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Kinetics and Mechanism of the Reactions of Bis(Cyclopentadienyl Carbonyl Nickel) with Alkynes

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The rates of the reaction of $Cp_2Ni_2(CO)_2$ ($Cp = \pi$-cyclopentadienyl) with alkynes are reported. The reaction proceeds by two different mechanisms, a two-stage mechanism, with first-order-rate-determining-step, and a bimolecular associative mechanism.

Either on both may prevail depending on the nature or the bulkiness of the ligand. First order path implies, more probably, the homolytic Ni-Ni fission as rate-determining.

The values of second order rate constant indicate that in coordinating alkyne the π-acceptor capacity is more important than the σ-donor capacity.

Introduction

In the last years a considerable interest has been addressed to the kinetic behaviour of the metal-metal bonded carbonyls, probably in order to discover the extent to which the homolytic fission of the metal-metal bond may provide a rate-determining-step and than to obtain information about the strength and nature of the bond. Therefore, in addition to the previous studies on the reactions of $Co_2(CO)_8$ with ^{14}CO.[1] triphenylphosphine[2] and acetylenes[3] and on the reactions of the acetylene derivatives of the type $Co_2(CO)_6RC_2R'$,[4] there have recently appeared the results of extensive investigation on the rates of the substitution reaction of $Mn_2(CO)_{10}$[5] and $Re_2(CO)_{10}$[6] with different ligands and of the insertion reaction of tin(II) halides into the metal-metal bonds of hexacarbonyl bis(tri-n-butylphosphine)dicobalt[7] and cyclopentadienyliron dicarbonyl dimer.[8]

In particular, the kinetic behaviour of bis(π-cyclopentadienyl carbonyl nickel) in the substitution reactions with monodentate ligands[9,10] and diphenylacetylene[10] and in the insertion with tin(II) halides[11] have been studied extensively. The mechanism of these reactions (except that with diphenylacetylene) is an associative one: it may be due to the presence of the π-cyclopentadienyl ligand, which is able to stabilize the transition state for the associative process, as previously suggested.[12]

On the contrary, the reaction with diphenylacetylene follows a two-stage-mechanism, in which a dissociative step is the rate-determining-step. In the previous work[10] we have proposed that the dissociative step could be: (a) the homolytic cleavage of the Ni-Ni bond; (b) the rupture of an Ni-CO bond; (c) a rapid preequilibrium of $Cp_2Ni_2(CO)_2$ with an isomer form without the bridging CO's, followed by dissociation of a terminal CO; (d) a π to σ rearrangement of a cyclopentadienyl ligand.

In this connection it seems of interest to extend the kinetic study of $Cp_2Ni_2(CO)_2$ to the substitution reaction with different acetylene derivatives, in order to elucidate the mechanism of that reaction and, if possible, to obtain information about the nature of the Ni-Ni bond. Moreover, we can evaluate the factors determining the reactivity of the acetylene derivatives in the reaction with metal carbonyls.

Experimental Section

Compounds and Solvents. Bis(π-cyclopentadienyl carbonyl nickel) was purchased from Alfa Inorganics, dissolved in toluene under nitrogen at room temperature and recrystallised at −20°C.

Diphenylacetylene (Fluka A.G.) was crystallised from n-heptane at −20°C; phenylacetylene (Fluka A.G.), 3-hexyne (K and K Lab.) and dimethyl acetylene dicarboxylate (Aldrich) were distilled at reduced pressure shortly before use. Propiolic acid methyl ester[13] and 1-phenylpropyne[14] were prepared according to the literature. All the reactants were stored in the dark under nitrogen.

The reagent grade n-heptane was used as solvent in all the kinetic experiments. It was refluxed over sodium and distilled in a nitrogen atmosphere.

High purity N_2, CO and CO-Ar mixtures were dried on $CaCl_2$-silica gel columns.

Kinetic Studies. Manipulations were made, as much as possible, under dry nitrogen in a glove-box.

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The reactions with acetylene ligands were allowed to take place in ampoules fitted with rubber caps, as illustrated before.[15] The complex solution was introduced in N_2 atmosphere before sealing and the ligand via the rubber cap by a microsyringe. The ampoules were kept at constant ($\pm 0.1°C$) temperature in the dark. At selected times samples were removed by means of a syringe inserted into the rubber cap, the samples so obtained being rapidly cooled at room temperature. In order to avoid a partial vacuum and introduction of air as a result of removal of aliquots the ampoules were sealed under a slight positive pressure of nitrogen.

The reaction with CO took place in sealed vials, $10 \div 12$ vials being used for each kinetic run. The vials were charged with the reaction mixture and sealed under a known CO or CO-Ar pressure. The volumes of the vial and of the solution and the solubility of CO in n-heptane at room temperature[16] made us able to estimate the concentration of dissolved carbon monoxide. The vials were completely immersed in a thermostat bath for appropriate lengths of time, before being removed, cooled to room temperature and opened for examination.

In all cases the reaction was followed by monitoring the disappearance of the strongest bridging carbonyl band of $Cp_2Ni_2(CO)_2$ at 1859 cm^{-1}. The absorbances of blanks containing ligand and solvent only were subtracted from all measurements. The infrared spectra were recorded by means of an IR 12 Beckman Spectrophotometer with KBr optics.

All the reaction went to completion and the data gave good linear plots of log A_t/A_o vs. time, where A_t is the absorbance at time t and A_o is the absorbance at the beginning of the reaction. Measurements were usually made over a period of about two half-lives. All the kinetic studies were carried out under pseudo-first-order conditions, using a large excess of ligand. In the reactions with CO it was obtained by using a large volume of gas with respect to that of solution, so the partial pressure of CO remained practically constant during the reaction. Duplicate runs carried out under the same condition showed that the values of the pseudo-first-order rate constant were generally reproducible within 5% or better.

Characterization of the Reaction Products. The products of the reactions of bis(cyclopentadienyl carbonyl nickel) with the acetylene ligands were only the derivatives $Cp_2Ni_2RC_2R'$, according to the reaction:

$$Cp_2Ni_2(CO)_2 + RC_2R' \rightarrow Cp_2Ni_2RC_2R' + 2CO \tag{1}$$

These compounds were isolated from the reaction mixtures and compared with the same compounds prepared as described in the literature.[17] In the case of the propiolic acid methyl ester we have isolated, together with the expected $Cp_2Ni_2HC_2COOCH_3$, other still unidentified trinuclear nickel cyclopentadienyl complexes.

It was possible that the CO developed in reaction (1) could react with $Cp_2Ni_2(CO)_2$ to give $Ni(CO)_4$ and $NiCp_2$.[9,10] To prevent this reaction we have used a large volume of gas in the ampoules, so as to minimize the partial pressure of CO. Really, by examining the zone between 2000 and 2100 cm^{-1}, we have found only after two half-lives at least very little traces of the intense CO stretching band of $Ni(CO)_4$ at 2046 cm^{-1}.

Results and Discussion

We have previously reported[10] that the reaction of $Cp_2Ni_2(CO)_2$ with diphenylacetylene follows a two-stage mechanism:

$$Cp_2Ni_2(CO)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cp_2Ni_2(CO)_2^*$$
$$Cp_2Ni_2(CO)_2^* + RC_2R' \xrightarrow{k_2} \text{products} \tag{2}$$

By applying the steady-state condition to the active intermediate $Cp_2Ni_2(CO)_2^*$, the rate of the reaction can be expressed by:

$$\text{rate} = k_{obs}[Cp_2Ni_2(CO)_2] = \frac{k_1k_2[Cp_2Ni_2(CO)_2][RC_2R']}{k_{-1}+k_2[RC_2R']} \tag{3}$$

Thus, at low $[RC_2R']$ values (i.e. $k_{-1} \gg k_2[RC_2R']$), k_{obs} varies linearly with $[RC_2R']$, but at high concentrations (i.e. $k_2[RC_2R'] \gg k_{-1}$) k_{obs} should reach a limiting value k_1.

Rearrangement of eq. (3) gives:

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}\frac{1}{[RC_2R']} \tag{4}$$

and plots of $1/k_{obs}$ vs. $1/[RC_2R']$ are expected to be linear, with y-intercept $1/k_1$ and slope k_{-1}/k_1k_2.

The total pseudo-first-order rate constants $k_{obs}(t)$ for the reaction 1 are reported in Table I. It should be noted that the values of $k_{obs}(t)$ in the cases of 3-hexyne, ethinylbenzene, 1-phenylpropine and propiolic acid methyl ester depend on the ligand concentration, but do no reach a limiting value; besides, at high ligand concentration $k_{obs}(t)$ varies linearly with $[RC_2R']$. That can be clearly seen in Figure 1, in which have been reported the plots of $k_{obs}(t)$ vs. $[C_2H_5C_2C_2H_5]$. So the plots of $1/k_{obs}(t)$ vs. $1/[RC_2R']$ do not show a linear relation-ship, as indicated by eq. (4), but the $1/k_{obs}(t)$ values fall down at low $1/[RC_2R']$ values. Figure 2 illustrates it well.

This behaviour strongly suggests that two mechanisms operate simultaneously in reaction 1: a two-stage mechanism, identical to that suggested for the $C_2(C_6H_5)_2$ reaction (eq. 2) and a bimolecular associative mechanism. Thus, the total rate of reaction can be expressed as:

$$-\frac{d[Cp_2Ni_2(CO)_2]}{dt} = k_{obs}(t)[Cp_2Ni_2(CO)_2] = k_{obs} + k''[Cp_2Ni_2(CO)_2][RC_2R'] \tag{5}$$

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Table I. Rate constants for reaction 1 in n-heptane at 80.0°C.

Alkyne	Alkyne conc., m*M*	$k_{obs}(t)\times 10^5$ sec^{-1}
$C_2H_5C_2C_2H_5$	65.0	4.84
	59.0	4.64
	50.0	4.32
	45.0	3.98
	40.0	3.84
	35.0	3.74
	30.0	3.14
	25.0	3.06
	20.0	2.67
	17.0	2.53
	15.0	2.49[a]
	12.0	2.35
	10.0	2.11
	7.0	2.02[a]
	5.0	1.82[a]
	4.0	1.58[a]
$CH_3C_2C_6H_5$	60.0	5.00
	50.0	4.72
	45.0	4.61
	40.0	4.55
	35.0	4.35
	30.0	4.15
	25.0	3.98
	20.0	3.22
	18.0	3.31
	16.0	2.99[a]
	14.0	2.88
	12.0	2.77
	10.0	2.54
	8.0	2.32
$HC_2C_6H_5$	65.0	7.53
	60.0	7.13
	55.0	6.88
	50.0	6.32
	45.0	6.05
	40.0	5.72
	35.0	5.48
	30.0	5.15
	25.0	4.81
	20.0	4.19
	15.0	3.80[a]
	12.5	3.60
	10.0	3.44[a]
	8.0	3.12
	7.5	3.07[a]
	6.0	2.83
	5.0	2.87[a]
HC_2COOCH_3	50.0	14.0[a]
	45.0	12.8
	40.0	11.7
	35.0	10.95
	30.0	9.27
	25.0	8.53
	20.0	6.76
	15.0	6.00[a]
	12.5	5.58
	10.0	4.84
	7.0	3.92[a]
	5.0	3.41[a]
$COOCH_3C_2COOCH_3$	55.0	89.8
	50.0	80.0
	45.0	73.7
	40.0	62.8
	35.0	56.3[a]
	30.0	45.6
	25.0	39.6
	20.0	30.9
	15.0	23.4
	10.0	16.8

[a] mean of two values.

in which

$$k_{obs}=k_1k_2[RC_2R']/k_{-1}+k_2[RC_2R'])$$

At high ligand concentration the contribution of the two-stage mechanism to the total rate is constant and equal to k_1, so that eq. (5) reduces to eq. (6):

$$k_{obs}(t)=k_1+k''[RC_2R'] \qquad (6)$$

The values of k_1 and k'' have been calculated as intercept and slope of this straight line by means of the least-squares method: only the plots with $[RC_2R']\geqslant 25\div 30\times 10^{-3}$ were used.

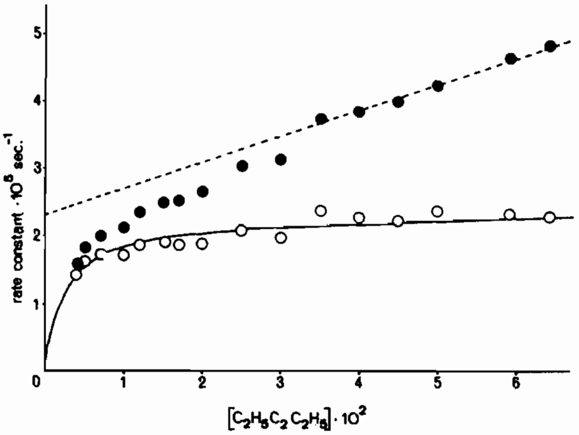

Figure 1. Plot of the observed rate constants vs the concentration of 3-hexyne. Filled circles, $k_{obs}(t)$; open circles, k_{obs}. Solid line and dotted line are calculated from eq. (3) and (6) respectively, with the rate constant values given in Table II.

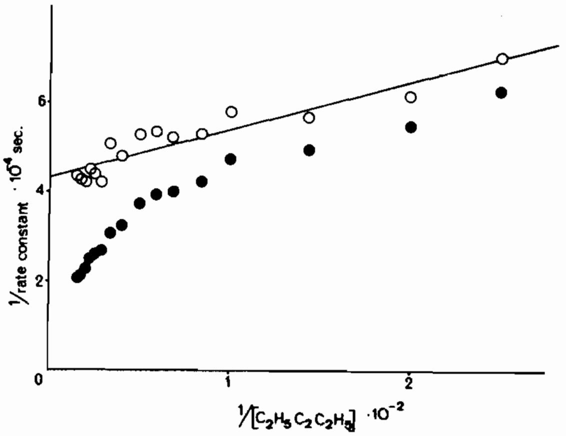

Figure 2. Plot of the reciprocal of the observed rate constants *vs* the reciprocal of the concentration of 3-hexyne. Filled circles, $1/k_{obs}(t)$; open circles, $1/k_{obs}$. Solid line is calculated from eq. (4), with rate constant values given in Table II.

Finally, we have determined the values of k_{obs} at different ligand concentrations by subtracting from $k_{obs}(t)$ the contribution of the bimolecular mechanism, given by $k''[RC_2R']$. Least-squares treatment applied to $1/k_{obs}$ vs. $1/[RC_2R']$ (eq. 4) enabled us to calculate the values of k_2/k_{-1}. The test of the correctness of this treatment is given by the behaviour of k_{obs} vs. $[RC_2R']$ and $1/k_{obs}$ vs. $1/[RC_2R']$, as illustrated in Figure 1 and 2.

Table II. Specific rate constants for reaction (1) in n-heptane at 80.0°C.

Alkyne RC_2R'	$k_1 \times 10^5$ sec^{-1}	$k_2/k_{-1} \times 10^{-2} M^{-1}$	$k'' \times 10^3 M^{-1} sec^{-1}$	$\sigma_R^* + \sigma_{R'}^*$
$C_2H_5C_2C_2H_5$	2.32±0.15	4.0±0.5	0.39±0.03	−0.200
$CH_3C_2C_6H_5$	3.32±0.23	1.4±0.1	0.29±0.05	+0.600
$HC_2C_6H_5$	3.09±0.11	6.2±0.7	0.67±0.02	+1.09
HC_2COOCH_3	2.94±0.50	6.6±2.1	2.21±0.13	+2.49
$COOCH_3C_2COOCH_3$	[a]	[a]	16.3±0.3	+4.00
$C_6H_5C_2C_6H_5$ [b]	2.92±0.12	1.3±0.1	[a]	+1.20

[a] not determined: see text. [b] from ref. 10.

The values of the different specific rate constants are reported in Table II[18]; the errors are the standard deviations.

The reaction between $Cp_2Ni_2(CO)_2$ and $C_2(COOCH_3)_2$ simply follows a second-order-rate-law, first order in both the reactants:

$$rate = k_{obs}(t)[Cp_2Ni_2(CO)_2] = \\ = k''[Cp_2Ni_2(CO)_2][C_2(COOCH_3)_2] \quad (7)$$

Good straight line with near-to-zero intercept is obtained by plotting $k_{obs}(t)$ vs. $[C_2(COOCH_3)_2]$. The second-order rate constant k″, calculated as slope of the line, is also reported in Table II.

It is possible to suppose that the reaction 1 with all the acetylene derivatives follows the same two simultaneous mechanisms: a two-stage mechanism (eq. 2), in which bond breaking in the reactant complex is prevailing, and an additive bimolecular mechanism, in which the formation of a new bond between the complex and the incoming acetylene is more important. In the reaction with diphenylacetylene the second-order mechanism should be regarded as practically inoperative, while with dimethyl acetylene dicarboxylate the high value of k″ should render unimportant the contribution to $k_{obs}(t)$ due to the two-stage mechanism (really, the value of k_1 is within the error of $k''[C_2(COOCH_3)_2]$).

The difference in reactivity of the acetylene derivatives can be rationalized in terms of changes in their σ and π bonding abilities. It is generally held that a metal-acetylene bond consists of two different components: a σ component, which is formed by overlap of an empty metal orbital atom with a π-orbital of the alkyne, and a π-type bond, by overlap of a filled metal orbital with an antibonding π*-molecular orbital of the alkyne.[19] Inclusion of electron withdrawing substituents in the alkyne lowers its antibonding levels: that increases the π-accepting capacity of the ligand and at same time decreases its σ-donor capacity.[19,20]

We have used Taft's polar constants σ*[21] as a measure of the inductive effect of the R and R′ groups in RC_2R' (fifth column in Table II) and we have found a good linear relation-ship between log k″ and $\sigma_R^* + \sigma_{R'}^*$, values (Figure 3). This suggests that the electron withdrawing power of the groups R and R′ is a good measure of the ligand reactivity and implies that the π-acceptor capacity of the alkyne is more important than the σ-donor capacity, so that the alkyne may be act as an electrophilic group in the reaction with $Cp_2Ni_2(CO)_2$. It could be possible that the cyclopentadienyl groups are able to stabilize the transition state of the reaction by concentrating the negative charge on the metal atoms to facilitate the electrophilic attack.

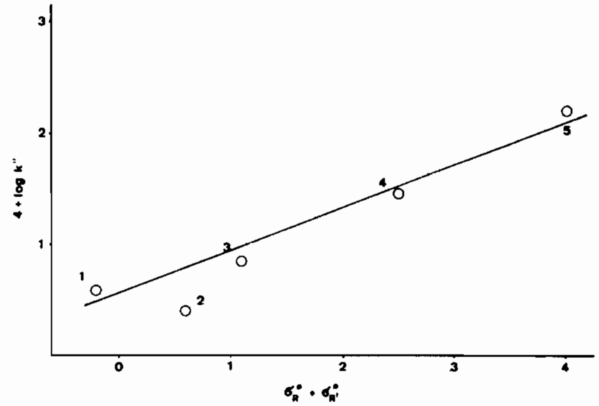

Figure 3. Plot of log k″ *vs* Taft's polar constant values of R and R′ groups. 1, 3-hexyne; 2, 1-phenyl propyne; 3, phenylacetylene; 4, propiolic acid methyl ester; 5, acetylene dicarboxylic acid dimethyl ester.

Diphenylacetylene is an exception in the previous trend (k″ value is zero for $C_2(C_6H_5)_2$, while the electron withdrawing ability of C_6H_5 is greater than those of H or C_2H_5): this is probably due to the steric hindrance of the bulky phenyl group. Taft have reported[21] the steric constant E_s, which is a near-quantitative measure of the net potential- and kinetic-energy steric effects of the group. The values are: H+1.24; $COOCH_3$+0.23 [22]; CH_3 0.00; C_2H_5 −0.07; C_6H_5 −2.55, more negative values indicating increase in steric interation. This may account for the inertness of $C_2(C_6H_5)_2$ to the coordination and, probably, for the smaller than expected value of k″ for $CH_3C_2C_6H_5$.

Four assumptions have been made (see Introduction) to explain the rate-determining-step of the two-stage mechanism in the reaction of bis(cyclopentadienyl carbonyl nickel) with diphenylacetylene.[10] The

(18) The value of k_1 can be calculated by applying both eq. 4 and eq. 6. The two equations give obviously very similar values, differences being due to the approximation in the calculations. The reported value is taken from eq. 6: it results more accurate because of the rather large approximation in the k_{obs} determination.

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(22) Approximate value: see R.W. Taft, *J. Amer. Chem. Soc.*, 74, 2729 and 3120 (1952).
L.P. Hammet, « Phsical Organic Chemistry » McGraw-Hill Ed. New York, N.Y. 1940, pp. 211-213.

nearly constant value of k_1 shows that the same mechanism should operate in the reaction with the other acetylenic ligands. In order to select between the previous hypothesis, it is interesting to examine the values of k_2/k_{-1}. It is logical to suppose that the value of k_{-1}, that measures the rate by which the active intermediate will return to the initial complex, will be the same for all the ligands, so that the relative values of k_2/k_{-1} are the measure of the ability of the alkyne to coordinate to the active intermediate. These values are: H C_2 $COOCH_3$ 5.1; H C_2 C_6H_5 4.8; $C_2(C_2H_5)_2$ 3.1; CH_3 C_2 C_6H_5 1.1; $C_2(C_6H_5)_2$ 1.0. This trend is about the same to that of k″, i.e. the coordinating ability of the alkynes with respect either the complex or the two-stage active intermediate should depend to the same factors. Thus, the probability of the mechanisms (b) and (d), in particular, should be very low because either a rupture of Ni-CO bond or a Cp $\pi \rightarrow \sigma$ conversion[23] would leave vacant orbitals on an Ni atom and facilitate nucleophilic instead of electrophilic attack.

Furthermore, diphenylacetylene coordinates much easier to the active intermediate than to the complex: it could mean that the active intermediate will have such a structure to minimize the steric repulsion with the incoming ligand. That occurs more probably in both the cases (a) and (c), while the two other hypothesis give active intermediates, in which the steric interference with the ligand should not be considerably changed.

Finally, to consider in particular the probability of the mechanism (c), we have studied the reaction of bis(cyclopentadienyl-carbonyl nickel) and carbon monoxide in n-heptane and the same reaction in a 50.0 mM n-heptane solution of diphenyl-acetylene, with such a ligand concentration that a contribution of the diphenylacetylene on the reaction rate will be constant and equal to k_1.[10] The results are given in Table III.

Table III. Observed rate constants for the reaction of $Cp_2Ni_2(CO)_2$ with CO and $C_2(C_6H_5)_2$ in n-heptane at 80.0°C.

CO conc., m*M*	$C_2(C_6H_5)_2$ conc., m*M*	$k_{obs}(t) \times 10^5$ sec^{-1}
—	50.0	2.80[a]
—	50.0	2.33[a]
—	50.0	2.38[a]
—	50.0	2.54[a]
0.113	—	6.46
0.099	—	5.66
0.085	—	4.78
0.082	—	4.83
0.063	—	3.51
0.044	—	2.72
0.112	50.0	8.36
0.106	50.0	8.48
0.096	50.0	7.94
0.087	50.0	7.39
0.072	50.0	6.43
0.062	50.0	5.80
0.061	50.0	5.56
0.052	50.0	5.17
0.045	50.0	5.10

[a] average value $2.54 \pm 0.22 \times 10^{-5}$ sec^{-1}.

It has been previously reported[9,10] that the reaction between $Cp_2Ni_2(CO)_2$ and CO follows a second-order rate law, first order in $Cp_2Ni_2(CO)_2$ and first order in CO:

$$\text{rate} = \varkappa_2[Cp_2Ni_2(CO)_2][CO] \qquad (8)$$

in which $\varkappa_2$ is the second-order rate constant. The total reaction rate of bis(cyclopentadienyl carbonyl nickel) with carbon monoxide and diphenylacetylene together can be expressed as:

$$\text{total rate} = k_{obs}(t)[Cp_2Ni_2(CO)_2] = (k_{obs} + \varkappa_2[CO])[Cp_2Ni_2(CO)_2] \qquad (9)$$

The test of the validity of the mechanism (a) is the plot of $k_{obs}(t)$ vs. [CO]: this plot should be a straight line with intercept $k_{obs} = k_1$ and slope $\varkappa_2$. If the mechanism (c) is operative, the reaction with diphenylacetylene should be inhibited by carbon monoxide and k_{obs} should dipend on [CO] and decreases by increasing the CO concentration. So the plots of $k_{obs}(t)$ vs. [CO] give a curve, which at high CO concentration transforms in a straight line with intercept zero.[26] Figure 4 reports the values from the Table III and clearly illustrates that the former hypothesis is valid. That is confirmed by the values of the specific rate constants: k_1 (from eq. 9) $2.38 \pm 0.24 \times 10^{-5}$ sec^{-1}; $\varkappa_2$ (from eq. 8) 0.561 ± 0.025 M^{-1} sec^{-1}; $\varkappa_2$ (from eq. 9) 0.561 ± 0.030 M^{-1} sec^{-1}.[27]

The failure of the mechanism (c) is in agreement with the recent infrared study of $Cp_2Ni_2(CO)_2$, which confirms that in the solid state or in solution only one species of $Cp_2Ni_2(CO)_2$ is present with both CO's bridging.[28]

(23) The possibility of a cyclopentadienyl π to σ rearrangement have been proposed by analogy with the kinetic mechanism postulated for the $NiCp_2$ reactions with phosphine[24] and mercaptans.[25] The same conclusions, however, can be drawn in the hypothesis of analogous rearrangements, e.g. a π - cyclopentadienyl conversion to monoolefin or to allylic group.

(24) Yu A. Ustynyuk, T.I. Voevodskava, N.A. Zharikova, and N.A. Ustynyuk, *Dokl. Akad. Nauk., SSSR 181*, 372 (1968).

(25) P.C. Ellgen and C.D. Gregory, *Inorg. Chem.*, *10*, 980 (1971).

(26) Mechanism (c) can be expressed by:

$$Cp_2Ni_2(CO)_2 \overset{K_e}{\rightleftarrows} Cp(CO)NiNi(CO)Cp$$

$$Cp(CO)NiNi(CO)Cp \underset{k_{-1}}{\overset{k'_1}{\rightleftarrows}} Cp(CO)NiNiCp^* + CO$$

$$Cp(CO)NiNiCp^* + RC_2R' \xrightarrow{k_2} \text{products.}$$

By applying the steady-state condition to the intermediate Cp(CO)NiNiCp, it can be obtained ($k'_1 k_e = k_1$)

$$\text{rate} = k_{obs}[Cp_2Ni_2(CO)_2] = \frac{k_1[Cp_2Ni_2(CO)_2][RC_2R']}{k_{-1}[CO] + k_2[RC_2R']}$$

At constant value of $[RC_2R']$ k_{obs} is:

$$k_{obs} = \frac{\text{const.}}{[CO] + \text{const}'.}$$

At high CO concentration k_{obs} becomes neardy zero and ep. 9 will trasform in eq. 8.

(27) The values of the CO concentrations and of the specific rate constant χ_2 have been calculated by assuming that the solubility of carbon monoxide in n-heptane at 80.0°C and at 1.00 CO atm. is 2.0 mM. Because this value have been obtained by extrapolation of the previously reported data at lower temperatures,[10] the measure of [CO] and of χ_2 can be not highly accurate. It is unimportant in this case because the aim of the experiment is only to compare the behaviour of k_{obs} (t) *vs* [CO] in the CO reaction of $Cp_2Ni_2(CO)_2$ with- and without diphenylacetylene.

(28) P. McArdle and A.R. Manning, *J. Chem. Soc.*, 717 (1971).