H=4.92, N=2.14% and M.W.=601, attributed to $Co(CO)NO[P(C_6H_5)_3]_2$ possibly impure for the chelate (theor. for the disubst. complex C=69.32, H=4.72, N=2.19 and M.W.=641; found m.p. 175-178°C [7]).

In the reaction of $Co(CO)_2NOP(OCH_3)_3$ with the diphos in defect of ligand, both the chelate complex and a disubstituted compound different from the chelate, but now well distinct spectroscopically from it (in toluene soln., for the chelate $\nu NO = 1711$ cm^{-1},[6] for the other compound 1727 cm^{-1}) were obtained. The disubstituted compound (M.W. found 374, near to that for $Co(CO)NO[P(OCH_3)_3]_2$), liquid at room temperature, was separated from the chelate and the excess monosubstituted complex chromatographing on Al_2O_3 (*n*-hexane as supporting liquid, CH_2Cl_2-*n*-hexane 2/5 mixture as eluent), followed by fractional crystallization to eliminate residual chelate.

The occurrence of these disubstitution products in the kinetic runs with $Co(CO)_2NOP(C_6H_5)_3$ and $Co(CO)_2NOP(OCH_3)_3$ should be due (see also the discussion below) to the fact that in these cases, the good reactivity of the starting complex at the reaction temperature (60°C or higher) allows for a relevant amount a disubstitution process with the ligand set free in the parallel reaction with the diphos.

The monosubstituted complexes were prepared as from literature;[5-8] the solid ones were purified recrystallizing from methanol, the liquid ones [$Co(CO)_2NOP(n{-}C_4H_9)_3$ and $Co(CO)_2NOP(OCH_3)_3$] chromatographing on Al_2O_3 as above. $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ was prepared and purified following.[9]

(b) *Conditions of the Kinetic Work.* The solvent employed for the kinetics was toluene, distilled over Na and collected under nitrogen to reduce the amount of dissolved oxygen and any decomposition of the compounds studied.[6]

The kinetic runs were followed with an IR method, measuring—with a Perkin-Elmer mod. 337 or 521 spectrophotometer—the rate of decrease of the high-frequency CO and of the NO stretching bands of the starting monosubstituted complexes, and the rate of increase of the NO stretching band of the produced disubstituted or chelate ones. Owing to the possibility in some cases of the parallel formation of two disubstituted products (see above), in every case it was checked whether the absorbance of the NO band of the disubstituted product measured at the end of the reaction, would correspond to what expected for the chelate complex. The kinetics were followed, because of the wide range of rates occurring, at two temperatures: 40.0°C for $Co(CO)_3NO$, $Co(CO)_2NOAs(C_6H_5)_3$, and $Co(CO)_2NOSb(C_6H_5)_3$, 60.1°C for $Co(CO)_2NOP(n{-}C_4H_9)_3$, $Co(CO)_2NOP(OCH_3)_3$, and $Co(CO)_2NOP(OC_6H_5)_3$; for $Co(CO)_2NOP(C_6H_5)_3$ it was also worked at higher temperatures, in order to evaluate the thermal parameters.

On account of the slowness of the reactions, they were carried out in dark ampoules sealed under nitrogen, to avoid changes of composition and reduce any decomposition. The kinetics were always followed for at least 40-70% of transformation. In the case of $Co(CO)_2NOAs(C_6H_5)_3$ and $Co(CO)_2NOSb(C_6H_5)_3$, which did not show simple kinetic behaviour, being neither first- or second-order and having the typical features of consecutive reactions, the zero-time of the kinetics was recorded; for this end the solutions of the starting complex and of the ligand were separately prethermostated in a reaction vessel sealed under nitrogen (see [6]).

The equations employed to evaluate, from the measured absorbancies, the first- and second-order rate constants, were the same as in [6]. In the case of consecutive reactions the equation

$$c = a\left[1 + \frac{1}{k_I - k_2}\left(k_2 e^{-k_I T} - k_I e^{-k_2 T}\right)\right] \qquad (I)$$

was used, where *a* is the initial concentration of the monosubstituted complex, *c* the chelate concentration at different times *t* of the kinetics, k_2 the first-order rate constant for the second step of the reaction, $k_I = k_1[\text{diphos}]$ the pseudo first-order rate constant for the first step. The rate constant k_2 of the chelation process was measured independently, studying that process for the reaction between $Co(CO)_3NO$ and the diphos. The *c* values were obtained from the absorbance of the NO band of the chelate. In these cases the decrease of the stretching bands of the monosubstituted complex could not be followed, because the first step of the kinetics involved displacement of $As(C_6H_5)_3$ or $Sb(C_6H_5)_3$ by the diphos, and the bands of $Co(CO)_2NOAs(C_6H_5)_3$ or $Co(CO)_2NOSb(C_6H_5)_3$ [6] overlapped those of $Co(CO)_2NOP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$.[10] From the experimental values and equation (I), using an IBM 1620 computer, values of k_I and consequently of k_1 could be obtained

Results and Discussion

The experimental results of the kinetics between $Co(CO)_2NOL$ and 1,2-bis(diphenylphosphino)ethane in toluene soln. are collected in Tables I to III. Table I gives the kinetic results at 40.0°C for $Co(CO)_3NO$ (second attack of the chelating ligand), $Co(CO)_2NOAs(C_6H_5)_3$ and $Co(CO)_2NOSb(C_6H_5)_3$, Table II those at 60.1°C for $Co(CO)_2NOP(OCH_3)_3$, $Co(CO)_2NOP(OC_6H_5)_3$, and $Co(CO)_2NOP(n{-}C_4H_9)_3$. In Table III are reported the values obtained for $Co(CO)_2NOP(C_6H_5)_3$; in this case the kinetics was studied in more detail and at different temperatures, to evaluate the thermal parameters of the process.

Table I shows that the second-order rate constants for $Co(CO)_2NOAs(C_6H_5)_3$ and $Co(CO)_2NOSb(C_6H_5)_3$ do not vary by changing the concentration of the complex or of the ligand. For $Co(CO)_2NOP(OCH_3)_3$ the second-order rate constants (see Table II) evaluated from the rate of de-

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(8) L. Malatesta and A. Araneo, *J. Chem. Soc.*, 3803 (1957).
(9) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).
(10) R. J. Mawby, D. Morris, E. M. Thorsteinson, and F. Basolo, *Inorg. Chem.*, 5, 27 (1966).

Table I. Rate constants for the reactions of $Co(CO)_3NO$, $Co(CO)_2NOAs(C_6H_5)_3$, and $Co(CO)_2NOSb(C_6H_5)_3$ with $P(C_6H_5)_2$-$CH_2CH_2P(C_6H_5)_2$ at 40.0°C in toluene soln.

Complex	$10^3\times[C]$ moles/liter	$10^2\times[L]$ moles/liter	k_1 $l\ mole^{-1}\ sec^{-1}$	$10^4\times k_2$ sec^{-1}
$Co(CO)_3NO$	6.20	10.37	1.73×10^{-2} [a]	3.10
»	18.28	4.98		2.95
$Co(CO)_2NOAs(C_6H_5)_3$	11.26	10.05	8.75×10^{-4} [b]	
»	8.08	8.24	8.62×10^{-4} [b]	
$Co(CO)_2NOSb(C_6H_5)_3$	10.13	10.10	3.90×10^{-2} [b]	
	5.05	5.02	3.80×10^{-2} [b]	

[a] From the thermal parameters of the reaction between $Co(CO)_3NO$ and $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ in benzene soln., see ref. (6). [b] From equation (I) and the above experimental rate constant value ($k_2=3\times10^{-4}\ sec^{-1}$) for the chelation step with $Co(CO)_3NO$.

Table II. Experimental second-order rate constants $k_{II}obs$ for reactions of $Co(CO)_2NOP(OCH_3)_3$, $Co(CO)_2NOP(OC_6H_5)_3$, and $Co(CO)_2NOP(n\text{—}C_4H_9)_3$ with $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ at 60.1°C in toluene soln.

Complex	$10^2\times[C]$ moles/liter	$10^2\times[L]$ moles/liter	$10^4\times k_{II}obs$ [a] $l\ mole^{-1}\ sec^{-1}$	$10^4\times k_{II}obs$ [b] $l\ mole^{-1}\ sec^{-1}$
$Co(CO)_2NOP(OCH_3)_3$	1.097	10.34	1.26	0.81
»	1.261	10.07	1.31	1.13
»	1.113	8.04	1.32	1.08
»	1.114	8.19	1.32	1.01
»	0.891	6.55	1.55	—
»	1.150	6.29	1.45	—
»	2.103	6.07	1.34	0.98
»	1.203	4.40	1.36	—
»	1.838	3.87	1.38	1.06
»	1.686	2.07	1.31	2.2 [c]
$Co(CO)_2NOP(OC_6H_5)_3$	0.955	15.59	4.71	4.13
»	0.963	12.79	4.61	4.10
»	0.972	10.23	4.90	4.00
$Co(CO)_2NOP(n\text{—}C_4H_9)_3$	1.060	15.60	0.64	0.48
»	0.979	15.57	0.62	0.51
»	1.071	9.91	0.64	0.53
»	1.403	9.88	0.62	0.49

[a] From the rate of decrease of the νCO(A′) and νNO bands of the starting monosubstituted complex. [b] From the rate of increase of the νNO band of the disubstituted chelate complex. [c] Value too high owing to competitive formation of the disubstituted complex $Co(CO)NO[P(OCH_3)_3]_2$ (see text).

Table III. Experimental second-order rate constants $k_{II}obs$ for the reaction of $Co(CO)_2NOP(C_6H_5)_3$ with $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ at different temperatures in toluene soln.

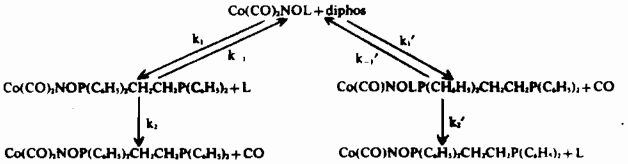
Temp. °C	$10^2\times[C]$ moles/liter	$10^2\times[L]$ moles/liter	$10^4\times k_{II}obs$ [a] $l\ mole^{-1}\ sec^{-1}$	$10^4\times k_{II}obs$ [b] $l\ mole^{-1}\ sec^{-1}$
72.5	0.838	9.03	5.13	5.13
»	0.766	7.92	5.84	5.24
»	1.047	7.53	5.64	5.53
»	0.714	7.30	5.69	5.14
»	0.958	6.60	6.21	6.04
»	0.892	6.08	6.36	5.71
69.3	0.972	8.89	3.87	3.66
»	1.954	6.54	4.16	4.27
»	1.380	5.51	4.57	4.66
»	2.007	3.82	4.81	4.75
»	2.000	3.27	4.88	5.23
»	2.023	2.33	5.52 [c]	6.40 [c]
»	1.999	2.22	6.90 [c]	6.65 [c]
»	1.999	2.01	7.90 [c]	9.12 [c]
63.6	0.801	10.68	2.21	2.21
»	0.803	10.18	2.27	2.11
»	1.002	8.90	2.25	2.25
»	1.004	8.48	2.39	2.16

[a] From the rate of decrease of the νCO(A′) and νNO bands of the starting monosubstituted complex. [b] From the rate of increase of the νNO band of the disubstituted chelate complex. [c] Values too high owing to competitive formation of the disubstituted complex $Co(CO)NO[P(C_6H_5)_3]_2$ (see text).

crease of the stretching bands (νCO(A′) and νNO) of the monosubstituted complex, remain constant within the limits of experimental uncertainty on varying the ligand concentration between 2×10^{-2} and 10^{-1} moles/liter. Also for $Co(CO)_2NOP(OC_6H_5)_3$ and $Co(CO)_2NOP(n-C_4H_9)_3$, although the ligand concentration range investigated was narrower, no variation of the rate constant values obtained in the same way was observed. In all cases a slight difference between the rate constants evaluated as above, and those deduced from the rate of increase of the NO stretching band of the disubstituted products was noticed; this was attributed to a slight decomposition of the monosubstituted complexes at the work temperature.

The data in Table III indicate that the rate constants obtained at 72.5°C from the rate of decrease of the stretching bands of the starting complex are in good agreement one another, differing slightly from those deduced from the rate of increase of the νNO band of the disubstituted product. This difference disappears by lowering the temperature to 63.6°C, pointing to a possible contribution of thermal decomposition at higher temperatures. For the possible significance of the slight residual dependence of $k_{II}obs$ from the entering ligand conc., which is reasonably linear *vs.* $1/[L]$ for $[L]/[C]>3/1$, see below.

For the present reactions two possible associative reaction paths are as follows:



For the path involving as its primary step ligand L displacement by the diphos, if $k_2\gg k_1[\text{diphos}]$[11] and in addition $k_2\gg k_{-1}[L]$ the kinetics is a second-order one and the rate of reaction is determined by the constant k_1 of the displacement step. If $k_2\simeq k_1[\text{diphos}]$, as found for the reactions with $Co(CO)_2NOAs(C_6H_5)_3$ and $Co(CO)_2NOSb(C_6H_5)_3$ at 40°C, the kinetics is a consecutive one; even in this case the first step of the reaction is not complicated by the settling of the equilibrium, because the basicity of the diphos is sufficiently higher than that of the substrate ligands to ensure a complete shift of the reaction towards the intermediate monosubstituted complex.

Also for the path involving primarily a CO disubstitution step, if $k_2'\gg k_1'[\text{diphos}]$ and moreover $k_2'\gg k'_{-1}[CO]$ the kinetics is again a second-order one, determined by the rate constant k_1'. If $k_2'\simeq k_1'[\text{diphos}]$ the process is a consecutive one. k_2' should be lower than k_2 owing to the greater difficulty for the bidentate entering ligand to displace a phosphinic ligand, with respect to a much less basic CO one.

The value of k_2' cannot be obtained independently, as it was instead the case for k_2 (see [6,10,11]).

The reactions with $Co(CO)_2NOAs(C_6H_5)_3$ and $Co(CO)_2NOSb(C_6H_5)_3$, owing to the remarkably higher basicity of the entering than of the substrate's ligand, appear to go primarily through ligand displacement. Working in ten times excess of the entering ligand to the monosubstituted complex, equation (I) above gives k_1 values for the displacement step as from Table I. These are constant within ±5%, both as far as the experimental points of a given kinetic run and kinetics performed with varied complex and ligand concentrations are concerned. Such a constancy supports by itself the mechanism indicated. The mean values at 40°C—8.68×10^{-4} and 3.85×10^{-2} l mole^{-1} sec^{-1} resp. for the arsine- and stibine-substrates—should be compared (see also below, and apart from a presumably small solvent contribution[12]) with the 1.73×10^{-2} l mole^{-1} sec^{-1} figure (see Table I) for the rate constant of the first attack in the reaction of $Co(CO)_3NO$ and diphos, as derived from the thermal parameters given in [6] in benzene soln.

With the substrate ligands having a phosphorus donor atom the choice between the two paths above is less evident, and the different situations which arise shall be examined separately.

The reaction path for $Co(CO)_2NOP(n-C_4H_9)_3$ involves ligand displacement as its first step, as it results indirectly by comparing the rate constants at 60.1°C (a) for the disubstitution reaction between this substrate and $P(n-C_4H_9)_3$ (4.25×10^{-6} l mole^{-1} sec^{-1} [13]) and (b) for the corresponding reaction with the diphos (5.00×10^{-5} l mole^{-1} sec^{-1}, see Table II and ref. [14]). Considering the higher basicity of $P(n-C_4H_9)_3$ with respect to the diphos,[15] if the first attack by the diphos would involve CO disubstitution its rate would be lower than the above one for the attack by $P(n-C_4H_9)_3$. Since the observed process has a rate constant about ten times higher than for disubstitution with $P(n-C_4H_9)_3$, it follows that the prevailing path is of ligand displacement followed by chelation.

For the complex $Co(CO)_2NOP(OC_6H_5)_3$ the rate constant for CO disubstitution with the substrate ligand is too low to be measured at 60.1°C.[13] This agrees with the low basicity of $P(OC_6H_5)_3$ but does not give indications as to the possible rate of CO disubstitution with the diphos, since for this last process both the higher basicity of the entering ligand[15] and the π-accepting ability of the substrate one[16,2] increase the rate of disubstitution. Anyway, the basicity of the diphos is sufficiently higher than that of $P(OC_6H_5)_3$ to ensure again, as with the arsine- and stibine-substrate ligands, that the ligand displacement path be the favoured one.

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(11) This is the case for the kinetic runs with monosubstituted substrates having phosphinic ligands, when the value of k_2 is found to be 1.8×10^{-3} sec^{-1} in benzene soln. at 60.1°C, as evaluated by extrapolating the thermal parameters[6] of the reaction between $Co(CO)_3NO$ and the diphos.

(12) R. J. Angelici and B. E. Leach, *J. Organometal. Chem.*, *11*, 203 (1968); R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, *84*, 2495 (1962).

(13) Unpublished results from this lab.

(14) Taking the value obtained from the rate of increase of the νNO band of the disubstituted product; the corresponding figure from the rate of decrease of the stretching bands of the starting complex should be possibly affected by partial thermal decomposition (see above).

(15) C. A. Streuli, *Anal. Chem.*, *32*, 985 (1960); W. A. Henderson, Jr. and C. A. Streuli, *J. Am. Chem. Soc.*, *82*, 5791 (1960); W. A. Henderson, Jr. and S. A. Buckler, *J. Am. Chem. Soc.*, *82*, 5794 (1960).

(16) W. D. Horrocks, Jr. and K. C. Taylor, *Inorg. Chem.*, *2*, 723 (1963).

In the case of $Co(CO)_2NOP(OCH_3)_3$ the rate constant for CO disubstitution with the substrate ligand is 4.57×10^{-5} l mole^{-1} sec^{-1} at 60.1°C,[13] while the corresponding figure for the reaction with the diphos is, at the same temperature, 1.01×10^{-4} l mole^{-1} sec^{-1} (see Table II and ref. [14]). On account of the somewhat higher basicity of the diphos with respect to the substrate ligand, the CO disubstitution path with the diphos involves, for this substrate, a rate constant competitive with that for the ligand displacement path.

The complex $Co(CO)_2NOP(C_6H_5)_3$ reacts with $P(C_6H_5)_3$ *via* a first-order kinetics, with a rate constant at 60.1°C of 2.3×10^{-6} sec^{-1};[13] this should only sligthly increase[6] for the corresponding reaction of mixed disubstitution with the diphos. Being at 63.6°C the kinetics with the diphos a second-order one with a rate constant 2.18×10^{-4} l mole^{-1} sec^{-1} (see Table III and ref. [14]; using the below reported thermal parameters, the figure at 60.1°C turns out 2.05×10^{-4} l mole^{-1} sec^{-1}), the path interested should be, as observed above for the substrate ligand $P(n\text{–}C_4H_9)_3$, the one involving primarily a ligand displacement step. The failure to observe, in the conditions of the present kinetic runs, appreciable disubstitution by the substrate ligand in the case of $P(n\text{–}C_4H_9)_3$, differently from $P(C_6H_5)_3$ (see the experimental section above) though the disubstitution rates for both ligands are near, should reflect the fact that for $P(C_6H_5)_3$ the disubstitution path is a dissociative one.[13] Also the previously cited slight residual dependence (as from Table III) of $k_{\rm II}$obs from the entering ligand conc., may be interpreted through a dissociative contribution (for an extent $<10\%$) in this specific case to the ligand displacement path by the diphos.

The data in Table III enable to evaluate the thermal parameters for the reaction $Co(CO)_2NOP(C_6H_5)_3$ + diphos, which turn out $\Delta H^* = 13\pm1$ kcal/mole and ΔS^* (336.5°K) $= -39$ eu/mole(the $k_{\rm II}$obs values employed here were extrapolated to high ligand conc.). These figures agree with those reported for the process of first attack in the reaction $Co(CO)_3NO$ + diphos,[6] and for the ligand displacement reaction $Co(CO)_2NOP(OCH_3)_3 + P(n\text{–}C_4H_9)_3$.[5]

For the complexes which, from the above evidence, react with the diphos prevailingly through a ligand displacement primary step, an order of reactivity can be deduced as a function of the substrate ligand; it gives informations on the characteristics of the ligands of importance for the reactivity. The order observed is the following: $Sb(C_6H_5)_3[3.85\times10^{-2}] > CO[1.73\times10^{-2}] > As(C_6H_5)_3[8.68\times10^{-4}] > P(OC_6H_5)_3[4.08\times10^{-4}] > P(C_6H_5)_3[2.05\times10^{-4}] > P(n\text{-}C_4H_9)_3[5.00\times10^{-5}]$, the first three complexes having been studied at 40.0°C, the second three at 60.1°C.

The above $k_{\rm I}$ values for substrate ligands with phosphorus donor atom give a good linear free-energy plot lg $k_{\rm I}$ *vs.* ΔHNP, being in these cases the Streuli's ΔHNP values[15] proportional both to the basicity and the polarizability of the ligands concerned.[17] Similar plots are reported by Graham and Angelici[18] for nitrogen substrate ligands in Cr, Mo, and W carbonyl complexes. The present linear dependence reflects the fact that, for a higher basicity of the substrate ligand, the increased charge density to the central metal atom disfavours the diphos associative attachment to the substrate.

The present order substantially agrees with that found (a) in typical dissociative processes of ligand displacement for disubstituted Ni(O) complexes, of the type $Ni(CO)_2L_2 + L'$,[2] (b) in associative processes of the type $Co(CO)_2NOL + L'$,[5] involving monodentate substrate and entering ligands. In the reactions studied by [2] and [5] the general influence of the varied basicity of the substrate ligands shows noticeable and different deviations, coming for instance with the Ni complexes from the unexpectedly low reactivity of the phosphite ligands, while for the Co complexes perturbations are caused by steric effects.

On going to As and Sb donor atoms, again it is apparent from the above order of reactivity that the basicity factor is the predominant one. Particular instead is the situation for the CO substrate ligand which, although being less basic than $Sb(C_6H_5)_3$ is displaced more difficultly. The order of steric hindrance would favour the CO displacement with respect to $Sb(C_6H_5)_3$, so that in this case the π-accepting ability of the substrate ligand seems to be the prevailing factor in determining the reactivity of the complex; this should strengthen the Co–CO bond, making it less reactive than the $Co\text{–}Sb(C_6H_5)_3$ one. In the series $Sb(C_6H_5)_3$, $As(C_6H_5)_3$, and $P(C_6H_5)_3$ the order of reactivity observed, considering the only slight differences of steric hindrance and π-accepting ability, corresponds to the increased basicity (and decreased polarizability) and reflects a bond strengthening in the order Co–P > Co–As > Co–Sb.

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