

Figure 1. Plot of  $(a-x)/(dx/dt)$  vs.  $1/(a-x)$  for  $\text{Si}(\text{OCH}_3)_4$  vs.  $\text{SiCl}_4$  exchange at  $38^\circ$ .

constants reported at  $72$  and  $100^\circ$  times  $1/[\text{HCl}]$ . The value of the third-order rate constant at  $38^\circ$ , calculated from the plot in Figure 1, is  $2.6 \pm 0.3 \times 10^{-3} \text{ l.}^2/\text{mole}^2 \text{ sec}$ .

A possible role for the second molecule of methyl silicate is that of solvating agent for any charge separation occurring in the  $k_3$  transition state. This hypothesis suggested an experiment in which a more polar solvent than carbon tetrachloride would be used. A sufficiently polar solvent would compete with the  $\text{Si}(\text{OCH}_3)_4$  as solvating agent, causing the reaction to become first order in methyl silicate. The exchange was carried out in benzonitrile at  $38^\circ$  and found to be

first order in methyl silicate while still zero order in silicon tetrachloride. A pseudo-first-order rate constant of  $5.3 \pm 0.4 \times 10^{-5} \text{ sec}^{-1}$  was obtained. A second-order rate constant could not be calculated since the  $[\text{HCl}]$  was not determined.

Because of the complexity of first exchange in the  $\text{Si}(\text{OCH}_3)_4$  vs.  $\text{SiCl}_4$  reaction, it was of interest to determine if the same type of mechanism would be operative in the subsequent, much slower, steps of the equilibration. To this end a sample<sup>13</sup> of  $(\text{CH}_3\text{O})_3\text{SiCl}$  was prepared by equilibrating<sup>14</sup> the appropriate mixture of methyl silicate and silicon tetrachloride at  $120^\circ$  for 200 hr. Initial rate measurements for the exchange between  $\text{Si}(\text{OCH}_3)_3\text{Cl}$  and  $\text{SiCl}_4$  at  $100^\circ$  in carbon tetrachloride to give  $\text{Si}(\text{OCH}_3)_2\text{Cl}_2$  and  $\text{Si}(\text{OCH}_3)\text{Cl}_3$  showed the reaction to be of the same form as the  $\text{Si}(\text{OCH}_3)_4$  vs.  $\text{SiCl}_4$  exchange, that is, zero order in  $\text{SiCl}_4$  and second order in  $\text{Si}(\text{OCH}_3)_3\text{Cl}$ . A third-order rate constant of  $1.8 \pm 0.2 \times 10^{-5} \text{ l.}^2/\text{mole}^2 \text{ sec}$  was calculated.

### Conclusion

While it appears likely that mechanisms involving four-center transition states will be common in scrambling chemistry it is not yet possible to predict the mechanism, or more precisely the form of the rate law, on an *a priori* basis.

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(13) This sample obtained by equilibration contained 84%  $\text{Si}(\text{OCH}_3)_3\text{Cl}$ , 9.7%  $\text{Si}(\text{OCH}_3)_4$ , and 6.3%  $(\text{CH}_3\text{O})_2\text{SiCl}_2$ ; therefore, it was necessary to make a correction for the  $\text{Si}(\text{OCH}_3)_4$  vs.  $\text{SiCl}_4$  reaction. An attempt to enrich the mixture in  $\text{Si}(\text{OCH}_3)_3\text{Cl}$  by distillation through a Vigreux column of one or two theoretical plates failed to show any noticeable change in concentration.

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## Carbon Monoxide Exchange with Some Metal–Metal Bonded Metal Carbonyls

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**Abstract:** Investigations on the kinetics of  $^{14}\text{CO}$  exchange with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  in solution are reported. The results show that all CO's exchange at the same rate, that the rate of exchange is first order, and that it is only slightly affected by the nature of the solvent. It is suggested that the mechanism for exchange perhaps involves an insertion (or ligand migration) reaction. The replacement of CO by phosphines gave complicated results that are not understood. Studied in less detail was the exchange of  $^{14}\text{CO}$  with the compounds  $\text{Cd}[\text{Co}(\text{CO})_4]_2$ ,  $(\text{CH}_3)_3\text{SnCo}(\text{CO})_4$ ,  $(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$ ,  $\text{CH}_3\text{COCO}(\text{CO})_4$ ,  $(\text{C}_6\text{H}_5)_3\text{PAuCo}(\text{CO})_4$ , and  $(\text{C}_6\text{H}_5)_3\text{PAuMn}(\text{CO})_5$ .

Investigations of the exchange of carbon monoxide with simple metal carbonyls containing metal–metal bonds are limited to the compounds  $\text{Co}_2(\text{CO})_8$ <sup>1</sup> and  $\text{Mn}_2(\text{CO})_{10}$ .<sup>2</sup> The cobalt compound undergoes rapid

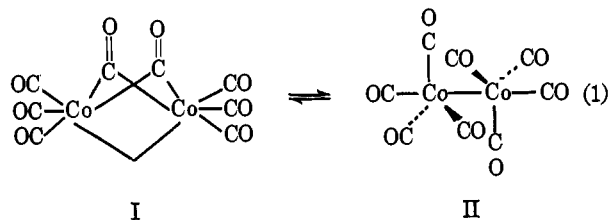
exchange with  $^{14}\text{CO}$ , whereas at room temperature in benzene solution the manganese compound exchanges with an estimated half-life greater than 10 years. A kinetic study shows that for  $\text{Co}_2(\text{CO})_8$  the rate of exchange is first order and all eight CO's exchange at the same rate. On this basis it was suggested<sup>1</sup> that the rapid rate of exchange was due to the bridged structure

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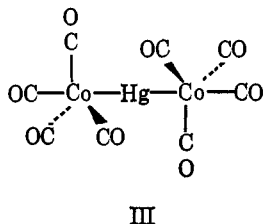
(I) of the carbonyl, and that the rate of exchange was the rate of opening of a carbonyl bridge.

However, subsequent studies by Noack<sup>3</sup> of the infrared spectra of a solution of  $\text{Co}_2(\text{CO})_8$  show that two species I and II in eq 1 exist in solution in rapid equilibrium. This introduces an alternative possibility for the



mechanism of CO exchange with  $\text{Co}_2(\text{CO})_8$ , namely one involving species II. In such a case it is of interest that the exchange of  $\text{Co}_2(\text{CO})_8$  is rapid, because structure II, except for the metal having a lower coordination number, is analogous with  $\text{Mn}_2(\text{CO})_{10}$  which does not exchange.

An indirect approach to obtaining some insight as to whether or not structure II can undergo rapid exchange is to examine the compound  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . The structure<sup>4</sup> (III) of this compound corresponds closely to



that of II. This paper reports the results of kinetic studies on the  $^{14}\text{C}$ O exchange with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and some of its related compounds, as well as some observations on substitution reactions.

## Experimental Section

**Compounds and Solvents.** The compounds  $\text{Co}_2(\text{CO})_8$  and  $\text{Mn}_2(\text{CO})_{10}$  were purchased from Alpha Inorganics, Inc., Beverly, Mass., and were purified by sublimation.  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ,<sup>6</sup>  $\text{Cd}[\text{Co}(\text{CO})_4]_2$ ,<sup>6</sup>  $(\text{C}_6\text{H}_5)_3\text{PAuCo}(\text{CO})_4$ ,<sup>6</sup>  $\text{CH}_3\text{COC}(\text{CO})_4$ ,<sup>7</sup> and  $(\text{C}_6\text{H}_5)_3\text{PAuMn}(\text{CO})_5$ <sup>6</sup> were prepared by the methods described in the literature. The compounds were purified and then characterized by comparing the infrared spectra with those reported.

$(\text{CH}_3)_3\text{SnCo}(\text{CO})_4$  and  $(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$  had not been previously reported and were prepared as follows. Both compounds were prepared under an atmosphere of nitrogen. The methyl compound was prepared by the reaction of 523 mg (2.7 mmoles) of  $\text{NaCo}(\text{CO})_4$  with 500 mg (2.5 mmoles) of  $(\text{CH}_3)_3\text{SnCl}$  in 30 ml of diethyl ether at room temperature for ca. 5 min. The ether was then evaporated and the residue was extracted with hexane. The filtered solution was again evaporated to remove the hexane, and the residue was readily sublimed at 40°. Because of the high vapor pressure of the compound, it was necessary to surround the upper part of the sublimation vessel with Dry Ice. A good yield of pale yellow needles was obtained. The compound is air sensitive, but under nitrogen it melts (74.5°) without decomposition. *Anal.* Calcd for  $(\text{CH}_3)_3\text{SnCo}(\text{CO})_4$ : C, 25.11; H, 2.71. Found: C,

24.77; H, 2.68. The infrared spectrum in the C–O stretching region in hexane shows 2085 s, 2024 s, 1992 vs, and 1957 w  $\text{cm}^{-1}$ .

The analogous phenyl compound was prepared by the addition of 2.0 g (5.2 mmoles) of  $(\text{C}_6\text{H}_5)_3\text{SnCl}$  to 50 ml of a tetrahydrofuran solution containing 2.6 g (13 mmoles) of  $\text{NaCo}(\text{CO})_4$ . After the mixture was allowed to stand for ca. 30 min at room temperature, 200 ml of water was added to precipitate the desired compound. The precipitate was collected on a filter and then dissolved in benzene. This solution was dried over  $\text{CaCl}_2$  and the benzene was removed by evaporation, yielding a yellow crystalline product which melts at 117–119° under nitrogen. *Anal.* Calcd for  $(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$ : C, 50.72; H, 2.9. Found: C, 51.72; H, 3.36. The infrared spectrum in the C–O stretching region in hexane has bands at 2090 s, 2028 ms, and 2000 vs  $\text{cm}^{-1}$ .

The reagents  $\text{P}(\eta\text{-C}_4\text{H}_9)_3$ ,  $\text{PC}_2\text{H}_5(\text{C}_6\text{H}_5)_2$ ,  $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$ , and  $\text{P}(\eta\text{-C}_4\text{H}_9)(\text{C}_6\text{H}_5)_2$  were prepared by the prescribed methods.<sup>8</sup> Other reagents and solvents were obtained from commercial sources. The solvents were dried, distilled, and kept under nitrogen. The  $^{14}\text{C}$ O (1.0 mcurie, 54.3 cc) purchased from Tracerlab, Inc., was transferred to a 2-l. storage flask, diluted to 1 atm with inactive CO, and used in this form.

**Carbon Monoxide Exchange.** The procedure used to investigate the rates of  $^{14}\text{C}$ O exchange with the metal carbonyls in solution was similar to that described earlier,<sup>1</sup> the chief modification being the apparatus used to monitor the radioactivity of the gas phase. This was done with a 100-cc DCF ion chamber and electrometer system, Dynacon Model 6010, obtained from Nuclear Chicago. The experimental infinite time activities were in good agreement with the calculated values based on the exchange of all the CO molecules in the compound. The only exception to this is the compound  $(\text{C}_6\text{H}_5)_3\text{PAuCo}(\text{CO})_4$  for which it appears that only three CO's undergo exchange readily.

All of the exchange reactions investigated were found to follow the McKay<sup>9</sup> equation and give satisfactory linear plots of  $\log(V_t - V_\infty)$  vs. time where  $V_t$  is the voltage of the gas phase recorded at time  $t$ , and  $V_\infty$  is the voltage at equilibrium. From these plots the half-lives for exchange were determined and used to estimate the values of  $k_{\text{true}}$  by eq 2, where  $t_{1/2}$  is the half-life for exchange,  $a$

$$k_{\text{true}} = \frac{0.69Xa^{1-\alpha}yb^{1-\beta}}{(Xa + by)t_{1/2}} \quad (2)$$

is the concentration of metal carbonyl,  $b$  is the concentration of CO in solution,  $X$  is the number of exchangeable CO's in the metal carbonyl,  $y$  is the ratio of total moles of CO in the enclosed system to the moles of CO in solution,  $\alpha$  represents the order in  $a$  and  $\beta$  the order in  $b$ . If  $\alpha$  equals 1 and  $\beta$  equals 0, then the rate of exchange is first order and the specific rate constant  $k_{\text{true}}$  is designated by  $k_1$  ( $\text{sec}^{-1}$ ); whereas if  $\alpha$  and  $\beta$  each equal 1, then the rate is second order and its constant is represented as  $k_2$  ( $M^{-1} \text{sec}^{-1}$ ) (see Table I).

For all of the solvents except dibutyl ether and  $n$ -hexane, the solubilities of CO were known.<sup>1,10</sup> The metal carbonyls are stable in solution during the exchange studies, except for a slow decomposition of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  in  $\text{CCl}_4$ . The reproducibility of the rate data obtained is satisfactory, but because of the inherent experimental difficulties it was necessary to make several duplicate (or almost duplicate) kinetic runs. The results show that most of the rate constants are reliable to better than 20%.

**Substitution Reactions.** Three different experimental techniques were used in an attempt to investigate the kinetics of substitution reactions of the type represented by eq 3. Unfortunately, it was



only possible to obtain quantitative kinetic data for the reaction of  $\text{CH}_3\text{COC}(\text{CO})_4$  with  $\text{P}(\text{C}_6\text{H}_5)_3$ . The other reactions studied were either too slow or too fast, or gave results that we were unable to treat in the usual manner to obtain meaningful linear log plots of the data.

The methods used were those described previously which involve measuring changes during the reaction as follows: (1) the infrared

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Table I. Rate of  $^{14}\text{CO}$  Exchange with  $\text{Hg}[\text{Co}(\text{CO})_4]_2^a$ 

Temp, °C	Solvent	[Cpd] <sup>b</sup>	[CO] <sub>s</sub> <sup>b</sup>	CO <sub>t</sub> <sup>b</sup>	$10^3 k_1$ , sec <sup>-1c</sup>	$10^3 k_2$ , M <sup>-1</sup> sec <sup>-1c</sup>
-21	Hexane	1.39	...	3.59	0.59	...
-20.5	Toluene	1.71	0.41	0.49	0.32	0.77
-12	CCl <sub>4</sub>	2.54	0.17	0.20	0.52	3.1
-12	CCl <sub>4</sub>	1.09	0.17	0.20	0.57	3.3
-12	Toluene	2.26	0.23	0.28	0.43	1.9
-12	Toluene	2.26	3.4	4.1	0.57	0.16
-12	Toluene	1.24	0.18	0.23	0.61	3.4
-5	CCl <sub>4</sub>	0.99	0.10	0.12	0.93	8.8
-5	CCl <sub>4</sub>	3.36	0.17	0.20	0.90	5.3
-5	Toluene	1.71	0.23	0.28	0.58	2.5
-5	Toluene	1.71	2.0	2.4	0.72	0.36
0	Toluene	2.5	3.3	4.2	2.1	0.62
0	Toluene	2.2	0.35	0.45	3.5	9.9
0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	1.98	...	0.24	2.3	...
0	Hexane	1.71	...	0.25	3.9	...
0	Hexane	1.71	...	4.9	4.8	...
5	Toluene	1.75	0.24	0.27	3.1	13
5	Toluene	1.75	2.8	3.1	4.1	1.4
10	Toluene	2.56	0.22	0.27	2.0	9.4
10	Toluene	2.56	2.9	3.52	4.8	1.6
20	CCl <sub>4</sub>	1.02	0.11	0.13	7.5	69
20	CCl <sub>4</sub>	1.02	0.11	0.13	7.0	64
20	Toluene	9.95	0.47	0.71	6.7	14
20	Toluene	1.51	0.09	0.13	7.1	80
20	Toluene	3.31	0.18	0.27	7.0	38
20	Toluene	3.31	2.5	3.7	8.5	3.4
20	Toluene	2.78	0.16	0.24	7.9	48
20	Toluene	2.78	4.6	6.9	9.2	2.0
20	Hexane	2.78	...	0.26	23	...
20	Hexane	2.78	...	4.2	36	...
20	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	2.68	...	0.26	11 <sup>d</sup>	...
20	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	2.68	...	5.9	15	...

<sup>a</sup> Activation parameters in toluene solution:  $\Delta H^* = 13 \pm 1$  kcal/mole;  $\Delta S^* = -24 \pm 2$  eu. <sup>b</sup> Concentrations mM: [Cpd] =  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ; [CO]<sub>s</sub> = dissolved CO; CO<sub>t</sub> = total CO in millimoles in enclosed system. <sup>c</sup> True first-, ( $k_1$ ) and second-order ( $k_2$ ) rate constants calculated from the observed half-life for exchange by eq 2. Note the large variation in  $k_2$  with changes in concentration of CO, whereas the values of  $k_1$  are reasonably constant supporting a first-order exchange. <sup>d</sup> This same experiment was repeated in the presence of 0.0065 M  $\text{PBu}_3$  and there was no detectable exchange. Also,  $\text{Hg}[\text{Co}(\text{CO})_4\text{PBu}_3]_2$  shows no exchange with  $^{14}\text{CO}$  in 1 hr.

spectra in the C-O stretching region,<sup>11</sup> (2) the visible and/or ultraviolet absorption spectra,<sup>12</sup> and (3) evolution of gaseous CO.<sup>13</sup>

The infrared technique could not be applied to the reaction of either  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  or  $\text{Cd}[\text{Co}(\text{CO})_4]_2$  with phosphines. Upon the addition of phosphine to the solution of metal carbonyl there is an immediate change in spectrum which complicates it such as to make it difficult to follow subsequent changes. This immediate change in spectrum may result from the addition of phosphine to Hg or Cd, forming  $\text{ML}_1$  or  $2[\text{Co}(\text{CO})_4]_2$ <sup>14</sup> which decreases the symmetry of the original substrate and causes splittings of the C-O stretching bonds. The infrared technique, however, was applicable to studies of reactions of compounds containing only one  $\text{Co}(\text{CO})_4$  group such as  $(\text{CH}_3)_3\text{SnCo}(\text{CO})_4$ .

Investigation by means of the visible and/or ultraviolet technique was tried only for reactions of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ , and it was not satisfactory. Again there was observed at different wavelengths a rapid change in spectrum, perhaps due to the formation of an addition compound as described above. This sufficiently complicated the observations that meaningful results were not obtained. The reactions were also light sensitive which further made this method unsatisfactory.

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The method that almost has to give reliable results is that of monitoring the evolution of CO gas. This did in fact work but, unfortunately, the results obtained were not amenable to quantitative treatment for the reactions of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . For example, its reaction in toluene with excess  $\text{P}(\text{n-C}_4\text{H}_9)_3$  gave data that do not produce a linear log plot for a pseudo-first-order reaction. Other attempts to treat the data, such as in terms of two consecutive reactions, were not successful. Various experimental approaches were used in an effort to gain some insight as to the nature of this reaction. The reaction does not appear to go to completion because it evolves less than the theoretical amount of two CO's per  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and because infrared spectra of the final reaction mixture always show the presence of some starting material. However, this does not appear to be a system at equilibrium because if the final reaction mixture is purged with  $\text{N}_2$  to expel CO, and/or more phosphine is added, there appears to be little or no additional reaction (the infrared spectrum does not change very much). Also the addition of a final reaction mixture to a freshly prepared reaction mixture does not appear to alter its rate or course of reaction. Therefore, it would not seem that an inhibitor is produced during reaction which tends to stop it. All of the experiments were done in a nitrogen atmosphere, in the absence of light, and in the absence of oxygen and water. However, the addition of small amounts of oxygen or water does not appear to affect the rate or the nature of the reaction. Because of such results the nature of these particular reactions is not known.

## Results

The rates of  $^{14}\text{CO}$  exchange with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  at many different experimental conditions are recorded in Table I. Kinetic data on the exchange of  $^{14}\text{CO}$  with some other compounds of  $\text{Co}(\text{CO})_4$  are given in Table II. Also included is the observation made on the compound  $(\text{C}_6\text{H}_5)_3\text{PAuMn}(\text{CO})_5$ . The temperature dependence of the rate of  $^{14}\text{CO}$  exchange with  $\text{Co}_2(\text{CO})_8$  in toluene solution is given in Table III. Because of the complications described above it was not possible to obtain meaningful quantitative data on the substitution reactions of  $\text{Co}(\text{CO})_4$  compounds with different reagents.

## Discussion

Kinetic data (Table I) on the rate of exchange of  $^{14}\text{CO}$  with  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  show (1) that all four CO's exchange at the same rate, (2) that the rate of exchange does not depend on the concentration of CO, and (3) that it is not greatly affected by the nature of the solvent. Such a first-order rate law is usually taken as a good indication of a dissociation mechanism, but some of the observations made suggest that exchange does not take place by a simple dissociation process. For example, the enthalpy of activation (13 kcal/mole) is less than that expected for the rupture of a Co-C bond,<sup>15</sup> and the entropy of activation (-24 eu) is negative. For a dissociation process in which the leaving group is only very slightly bound in the transition state, there is generally an increase in entropy and the entropy of activation would be positive or about zero, but not a large negative value as is found.<sup>16</sup> Also if the exchange did involve a simple dissociation mechanism, then substitution reactions to give thermodynamically stable products should take place at the same rate as the rate of exchange. In contrast to this, quite different and complicated behaviors were observed for the reactions of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  with various phosphines.

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Table II.<sup>a</sup> Rates of <sup>14</sup>CO Exchange with Compounds of [Co(CO)<sub>4</sub>]<sup>-</sup>

Compounds	Temp, °C	Solvent	[Cpd]	[CO] <sub>g</sub>	CO <sub>t</sub>	10 <sup>3</sup> k <sub>1</sub> , sec <sup>-1</sup>
Cd[Co(CO) <sub>4</sub> ] <sup>b</sup>	-21.5	Toluene	1.65	0.17	0.21	0.5
	-21.5	CCl <sub>4</sub>	1.40	0.17	0.20	6.8
	-21.5	Hexane	1.09	...	0.19	Fast <sup>c</sup>
	-20.5	Toluene	1.23	2.6	3.2	1.9
	-20.5	Toluene	1.71	0.42	0.50	2.1
	-20.5	Toluene	1.47	0.19	0.23	1.5
	-20.5	Toluene	1.36	0.19	0.23	1.5
	-11.5	Toluene	1.20	0.18	0.23	4.7
	-11.5	Toluene	1.20	0.19	0.23	3.4
	20.0	Toluene	1.39	0.09	0.13	7.0
(CH <sub>3</sub> ) <sub>2</sub> SnCo(CO) <sub>4</sub>	20.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	5.8	...	0.23	0.21
	20.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	3.4	...	0.23	0.21
	20.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	3.7	...	0.22	0.15
	20.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	3.7	...	6.5	0.42
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnCo(CO) <sub>4</sub>	40.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	3.7	...	0.22	1.0
	40.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	3.7	...	5.8	1.6
CH <sub>3</sub> COCo(CO) <sub>4</sub> <sup>d</sup>	0.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	4.6	...	0.26	0.85
	0.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	4.6	...	0.28	0.88
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PAuCo(CO) <sub>4</sub>	20.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	3.2	...	0.25	7.4 <sup>e</sup>
	20.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	3.2	...	6.7	11 <sup>e</sup>
	20.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	2.8	...	6.0	6.7 <sup>e</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PAuMn(CO) <sub>5</sub>	20.0	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	1.9	...	0.22	N.E. <sup>f</sup>

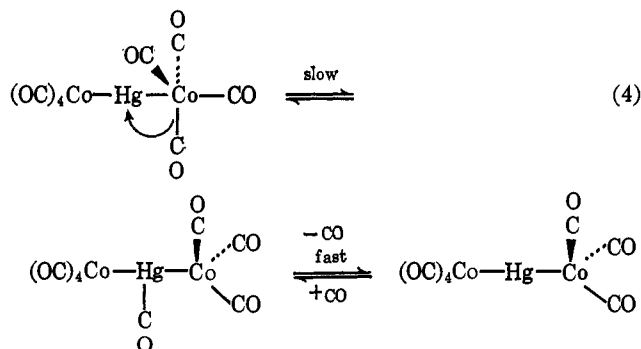
<sup>a</sup> Notations to Table I also apply here. Except for footnote *d*, values of *k*<sub>2</sub> are not constant suggesting a first-order exchange. <sup>b</sup> Δ*H*\* = 11 kcal/mole; Δ*S*\* = -28 eu. <sup>c</sup> Exchange was too fast to measure by this technique. <sup>d</sup> Rate constant for the reaction with P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> is 7.6 × 10<sup>-4</sup> sec<sup>-1</sup>. <sup>e</sup> Values of *k*<sub>1</sub> are not constant, indicating a second-order process. The values reported here are for *k*<sub>2</sub> in M<sup>-1</sup> sec<sup>-1</sup> and are to be taken as shown and not to be multiplied by 10<sup>-3</sup>. <sup>f</sup> No detectable exchange in 27 hr.

Table III.<sup>a</sup> Rate of <sup>14</sup>CO Exchange with Co<sub>2</sub>(CO)<sub>8</sub> in Toluene Solution

Temp, °C	[Co <sub>2</sub> (CO) <sub>8</sub> ] <sup>b</sup>	[CO] <sub>g</sub> <sup>b</sup>	[CO] <sub>t</sub> <sup>c</sup>	<i>k</i> <sub>1</sub> , sec <sup>-1</sup>
-20	2.96	0.21	0.26	5.8 × 10 <sup>-5</sup>
-5	4.33	0.2	0.26	7.5 × 10 <sup>-4</sup>
-5	4.33	5.2	8.6	9.4 × 10 <sup>-4</sup>
+5	5.67	0.19	0.26	2.5 × 10 <sup>-3</sup>
+5	5.67	6	7.4	4.6 × 10 <sup>-3</sup>

<sup>a</sup> The activation energy parameters estimated from these values are Δ*H*\* = 23 ± 2 kcal/mole; Δ*S*\* = -13 ± 4 eu. <sup>b</sup> Concentrations in mM. <sup>c</sup> [CO]<sub>t</sub> = total CO in millimoles in enclosed system.

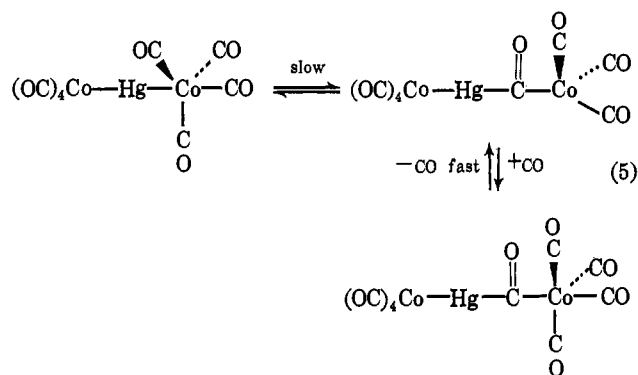
Alternative explanations can be given to account for the results obtained. A possible mechanism of CO exchange with Hg[Co(CO)<sub>4</sub>]<sub>2</sub> is that represented by the



equilibria in eq 4. The slow step of transferring one molecule of CO from Co to Hg is rate determining and does not depend on the concentration of CO. The molecule of CO on Hg is then labile and rapidly exchanges with <sup>14</sup>CO in solution. Thus the intramolecular transfer of a CO molecule from Co to Hg may well take place with a low enthalpy of activation, because this amounts to breaking a Co-C bond and making a Hg-C bond. The negative entropy of activation is also

in accord with such a process where the motion in the transition state is severely restricted relative to the ground state. Finally, the inhibition of exchange by the presence of a phosphine may mean that the phosphine adds to the mercury and prevents a transfer of carbon monoxide to it. This seems plausible because addition compounds of the type CdL<sub>2</sub>[Co(CO)<sub>4</sub>]<sub>2</sub>, where L = amines or phosphines, have been prepared and characterized.<sup>14</sup>

Another mechanism which would also be in accord with the results obtained is shown by reaction scheme 5.



Insertion<sup>17a</sup> (or ligand migration<sup>17b</sup>) reactions of this type are very common, and this can provide a low-energy path for carbon monoxide exchange. Halpern and Kettle<sup>17c</sup> have suggested that the fact that a methanol solution of Hg(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> can take up CO and then liberate it at elevated temperatures or on the addition of halide ion is due to an insertion reaction. Because of this precedence for insertion reactions in such systems, chemical intuition prompts us to favor mechanism 5 over 4. But it must be understood that both are con-

(17) (a) R. F. Heck, *Advances in Chemistry Series*, No. 49, American Chemical Society, Washington, D. C., 1965, p 181; (b) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964); (c) J. Halpern and S. F. A. Kettle, *Chem. Ind.* (London), 668 (1961).

sistent with the experimental data and that other processes are also possible.

The activation parameters found for exchange in this system are very similar to those reported for the exchange of  $^{14}\text{CO}$  with  $\text{Ni}(\text{CO})_4$  ( $\Delta H^* = 12$  kcal/mole,  $\Delta S^* = -26$  eu) in toluene solution. The rate of this exchange is also first order in carbonyl and zero order in carbon monoxide concentrations. It was believed<sup>1</sup> that exchange takes place by a dissociation mechanism, but recent studies<sup>18</sup> indicate that this is not correct. Substitution reactions of  $\text{Ni}(\text{CO})_4$  with different phosphines and phosphites to yield  $\text{Ni}(\text{CO})_3\text{L}$  are also first order but have values of  $\Delta H^* \sim 21$  kcal/mole and  $\Delta S^* \sim +2$  eu. It is clear that the mechanism for substitution differs from that for exchange which takes place by a path of much lower energy. The nature of this path is not known, but one possibility is that in solution tetrahedral  $\text{Ni}(\text{CO})_4$  rearranges to a square-planar (or six-coordinated with two molecules of solvent along the  $z$  axis) structure and readily adds CO leading to exchange. Whatever the explanation, the facts resemble the exchange for  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ , and special mechanisms appear to be required for both.

One of the initial reasons for this research was to compare the characteristics of the  $^{14}\text{CO}$  exchange for  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  with that for  $\text{Co}_2(\text{CO})_8$ , since the two carbonyls have somewhat analogous structures (III and II). The activation parameters reported earlier<sup>1</sup> for the exchange of  $\text{Co}_2(\text{CO})_8$  were estimated from kinetic data at only two temperatures, and only one run made at one of the temperatures. For this reason the study was repeated and the results obtained are shown in Table III. All eight CO's exchange at the same rate and by a first-order process. The activation parameters ( $\Delta H^* = 23$  kcal/mole,  $\Delta S^* = +13$  eu) have values that appear normal for a dissociation mechanism. This suggests that species II may undergo exchange by a dissociation process and that a low-energy mechanism for exchange of the type represented by either (4) or (5) is not available to this species.

The rates of exchange of  $^{14}\text{CO}$  with other compounds

(18) L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson, and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2334 (1966).

of  $\text{Co}(\text{CO})_4$  are summarized in Table II. These systems were not studied in much detail, but a few comments can be made relative to the discussion here on the compound  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . The corresponding  $\text{Cd}[\text{Co}(\text{CO})_4]_2$  appears to be somewhat more labile but otherwise to behave in much the same manner as does the Hg compound. The tin compounds,  $(\text{CH}_3)_3\text{SnCo}(\text{CO})_4$  and  $(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$ , are much slower to exchange. Since the tin compounds do not undergo substitution reactions at these conditions, it follows that an independent path is available for CO exchange which is not available for substitution.

The rate of  $^{14}\text{CO}$  exchange with  $\text{CH}_3\text{COCO}(\text{CO})_4$  in dibutyl ether solution is in good agreement with its rate of reaction with triphenylphosphine to yield  $\text{CH}_3\text{COCO}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ . Presumably, both exchange and substitution take place by a dissociation mechanism, as was described by Heck.<sup>19</sup>

The compound  $(\text{C}_6\text{H}_5)_3\text{PAuCo}(\text{CO})_4$  appears to be anomalous in its behavior and should be studied further. Only three CO's seem to exchange, and an approximate second-order rate of exchange is observed. Finally, the compound  $(\text{C}_6\text{H}_5)_3\text{PAuMn}(\text{CO})_5$  was investigated because it had been suggested<sup>20</sup> on the basis of the infrared spectrum of this compound in the C-O stretching region that it is analogous to  $\text{Mn}(\text{CO})_5\text{I}$ . However, under conditions that the iodine compound undergoes CO exchange,<sup>21</sup> there is no exchange for the gold compound (Table II). This suggests that infrared spectral data, although a guide,<sup>22</sup> must be used with caution in attempts to estimate the lability of metal carbonyls.

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(19) R. F. Heck, *ibid.*, **85**, 651 (1963).

(20) C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1741 (1964).

(21) A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

(22) A. T. Brault, E. M. Thorsteinson, and F. Basolo, *Inorg. Chem.*, **3**, 770 (1964).