(1600 cm^{-1}) and CH_2 rocking (800 cm^{-1}) regions.[8,9] This was expected since Bauer[1] did not observe cis–trans isomerism of similar $[Ir(en)_2X_2]^{n+}$ complexes under any conditions and since the ligand transformation is believed to take place without Ir–N bond rupture. The ultraviolet spectrum exhibits a broad shoulder at 325 nm (ϵ 35) and a band at 225 nm (ϵ 390).

Acknowledgment.—This research was supported by a grant from the National Science Foundation. We wish to thank Dr. J. W. McDonald for helpful discussions. The iridium used was loaned to us by the Matthey Bishop Co.

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Kinetics and Mechanism of the Reaction of Di-μ-carbonyl-bis(cyclopentadienyl)dinickel with Alkynes

BY PAUL C. ELLGEN

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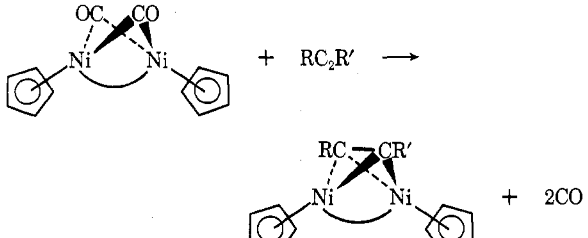
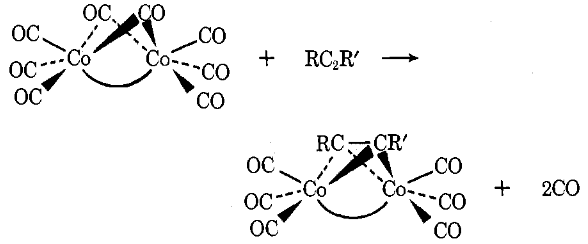
At least in the solid state, the complexes $Co_2(CO)_8$ and $Ni_2(CO)_2(C_5H_5)_2$ are structurally analogous,[1,2] each having a metal–metal bond and two bridging carbon monoxide ligands. Moreover, each reacts with alkynes[3,4] to displace the bridging carbon monoxid-groups and give products whose structural similarity parallels that of the original metal carbonyls.[2,5] Equations 1 and 2 attempt to display these parallels.



(1)



(2)

On the basis of an elegant analysis of rate data for (2), Tirpak and coworkers[6] originally proposed the mechanism shown as eq 3 for this reaction.

$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_8{}^* \quad (3a)$$

$$Co_2(CO)_8{}^* + RC_2R' \rightleftharpoons Co_2(CO)_7RC_2R' + CO \quad (3b)$$

$$Co_2(CO)_7RC_2R' \longrightarrow Co_2(CO)_6RC_2R' + CO \quad (3c)$$

Recently, Cetini and coworkers[7] have reported that reaction 1 follows rate law 4 (for R = R′ = C_6H_5).

$$-d[Ni_2(CO)_2(C_5H_5)_2]/dt = k_{obsd}[Ni_2(CO)_2(C_5H_5)_2] \quad (4a)$$

$$k_{obsd} = \frac{k_1k_2[C_2(C_6H_5)_2]}{k_{-1} + k_2[C_2(C_6H_5)_2]} \quad (4b)$$

From this rate law, the mechanism shown as eq 5 was

$$Ni_2(CO)_2(C_5H_5)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni_2(CO)_2(C_5H_5)_2{}^* \quad (5a)$$

$$Ni_2(CO)_2(C_5H_5)_2{}^* + C_2(C_6H_5)_2 \xrightarrow{k_2} Ni_2(C_2(C_6H_5)_2)(C_5H_5)_2 + 2CO \quad (5b)$$

inferred. In these proposed mechanisms, the symbols "$Ni_2(CO)_2(C_5H_5)_2{}^*$" and "$Co_2(CO_8{}^*$" represent reactive isomers present at concentrations sufficiently low to be well approximated by a steady-state treatment.

Both of these reactions have been intensively studied in this laboratory. Reinvestigation of reaction 2 has established that the mechanism of eq 3 is incorrect. Instead, the stoichiometric mechanism depicted by eq 6 now appears to be securely established.[8] It should be noted that the original kinetic study of (2) was carried out at constant carbon monoxide pressure.[6] Under these conditions, the mechanisms of eq 6 and eq 3 are

$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO \quad (6a)$$

$$Co_2(CO)_7 + RC_2R' \rightleftharpoons Co_2(CO)_7RC_2R' \quad (6b)$$

$$Co_2(CO)_7RC_2R' \longrightarrow Co_2(CO)_6RC_2R' + CO \quad (6c)$$

kinetically equivalent.

It is the purpose of this paper to point out that rate law 4 proposed for reaction 1 is incorrect. Cetini and coworkers monitored the disappearance of the 1855-cm^{-1} ir band of $Ni_2(CO)_2(C_5H_5)_2$ in the presence of large excesses of diphenylacetylene and calculated pseudo-first-order rate constants for this decay. Figure 1 presents their reported values for the pseudo-first-order rate constants plotted against the diphenylacetylene concentration for experiments done at 80° in heptane solution. The dashed line in this plot is the best fit to these data afforded by rate law 4. The salient feature of this rate law is the prediction that the pseudo-first-order rate constant becomes essentially independent of the diphenylacetylene concentration when the latter exceeds 5.0×10^{-2} *M*. Since this contradicts unreported observations previously made in these laboratories, a brief reinvestigation of (1) under the conditions used by Cetini has been undertaken.

Pseudo-first-order rate constants calculated for the disappearance of $Ni_2(CO)_2(C_5H_5)_2$ do not approach a constant value at high concentrations of diphenylacetylene. (See Table I.) At $[C_2(C_6H_5)_2]$ = 0.50 *M* and 80°, the pseudo-first-order rate constant observed is almost 6 times that expected from (4) and the data of ref 7. It is concluded that rate law 4 is incorrect and that the fit afforded by the dashed line in Figure 1 is accidental.

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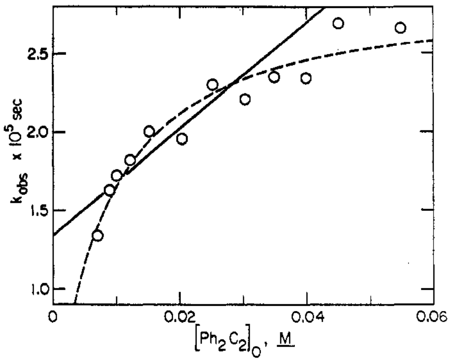

Figure 1.—Pseudo-first-order rate constant for disappearance of $Ni_2(CO)_2(C_5H_5)_2$ plotted *vs.* concentration of diphenylacetylene. Data from ref 7. The dashed line is the best fit of these data to the rate law of eq 4 computed from the rate constants given in ref 7. The solid line is the least-squares fit of all of the 80° data in Table I and ref 7 to eq 9 ($k_d = 1.3 \times 10^{-5}$ sec^{-1}; $k_r = 3.4 \times 10^{-4}$ M^{-1} sec^{-1}).

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS CALCULATED FOR THE DISAPPEARANCE OF THE 1855-CM^{-1} BAND OF $Ni_2(CO)_2(C_5H_5)_2$

$10^3[Ni_2(CO)_2(C_5H_5)_2]_0$, M^{-1}	$[C_2(C_6H_5)_2]_0$, M	$10^5 k_{obsd}$, sec
2.7	0.00	0.45[a]
2.3	0.204	9.0[b]
2.8	0.206	8.2[a]
2.9	0.346	13.3[a]
2.1	0.352	12.4[b]
2.9	0.500	16.6[b]
2.4	0.503	14.8[a]

[a] Aliquots in tubes which were fused shut under nitrogen. [b] Aliquots in tubes which were sealed with rubber serum caps.

Study of the kinetics of (1) is attended by a number of acute difficulties. The first of these is that the reaction takes place at a convenient rate only at temperatures which are sufficiently high that the decomposition of $Ni_2(CO)_2(C_5H_5)_2$ is difficult to avoid. Even with extreme measures to exclude oxygen from reaction solutions, the decomposition of $Ni_2(CO)_2(C_5H_5)_2$ (presumably[9] according to eq 7) takes place at a rate which is nonnegligible in comparison to the rate of (1). (See Table I.)

$$4Ni_2(CO)_2(C_5H_5)_2 \longrightarrow 2Ni_3(CO)_2(C_5H_5)_3 + Ni(CO_4) + Ni(C_5H_5)_2 \quad (7)$$

A second serious difficulty arises from the fact that reaction 1 liberates 2 mol of carbon monoxide for each mole of $Ni_2(CO)_2(C_5H_5)_2$ consumed by reaction with alkyne. The carbon monoxide thus produced reacts readily with $Ni_2(CO)_2(C_5H_5)_2$ according to eq 8 (with

$$Ni_2(CO)_2(C_5H_5)_2 + 2L \longrightarrow Ni(CO)_2L_2 + Ni(C_5H_5)_2 \quad (8)$$

L = CO).[10] The ir spectra of reaction mixtures invariably develop a prominent peak at 2057 cm^{-1} due to the $Ni(CO)_4$ produced. Clearly, a thorough study of the kinetics of reaction 1 must include a quantitative allowance for the occurrence of reaction 8.

A third source of difficulty is the decomposition of $Ni(CO)_4$ produced *via* (8) to nickel metal and carbon monoxide. Although the extent of this decomposition appears small in the rate experiments reported here, it must be anticipated that the decomposition rate will be very difficult to reproduce[11] under these reaction conditions. When it occurs, this decomposition provides an additional source of free carbon monoxide and leads to increased loss of substrate *via* (8).

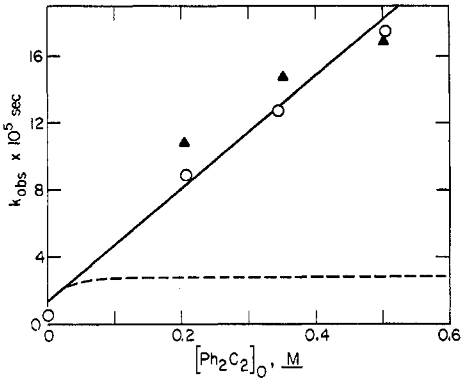

Figure 2.—Pseudo-first-order rate constants for disappearance of $Ni_2(CO)_2(C_5H_5)_2$ plotted *vs.* concentration of diphenylacetylene. Data from Table I. The dashed and solid lines have the same significance as in Figure 1.

Cetini and coworkers also reported kinetic data for reaction 8 with L = CO, $PCl(C_6H_5)_2$, $P(C_6H_5)_3$, and $P(n\text{-}C_4H_9)_3$. In general these results are in good agreement with those reported[10] earlier from this laboratory for this reaction. Although there is reason to believe that the mechanism for (8) may be quite complex,[10] the initial step in the reaction of monodentate ligands with $Ni_2(CO)_2(C_5H_5)$ is most simply assumed to be a direct attack of the incoming ligand on the bridged form of $Ni_2(CO)_2(C_5H_5)_2$. In view of the results reported here, there is no reason to assume that the initial step in the reaction of diphenylacetylene with $Ni_2(CO)_2(C_5H_5)_2$ is of a fundamentally different character.

These considerations suggest that the dependence on the diphenylacetylene concentration of the pseudo-first-order rate constant for disappearance of $Ni_2(CO)_2(C_5H_5)_2$ is probably best summarized by an equation of the form (9). The k_d term is the rate constant for

$$k_{obsd} = k_d + k_r[C_2(C_6H_5)_2] \quad (9)$$

$Ni_2(CO)_2(C_5H_5)_2$ decomposition in the absence of alkyne, and the k_r term is most simply interpreted as twice the second-order rate constant for attack of diphenylacetylene on $Ni_2(CO)_2(C_5H_5)_2$. This interpretation would assume that the carbon monoxide liberated by (1) reacts rapidly and quantitatively with $Ni_2(CO)_2(C_5H_5)_2$ according to (8). The solid lines in Figures 1 and 2 are the least-squares fit of eq 9 to all of the 80° data reported in Table I and in Cetini's report.

Experimental Section

Materials.—$Ni_2(CO)_2(C_5H_5)_2$ was prepared as previously described.[10] Diphenylacetylene (Farchan Research Laboratories) and heptane ("Analytical Reagent" grade from Mallinckrodt Chemical Works) were used as received.

Kinetic Runs.—Solutions for kinetic runs were prepared by dissolving weighed quantities of each reagent in a known volume of heptane. These solutions were then deoxygenated by three freeze–thaw cycles and aliquots apportioned among 10–12 7 × 130 mm Pyrex tubes. This transfer was effected with a syringe and stainless steel needle under an atmosphere of nitrogen. In some cases these tubes were sealed with rubber serum caps

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secured by twists of copper wire. In other cases (see Table I and Figure 2), the aliquots were individually subjected to an additional freeze–thaw cycle before the tubes were fused shut under an atmosphere of nitrogen. The sealed tubes were then placed in an 80° bath for known periods of time. Upon removal from the 80° bath, the tubes were stored at −78°. Infrared spectra over the region 2100–1800 cm^{-1} were recorded for all of the samples of a given run at the same time.

For reasons set forth in the discussion, the kinetic data collected cannot be said to be of high quality. However, plots of ln $(A - A_\infty)$ *vs.* time were approximately linear for 2–3 half-lives. (In all cases, the 1855-cm^{-1} band of $Ni_2(CO)_2(C_5H_5)_2$ was used to monitor the extent of substrate consumption. It should be noted that diphenylacetylene absorbs weakly at this frequency so that A_∞ was not zero for the kinetic runs reported here.)

The reported pseudo-first-order rate constants and the fit to eq 9 were obtained from standard least-squares analyses.

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Stereochemistry of the Mercury-Catalyzed Aquation of *cis*-$[Ru(en)_2Cl_2]^+$

BY L. A. P. KANE-MAGUIRE[1]

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There has been considerable interest recently in the mechanism of the Hg^{2+}-catalyzed aquation reactions of chloro(amine)cobalt(III) complexes. Posey and Taube[2] have shown these reactions to be SN1(lim) in character, while stereochemical studies[3-5] have indicated that they generally involve intermediates different in geometry from those encountered in the uncatalyzed aquations. Thus, the Hg^{2+}-induced aquation of D-$[Co(en)_2Cl_2]^+$ yielded a mixture of 70% D-$[Co(en)_2(H_2O)Cl]^{2+}$ and 30% *trans*-$[Co(en)_2(H_2O)Cl]^{2+}$, compared with the complete retention observed in the spontaneous reaction.[3] Both square-pyramidal[5] and trigonal-bipyramidal[3] geometries have been inferred for the five-coordinate intermediates. However, except for a kinetic study of the Hg^{2+}-catalyzed aquation of $[Rh(NH_3)_5Cl]^{2+}$ in mixed solvents,[6] no studies have been made of the corresponding reactions of the complexes of the second- and third-row transition elements. This paper reports the stereochemical results of the Hg^{2+}-catalyzed aquation of *cis*-$[Ru(en)_2Cl_2]^+$ and compares these with previous data[7] for the spontaneous aquation.

Experimental Section

Materials.—*cis*-$[Ru(en)_2Cl_2]Cl \cdot H_2O$ and D(−)-$[Ru(en)_2Cl_2]I$ were prepared by published methods.[8] All other reagents were analytical grade.

Geometrical Retention Experiment.—Fresh solutions of *cis*-$[Ru(en)_2Cl_2]Cl \cdot H_2O$ and $Hg(NO_3)_2$ in 0.2 *M* H_2SO_4 were mixed to give the final concentrations $[Ru^{3+}] = 7.5 \times 10^{-4}$ *M* and $[Hg^{2+}] = 1.5 \times 10^{-3}$ *M*. The uv–vis spectrum of the solution was measured periodically on a Cary 14 spectrophotometer. After 30 min, concentrated HCl was added to give a final [HCl] = 2.5 *M*. The uv–vis spectrum was then recorded periodically for 24 hr to observe the regeneration of $[Ru(en)_2Cl_2]^+$.

Optical Retention Experiment.—The ord spectrum of D(−)-$[Ru(en)_2Cl_2]I$ (8.2×10^{-4} *M*) in 0.2 *M* H_2SO_4 was recorded using a Cary ORD/CD instrument. A fresh solution of $Hg(NO_3)_2$ in 0.2 *M* H_2SO_4 was added to give the final concentration $[Ru^{3+}] = 6.6 \times 10^{-4}$ *M* and $[Hg^{2+}] = 1.3 \times 10^{-3}$ *M*. After 30 min concentrated HCl was added (2 *M*) and the ord spectrum was recorded after a further 4 hr (Table I).

TABLE I
COMPARISON OF THEORETICAL AND REGENERATED SPECIFIC ROTATIONS AT ROTATIONAL MAXIMA

Wavelength, nm	[α] of pure D(−)-$[Ru(en)_2Cl_2]^+$	[α] regenerated by addition of HCl to aquated soln
368	−1590 ± 50	−1640 ± 50
333	+250	+150
307	+1350	+1280
280	−1620	−1530

Results and Discussion

Addition of Hg^{2+} to an acidic solution of *cis*-$[Ru(en)_2Cl_2]^+$ caused the uv–vis spectrum to change rapidly over 10 min to that of *cis*-$[Ru(en)_2(H_2O)Cl]^{2+}$ (ϵ_{329} 1650). This peak at 329 nm then slowly decreased, probably due to conversion to *cis*-$[Ru(en)_2(H_2O)_2]^{3+}$. The addition of excess HCl at this stage regenerated the calculated uv–vis spectrum of *cis*-$[Ru(en)_2Cl_2]^+$ within 24 hr. No evidence was found for the presence of the trans isomer.

The rapid production of *cis*-$[Ru(en)_2(H_2O)Cl]^{2+}$ *via* the Hg^{2+}-induced aquation of *cis*-$[Ru(en)_2Cl_2]^+$ was also evident from the ord studies. Thus, the ord spectrum had changed after 15 min to a curve with rotational maxima at 340, 303, and 260 nm ([α] = −550, +670, −970, respectively). The optical retention experiment (Table I) therefore shows that, within experimental error, the reaction sequence

$$cis\text{-}[Ru(en)_2Cl_2]^+ + Hg^{2+} + H_2O \longrightarrow [Ru(en)_2(H_2O)Cl]^{2+} + HgCl^+$$

$$[Ru(en)_2(H_2O)Cl]^{2+} + HCl \longrightarrow [Ru(en)_2Cl_2]^+$$

occurs with overall retention of geometric and optical configuration. This is most readily interpreted in terms of complete retention in each step.

A previous study[7] has shown that the spontaneous aquation of *cis*-$[Ru(en)_2Cl_2]^+$ also occurs with retention of geometric and optical configuration. The similar stereochemical course of the aquation in the presence and absence of Hg^{2+} is further confirmed by the observation of the same isosbestic points (341 and 317 nm) in both cases. However, identical mechanisms are unlikely since the earlier kinetic studies[7] suggest an SN2 mechanism for the spontaneous aquation of *cis*-$[Ru(en)_2Cl_2]^+$. This seems very improbable in the presence of Hg^{2+}, and the retention of configuration observed here is best explained in terms of an SN1 mechanism involving a square-pyramidal intermediate. It is inconsistent with a trigonal-bipyramidal interme-

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