CONTRIBUTION FROM THE INSTITUTE OF CHEMISTRY,
UNIVERSITY OF TURIN, 10125 TURIN, ITALY

Kinetic Study of the Reactions of Bis(cyclopentadienylcarbonylnickel) with Ligands

BY P. L. STANGHELLINI, R. ROSSETTI, O. GAMBINO, AND G. CETINI*

Received September 16, 1970

The kinetics of the reactions between $Cp_2Ni_2(CO)_2$ (Cp = cyclopentadienyl) and mono- and bidentate ligands have been studied. The reaction with monodentate ligands proceeds by an SN2 mechanism, but the reaction with bidentate (acetylenic) ligands appears to be a two-stage mechanism with a reversible, first-order process as rate-determining step. The more probable mechanisms are discussed on the basis of the values of the activation parameters and the steric hindrance of the ligand.

Introduction

The chemical reactivity of $Co_2(CO)_8$ has been the subject of thorough study over the last 10 years: there have been kinetic studies of the CO-exchange reaction,[1] the substitution of terminal CO's with monodentate ligands,[2] and the substitution of bridging CO's with bidentate ligands, such as the acetylenic derivatives.[3]

On the other hand, a carbonyl derivative of Ni with formula $Cp_2Ni_2(CO)_2$ (Cp = cyclopentadienyl group) has been held to have exactly the same structure and electronic configuration as $Co_2(CO)_8$.[4] The metal atoms in the two complexes may, in fact, be treated as isoelectronic according to the noble gas formalism; their similarity of structure (two bridging CO's, not coplanar with the metal atoms, with the other ligands in symmetric coordination with them: idealized symmetry C_{2v}) is proved by the fact that in both complexes the two bridging CO's can be substituted with an acetylenic derivative.[5] Derivatives with an analogous structure, generally indicated as $Co_2(CO)_6C_2RR'$ and $Cp_2Ni_2C_2RR'$, can readily be obtained.[6]

The present paper, therefore, is a first step in a comparative study of the kinetic behavior of $Cp_2Ni_2(CO)_2$ and $Co_2(CO)_8$. Later work will compare the acetylenic derivatives of the two complexes, as a follow-up of our earlier study of the acetylenic complexes of dicobaltoctacarbonyl.[7,8]

Experimental Section

Compounds and Solvents.—$Cp_2Ni_2(CO_2)$ was prepared and purified as described in the literature.[9] Its purity was checked by ir spectrophotometry, elemental analysis, and thin-layer chromatography (adsorbent, silica gel G according to Stahl; developer, petroleum ether (bp 40–70°)). Decomposition of the complex was prevented by carrying out the chromatographic runs in an inert atmosphere.

$Ni(CO)_4$ and $NiCp_2$ were supplied by Alfa Inorganics Co. and used without further purification. $P(C_6H_5)_3$ (Fluka AG) and $C_2(C_6H_5)_2$ (Aldrich Chemical Co.) was crystallized from petroleum ether; $PCl(C_6H_5)_2$ and $P(n\text{-}C_4H_9)_3$ (K & K Laboratories) were distilled at reduced pressure before use.

Solvents (petroleum ether, *n*-heptane, etc.) were dried, distilled, and stored according to standard techniques.[10]

N_2 and CO were dried on silica gel and $CaCl_2$ columns before use.

Kinetic Measurements.—The reactions with carbon monoxide were run in glass vials in accordance with a previously reported technique;[7] pure CO or CO and Ar mixtures of known composition were employed. The solubilities of CO in *n*-heptane at various temperatures were determined by us.[11]

With the other ligands the vials were provided with a valve and a rubber plug so that withdrawals could be made at set times.[8] The complex and the ligand, dissolved in *n*-heptane, were placed in the vials under an inert atmosphere (N_2); in the case of very fast reactions, the ligand (in solution) was inserted into the prethermostated complex solution *via* the valve with a syringe before starting the measurements.

The vials were placed in a constant-temperature (±0.2°) bath. Light was strictly excluded.

Reaction rates were determined by measuring the intensity of the 1859-cm^{-1} ir band and plotting ln $[(A_t - A_\infty)/(A_0 - A_\infty)]$ *vs.* time, where A_0, A_t, and A_∞ are the absorbances at $t = 0$, $t = t$, and $t = \infty$, respectively ($A_\infty = 0$ in all the reactions studied in the present experiment). The spectra were taken with a double-beam ir 12 Beckman spectrophotometer with KBr optics. All kinetic plots were linear, at least up to 60–70% conversion. The specific rate value k_{obsd} was calculated by the least-squares method as the slope of the best straight line. The uncertainty of each value is about 5%.

All kinetic measurements were done under pseudo-first-order conditions, *i.e.*, with the ligand concentration essentially constant throughout the reaction; in the case of CO, this condition was ensured by using a high gas to solution volume ratio in the vials.

Reaction products were first identified by ir spectrophotometry. This was followed by conventional methods of product separation (fractioned crystallization, tlc, etc.), together with comparison with separately prepared pure samples. $Ni(CO)_2(P(C_6H_5)_3)_2$ and $Ni(CO)_2(P(n\text{-}C_4H_9)_3)_2$ were prepared in accordance with literature methods.[12] $Ni(CO)_2(PCl(C_6H_5)_2)_2$ has not previously been described and was prepared as follows.

Preparation of $Ni(CO)_2(PCl(C_6H_5)_2)_2$.—Nickel carbonyl (7 ml, 54 mmol) and chlorodiphenylphosphine (19 ml, 108 mmol) were allowed to react at room temperature in a glass flask, with gas inlet and outlet, reflux, and Hg valve, previously purged of air by a current of N_2. The mixture was shaken vigorously with a magnetic stirrer and allowed to react until practically no more gas was produced. Unreacted material was removed by vacuum evaporation. Repeated washings with absolute ethyl alcohol were employed to remove the final traces of ligand from the semisolid mixture. The microcrystalline powder was dried and purified by crystallization from *n*-heptane at −20°.

We have thus obtained pure $Ni(CO)_2(PCl(C_6H_5)_2)_2$ as white-yellow crystals, moderately stable in air, soluble in CS_2 and CCl_4, but poorly soluble in *n*-heptane and alcohol.

---

[1] F. Basolo and A. Wojcicki, *J. Amer. Chem. Soc.*, **83**, 520 (1961); S. Breitschaft and F. Basolo, *ibid.*, **88**, 2702 (1966).

[2] R. F. Heck, *ibid.*, **85**, 657 (1963).

[3] M. R. Tirpak, J. H. Wotiz, and C. A. Hollingsworth, *ibid.*, **80**, 4265 (1968).

[4] J. Chatt, P. L. Pauson, and L. M. Venanzi in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, p 473.

[5] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. Wotiz, R. Markby, and I. Wender, *J. Amer. Chem. Soc.*, **78**, 120 (1956); J. F. Tilney-Bassett, *J. Chem. Soc.*, 577 (1961).

[6] W. G. Sly *J. Amer. Chem. Soc.*, **81**, 14 (1959); O. S. Mills and B. W. Shaw, *J. Organometal. Chem.*, **11**, 595 (1968).

[7] G. Cetini, O. Gambino, P. L. Stanghellini, and G. A. Vaglio, *Inorg. Chem.*, **6**, 1225 (1967).

[8] G. Cetini, O. Gambino, R. Rossetti, and E. Sappa, *J. Organometal. Chem.*, **8**, 149 (1967).

[9] E. O. Fischer and C. Palm, *Chem. Ber.*, **91**, 1725 (1956).

[10] A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. VII, Interscience, New York, N. Y., 1955.

[11] The apparatus is similar to that previously described by Basolo and Wojcicki.[1] We have found the following values for the solubility of CO in *n*-heptane: 13 m*M* at 23.0°, 11 m*M* at 34.0°, and 9 m*M* at 44.0° (the uncertainty is about 15%).

[12] L. S. Meriwheter and M. L. Fiene, *J. Amer. Chem. Soc.*, **81**, 4200 (1959).

TABLE I

VALUES OF THE PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTIONS OF $Cp_2Ni_2(CO)_2$ WITH LIGANDS

Ligand	Temp, °C	Ligand concn × 10^3, *M*	10^5k_{obsd}, sec^{-1}
$C_2(C_6H_5)_2$	70.0	3.03	0.434
		6.85	0.571
		10.1	0.592
		14.7	0.654
		20.3	0.660
		30.0	0.730
		35.0	0.689
		40.0	0.793
		45.2	0.732
		50.1	0.777
		55.3	0.706
	75.0	2.43	0.585
		2.94	0.740
		3.89	0.703
		4.63	0.857
		6.04	1.03
		10.2	1.08
		12.5	1.12
		15.1	1.18
		20.0	1.12
		25.2	1.29
		30.3	1.38
		35.5	1.30
		40.2	1.53
		45.2	1.47
		50.4	1.44
		55.6	1.55
	80.0	7.06	1.34
		9.03	1.63
		10.0	1.72
		12.3	1.82
		15.2	2.00
		20.4	1.95
		25.3	2.30
		30.4	2.20
		34.9	2.35
		40.0	2.34
		45.2	2.69
		55.0	2.66
CO	31.7	2.8	0.59
		4.9	0.89
		7.7	1.38
		10.7	1.96
	40.0	2.5	1.15
		4.4	2.03
		6.7	3.18
		9.4	4.18
	48.0	2.2	2.59
		3.8	4.53
		5.8	6.93
$PCl(C_6H_5)_2$	23.5	3.95	5.11
		8.01	10.3
		12.1	17.6
		16.0	25.0
		19.5	31.0
$P(C_6H_5)_3$	23.5	4.00	13.0
		8.00	24.0
		12.0	38.2
		16.0	49.0
		20.0	67.0
		25.0	82.5
$P(n\text{-}C_4H_9)_3$	23.5	3.75	21
		5.71	41
		7.7	52
		9.8	76

The infrared spectrum contained bands in the carbonyl stretching region at 1986 and 2035 cm^{-1} (CCl_4).

Anal. Calcd for $C_{26}H_{20}Cl_2NiP_2O_2$: C, 56.16; H, 3.63; Cl, 12.75; Ni, 10.56; O, 5.75; P, 11.14. Found: C, 56.22; H, 3.71; Cl, 12.84; Ni, 10.57, O, 5.77; P, 10.77.

Results

The reaction between $Cp_2Ni_2(CO)_2$ and diphenylacetylene is represented by

$$Cp_2Ni_2(CO)_2 + C_2(C_6H_5)_2 \longrightarrow Cp_2Ni_2C_2(C_6H_5)_2 + 2CO \quad (1)$$

Table I gives the k_{obsd} values for eq 1 and Figure 1 shows the behavior of k_{obsd} as a function of $[C_2(C_6H_5)_2]$. The experimental data show that the pseudo-first-order constant increases with increasing $[C_2(C_6H_5)_2]$ but begins to level off at high concentration of the ligand. This can be explained by the slow formation (k_1) of an intermediate, which can either return to the starting complex (k_{-1}) or react further with the ligand to form products (k_2), as illustrated by

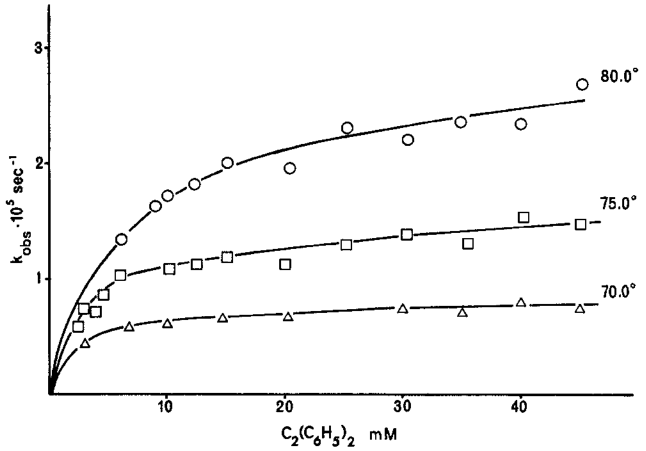


Figure 1.—Variation of the observed pseudo-first-order rate constant with the concentration of diphenylacetylene for reaction 1.

$$Cp_2Ni_2(CO_2) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cp_2Ni_2(CO)_2{}^*$$

$$Cp_2Ni_2(CO)_2{}^* + C_2(C_6H_5)_2 \xrightarrow{k_2} Cp_2Ni_2C_2(C_6H_5)_2 + 2CO$$

Using the steady-state approximation for the active intermediate, *i.e.*, $[Cp_2Ni_2(CO)_2{}^*]$ = constant, the rate for (1) can be expressed as

$$\text{rate} = k_{obsd}[Cp_2Ni_2(CO)_2] = \frac{k_1k_2[C_2(C_6H_5)_2][Cp_2Ni_2(CO)_2]}{k_{-1} + k_2[C_2(C_6H_5)_2]}$$

from which

$$k_{obsd} = \frac{k_1k_2[C_2(C_6H_5)_2]}{k_{-1} + k_2[C_2(C_6H_5)_2]} \quad (2)$$

The behavior of k_{obsd} *vs.* $[C_2(C_6H_5)_2]$ according to (2) is similar to that in Figure 1.

Equation 2 can be rearranged to give

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}\frac{1}{[C_2(C_6H_5)_2]} \quad (3)$$

If we plot $1/k_{obsd}$ *vs.* $1/[C_2(C_6H_5)_2]$, we obtain a straight line (Figure 2), of k_{-1}/k_1k_2 slope and $1/k_1$ intercept, from which the values of k_1 and k_{-1}/k_2 can be calculated. These values are reported in Table II, together with the activation parameters; the error is always the standard deviation, calculated by means of the least-squares method.

Equation 4 represents the reaction between $Cp_2Ni_2(CO)_2$ and a monodentate ligand (when L = CO,

$$Cp_2Ni_2(CO)_2 + 2L \longrightarrow NiCp_2 + Ni(CO)_2L_2 \quad (4)$$

TABLE II

SPECIFIC RATE CONSTANT VALUES FOR THE REACTIONS OF $Cp_2Ni_2(CO)_2$ WITH LIGANDS

Ligand	Temp, °C	10^5k_1, sec^{-1}	$10^3k_{-1}/k_2$, mol l.$^{-1}$	10^2k_3, mol^{-1} l. sec^{-1}
$C_2(C_6H_5)_2$[a]	70.0	0.767 ± 0.017	2.38 ± 0.20	
	75.0	1.51 ± 0.06	3.67 ± 0.28	
	80.0	2.92 ± 0.12	7.68 ± 0.66	
CO[b]	31.7			0.183 ± 0.01
	40.0			0.445 ± 0.028
	48.0			1.19 ± 0.01
$PCl(C_6H_5)_2$	23.5			1.70 ± 0.08
$P(C_6H_5)_3$	23.5			3.4 ± 0.1
$P(n\text{-}C_4H_9)_3$	23.5			9 ± 1

[a] $\Delta H_1^* = 32 \pm 2$ kcal/mol; $\Delta S_1^* = 9 \pm 3$ eu; $\Delta H_{-1}^* - \Delta H_2^* = 28 \pm 8$ kcal/mol; $\Delta S_{-1}^* - \Delta S_2^* = 9 \pm 13$ eu. [b] $\Delta H_3^* = 22 \pm 1$ kcal/mol; $\Delta S_3^* = -1 \pm 2$ eu.

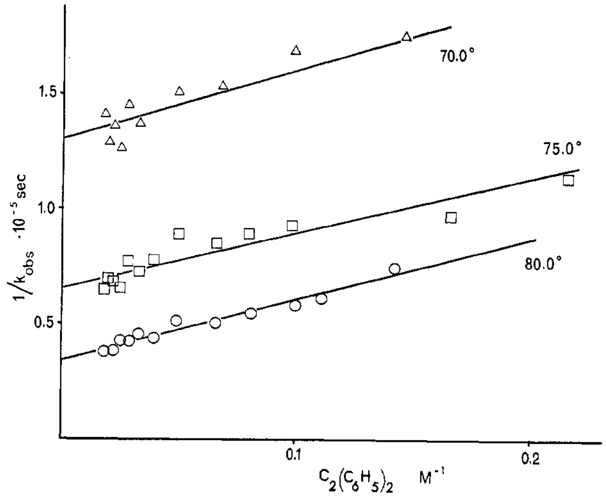


Figure 2.—The linear relationship between values of $1/k_{obsd}$ and and $1/[C_2(C_6H_5)_2]$ taken from Figure 1.

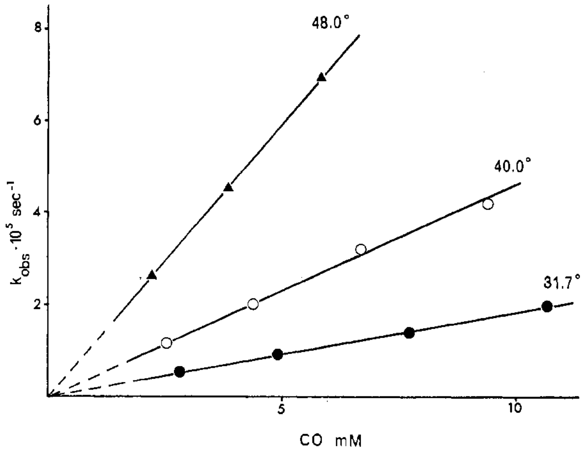


Figure 3.—Variation of the observed pseudo-first-order rate constant with the CO concentration for reaction 4.

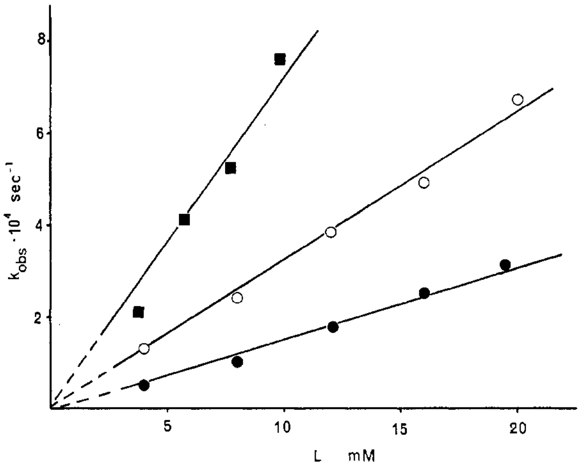


Figure 4.—Variation of the observed pseudo-first-order rate constant with the concentration of the ligand for reaction 4: ■, $P(n\text{-}C_4H_9)_3$; ○, $P(C_6H_5)_3$; ●, $PCl(C_6H_5)_2$.

this equation is the inverse of the reaction generally used to prepare $Cp_2Ni(CO)_2$).

It is possible that the excess ligand takes part in the additional reactions

$$Ni(CO)_2L_2 + L \longrightarrow Ni(CO)L_3 + CO, \text{ etc.}$$

$$NiCp_2 + 4L \longrightarrow NiL_4 + \text{products}$$

as reported elsewhere.[13]

The k_{obsd} values for eq 4 as calculated by the method described in the Experimental Section are dependent on ligand concentration, but this case differs considerably from that of $C_2(C_6H_5)_2$, because there is no leveling off of the rate constant at high ligand concentration. In effect linear behavior is observed by plotting k_{obsd} *vs.* [L], as illustrated in Figures 3 and 4. The near-zero intercept values of the straight lines fall within the standard error and can therefore be ignored. The kinetics of reaction 4 can thus be expressed as

$$\text{rate} = k_{obsd}[Cp_2Ni_2(CO)_2] = k_3[Cp_2Ni_2(CO)_2][L]$$

The k_3 values, calculated from the best slope of the lines, are reported in Table II, together with the activation enthalpy and entropy for the CO reaction; the error is the standard deviation in each case.

Discussion

The data in the Figures 1, 3, and 4 show that the reaction mechanisms between $Cp_2Ni_2(CO)_2$ and CO (and monodentate ligands) and with acetylenic derivatives are entirely different. The mechanism of the reaction between $Cp_2Ni_2(CO)_2$ and $C_2(C_6H_5)_2$ has been illustrated above. A first-order process is rate determining, and the activation parameters are consistent with such a process.

Reactions with monodentate ligands are, therefore, of the associative type, which implies coordination of the ligand on the Ni atom as the rate-determining step.[14,15] It is probable that two mechanisms are si-

---

[13] M. Bigorgne and A. Zelwer, *Bull. Soc. Chim. Fr.*, 1986 (1960); J. F. Nixon, *Chem. Commun.*, 34 (1966); J. R. Olechowski, C. G. McAlister, and R. F. Clark, *Inorg. Chem.*, **4**, 246 (1965).

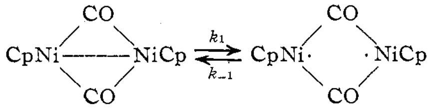
[14] Brief kinetic data for the isotopic exchange reaction between $Cp_2Ni_2(CO)_2$ and labeled CO are previously reported.[15] These data agree with ours as far as the second-order kinetics and the value of the activation enthalpy are concerned, though the specific rate constants are a little higher.

[15] A. Wojcicki and F. Basolo, *J. Inorg. Nucl. Chem.*, **17**, 77 (1961).

multaneously present in this case: a two-stage mechanism, identical with that suggested for the $C_2(C_6H_5)_2$ reaction, and a bimolecular associative mechanism. Since $k_1 \ll k_3$, the contribution of k_1 to k_{obsd} is negligible. It has already been shown[16] that the approach of a nucleophilic ligand may cause a transfer of an electron pair from metal to cyclopentadienyl group; this leaves a low-energy orbital vacant on the metal. In all probability, increased metal positive charge is the result of a decreased σ and π cyclopentadienyl→metal donation and an increased δ metal→cyclopentadienyl back-donation, rather than a complete transfer of an electron pair. Increased positive charge on the Ni atom favors the direct ligand attachment; this is confirmed by the fact that the reaction rate increases with increasing ligand basicity; specific rate values are in the order $P(n\text{-}C_4H_9)_3 > P(C_6H_5)_3 > PCl(C_6H_5)_2 > CO$.

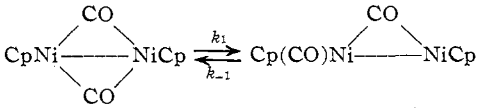
Activation parameter values for the CO reaction are consistent with an SN2 reaction, yet it should be noted that these values are fairly high, though they do not fall outside the experimentally observed limits for nucleophilic substitution on complexes.[17] This is not uncommon in SN2 reactions in which the ligand is CO.[18] The fairly high ΔH_3^* value is most likely the result of the poor nucleophilic power of CO; the small steric hindrance of this molecule, on the other hand, may facilitate the reaction and be responsible for the increased ΔS_3^* value.[19]

Among the possible mechanisms for reaction 1, those that seem most likely are as follows: (a) homolytic fission of the Ni–Ni bond



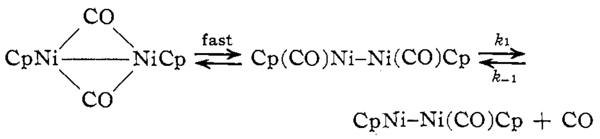
(5)

(b) rupture of a Ni–CO bond with reversible formation of an intermediate in which one bridging CO has become terminal



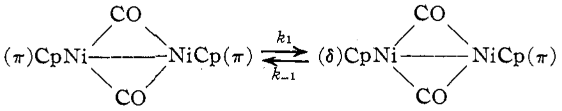
(6)

(c) a rapid preequilibrium involving a small amount of unabridged complex (only this form can react by a slow dissociation of one terminal CO)



(7)

(d) $\pi \rightarrow \sigma$ conversion of the Cp–Ni bond



(8)

Mechanisms like these have been previously proposed: (5), for the reaction between $Co_2(CO)_8$ and acetylenic derivatives;[3] (6) and (7), for the CO isotopic exchange reaction on $Co_2(CO)_8$;[20] (8), for the reaction between $NiCp_2$ and $P(C_6H_5)_3$.[21]

Some considerations can be made at this point on the probability of such mechanisms. It should be noted that the positive value of $\Delta H_{-1}^* - \Delta H_2$ is consistent with a nondissociative mechanism (*i.e.* (5), (6), and (8)). In the case of CO dissociation the value of the activation enthalpy for the reactive intermediate to react further is greater than the value to re-form the initial complex.[22]

Moreover, the fact that the value of $\Delta S_{-1}^* - \Delta S_2^*$ is greater than zero provides another argument in favor of the (5), (6), and (8) mechanisms, since the k_2 path will certainly have in these cases a more negative entropy. This follows from the fact that the k_2 path has more degrees of freedom than the k_{-1} path.

The steric hindrance of the $C_2(C_6H_5)_2$ molecule, also, plays probably a not negligible role in determining the path of the reaction. In fact there is the possibility that the diphenylacetylene cannot attack (*i.e.*, SN2 mechanism) the complex directly because of its steric hindrance. Thus (5) could be more favored (if $C_2(C_6H_5)_2$ approaches the Ni atoms from the side opposite to that in which are the bridging CO's) and (7) could be more favored (if $C_2(C_6H_5)_2$ coordinates to the Ni without CO) than mechanisms (6) and, especially, (8) (the size of the σ-Cp group and/or of the bridging CO still bonded to the coordinating Ni atom would make the diphenylacetylene coordination more difficult).

At this point there is no definitive evidence of any of the proposed mechanisms. Even if the previous considerations should favor mechanism 5, this conclusion must remain tentative until the mechanism is more firmly established.

---

[16] H. G. Schuster-Woldan and F. Basolo, *J. Amer. Chem. Soc.*, **88**, 1657 (1966).

[17] R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

[18] G. Cetini, P. L. Stanghellini, R. Rossetti, and O. Gambino, *Inorg. Chim. Acta*, **4**, 433 (1968).

[19] The possibility that the reaction with monodentate ligands can be a reversible, first-order formation of a reactive intermediate followed by the attack of the ligand should not be excluded. It is necessary that the reverse step is much faster so a limiting rate is not reached at the ligand concentration used; the high value of ΔH_3^* is consistent with this mechanism. In this case, however, two different first-order determining steps for the two reactions must be proposed, because the limiting specific rate value with monodentate ligands should be very much higher than the corresponding value of k_1.

[20] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, pp 549–551.

[21] Yu. A. Ustynyuk, T. I. Voevodskaya, N. A. Zharikova, and N. A. Ustynyuk, *Dokl. Akad. Nauk SSSR*, **181**, 372 (1968).

[22] J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **90**, 6933 (1968).