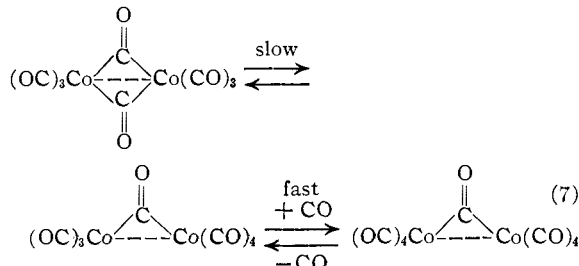
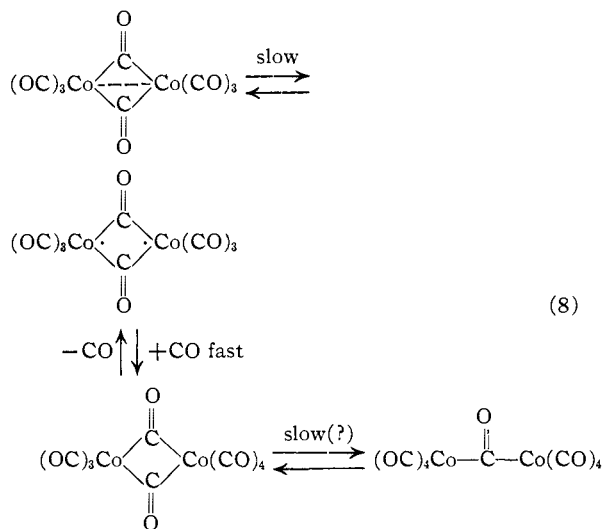


Therefore it would appear that at least one carbonyl bridge is required for the rapid exchange of CO in these binuclear cobalt systems.

In keeping with these observations, a possible mechanism may be



Since all eight CO's exchange at the same rate (Fig. 2), it is necessary that free rotation about the cobalts in the active intermediates be assumed possible. The reaction between 1- and 2-hexyne and  $\text{Co}_2(\text{CO})_8$  was investigated<sup>4</sup> and it was postulated that these reactions may involve a reactive biradical intermediate. On this basis, it is possible that the CO exchange may follow the reaction scheme (8). These two mechanisms are very similar and cannot be distinguished with the data now available. Other mechanisms, also in accord with the experimental observations, could be cited but this would serve no useful purpose because the details of the



exchange process cannot yet be assigned. The two mechanisms proposed are intended to represent in a general way the type of process that is perhaps involved and both are consistent with the existence of  $\text{Co}_2(\text{CO})_8$ .

**Acknowledgments.**—The authors are thankful for the helpful discussions during the early stages of this research with the following: Prof. E. O. Fischer, Dr. R. E. Johnson, Prof. R. G. Pearson, Dr. L. S. Meriwether, Dr. H. W. Sternberg and Dr. I. Wender. Suggestions made by Professors R. L. Burwell, Jr., and H. Pines with regard to the exchange apparatus were also most helpful.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

### Metal Carbonyls. III. Carbon Monoxide Exchange with Some Metal Carbonyl Halides<sup>1,2</sup>

BY ANDREW WOJCICKI<sup>3</sup> AND FRED BASOLO

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Kinetic studies on the exchange of  $^{14}\text{CO}$  with metal carbonyl halides in solution are reported. The exchange of  $\text{Mn}(\text{CO})_5\text{X}$  proceeds by an  $\text{S}_{\text{N}}1$  path whereas that of  $\text{Fe}(\text{CO})_4\text{I}_2$  involves an  $\text{S}_{\text{N}}2$  mechanism. The relative rates of exchange of the  $\text{Mn}(\text{CO})_5\text{X}$  compounds decrease in the order:  $\text{Mn}(\text{CO})_5\text{Cl} > \text{Mn}(\text{CO})_5\text{Br} > \text{Mn}(\text{CO})_5\text{I}$ . This same order was found for  $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ ; moreover,  $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{I} > \text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{CN}$ . The exchange for some square planar compounds was too fast to measure.

The kinetics and mechanism of carbon monoxide exchange with metal carbonyls<sup>4,5</sup> and with cyclopentadienyl metal carbonyls<sup>1</sup> were reported recently. This paper describes the investigation of  $^{14}\text{CO}$  exchange with solutions of  $\text{Mn}(\text{CO})_5\text{X}$ ,  $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ ,  $\text{Fe}(\text{CO})_4\text{I}_2$ ,  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ,  $\text{Rh}(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{COCl}$  and  $\text{Pt}_2(\text{CO})_2\text{Cl}_4$ .

(1) For paper II on cyclopentadienyl carbonyls see A. Wojcicki and F. Basolo, *J. Inorg. Nuclear Chem.*, in press.

(2) Presented in part as paper No. 139 at the XVIIth Congress of the International Union of Pure and Applied Chemistry, Munich, Germany, 1959.

(3) Based upon a portion of a thesis submitted by A. W. to Northwestern University in June 1960, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) D. F. Keeley and R. E. Johnson, *J. Inorg. Nuclear Chem.*, **11**, 33 (1959).

(5) F. Basolo and A. Wojcicki, *THIS JOURNAL*, **83**, 520 (1961).

### Experimental

**Compounds and Solvents.**—The metal carbonyl halides used in this study are all known compounds. They were prepared by the methods described in the literature and characterized by analyses and/or infrared spectra.<sup>6</sup> We also wish to acknowledge the gift of a sample of  $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$  by Professor E. O. Fischer and of a sample of  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  by Dr. H. W. Sternberg. The solvents used were all puri-

(6)  $\text{Mn}(\text{CO})_5\text{Cl}$  and  $\text{Mn}(\text{CO})_5\text{Br}$ , E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959);  $\text{Mn}(\text{CO})_5\text{I}$ , E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, *THIS JOURNAL*, **76**, 3831 (1954);  $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{X}$  (where X = Cl, CN), T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nuclear Chem.*, **1**, 165 (1955);  $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ , T. S. Piper and G. Wilkinson, *ibid.*, **2**, 38 (1956);  $\text{Fe}(\text{CO})_4\text{I}_2$ , W. Hieber and G. Bader, *Ber.*, **61B**, 1717 (1928);  $\text{Rh}(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{COCl}$ , L. Vallarino, *J. Chem. Soc.*, 2287 (1957);  $\text{Pt}_2(\text{CO})_2\text{Cl}_4$ , F. Mylius and F. Foerster, *Ber.*, **24**, 2424 (1891).

fied. The method described by Fieser<sup>7</sup> was used to purify toluene. Thiophene free benzene was refluxed over sodium for several hours and then fractionally distilled. Chloroform was dried over CaCl<sub>2</sub> and distilled.

Carbon monoxide of C.P. grade, obtained from Matheson Co., was passed through concentrated H<sub>2</sub>SO<sub>4</sub> prior to use. Carbon-14 monoxide (1.0 millicurie, 54.3 ml.), purchased from Tracerlab, Inc., was transferred to a two liter storage flask, diluted to one atmosphere with inactive CO and used in this form. Argon from the Matheson Co. was also bubbled through concentrated H<sub>2</sub>SO<sub>4</sub>.

**Exchange and Kinetics.**—The apparatus used and the experimental procedure for determining CO exchange in these systems was the same as that described in some detail earlier.<sup>5</sup> Briefly, this involved measuring the rate of decrease of radioactivity at constant temperature in a closed system starting with radiocarbon monoxide and inactive metal carbonyl halide in solution. All exchanges are run at 1 atm. and the partial pressure of CO is varied by dilution with Ar. In a closed system, the gas is rapidly circulated through the solution so that the rate of diffusion is much greater than the rate of exchange. Light is excluded and the infrared spectra are determined at the end of each run to establish whether or not there is any chemical decomposition of the metal carbonyl halide.

All of the exchange reactions investigated were found to follow the McKay<sup>8</sup> equation and give linear plots of log  $[A_0 - A_{00}/A - A_{00}]$  versus time, where  $A_0$  is the initial radioactivity,  $A$  is the radioactivity at time  $t$ , and  $A_{00}$  is the radioactivity at equilibrium. The slope of these lines equals  $k_{\text{apparent}}/2.303$ , which is related to  $k_{\text{true}}$  by the equation

$$k_{\text{true}} = k_{\text{apparent}} \frac{x a^{1-\alpha} y b^{1-\beta}}{x a + y b} \quad (1)$$

where  $a$  is the concentration of metal carbonyl halide,  $\alpha$  is the order in  $a$ ,  $b$  is the concentration of carbon monoxide in solution,  $\beta$  is the order in  $b$ ,  $x$  is the number of exchangeable CO's in the carbonyl, and  $y$  is the ratio of total moles of carbon monoxide in the enclosed system to moles of carbon monoxide in solution. Equation (1) is used instead of the usual statistical factor because the carbon monoxide in the experiments was distributed between two phases. Duplicate kinetic runs were made with a 10% precision.

### Results

Except for Mn(CO)<sub>5</sub>X, the experimental infinite time radioactivity corresponds to the value calculated on the basis that all CO's in the metal carbonyl halide exchange. For Mn(CO)<sub>5</sub>X, as shown in Fig. 1, one CO exchanges much more slowly than do the other four. Therefore the values of  $k_{\text{true}}$  reported in Table I are calculated on the basis of four CO's undergoing exchange. Data for the exchange of Fe(CO)<sub>4</sub>I<sub>2</sub> are given in Table I. Under the exchange conditions, there is some decomposition of the compounds C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>X. Because of this, the data shown in Table I are only approximate and no attempt was made to investigate the dependence of rate on the CO concentration. As shown in Table II, the exchange rates for the square metal carbonyl halides are much too fast to measure by this technique.

### Discussion

The metal carbonyl halides that were investigated are believed to have three different types of structure. The compounds Mn(CO)<sub>5</sub>X and Fe(CO)<sub>4</sub>I<sub>2</sub> are octahedra, C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>X compounds "distorted tetrahedra," and the Rh(I) and Pt(II) compounds are square planar. It is not possible to make a quantitative comparison of rates of exchange for these systems but qualitatively the rates decrease in the order Rh(I) and Pt(II) carbonyls

(7) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, New York, N. Y., 1941, p. 364.

(8) H. A. C. McKay, *Nature*, **142**, 997 (1938).

TABLE I  
RATES OF CO EXCHANGE WITH SOME METAL CARBONYL HALIDES IN TOLUENE AT 31.8°

Compound	Concn. (mmole/l.)			$k_{\text{apparent}}$ (sec. <sup>-1</sup> )	$k_{\text{true}}$ (sec. <sup>-1</sup> )
	Compound	(CO) <sub>a</sub>	(CO) <sub>b</sub>		
Mn(CO) <sub>5</sub> Cl <sup>a,b</sup>	12.6	6.2	2.4	$1.3 \times 10^{-2}$	$3.0 \times 10^{-3}$
Mn(CO) <sub>5</sub> Br <sup>a,b</sup>	13.3	6.6	3.1	$3.6 \times 10^{-1}$	$1.1 \times 10^{-4}$
	16.6	6.2	2.6	$4.8 \times 10^{-1}$	$1.1 \times 10^{-4}$
	15.2	0.85	0.32	$2.8 \times 10^{-4}$	$1.5 \times 10^{-4}$
Mn(CO) <sub>5</sub> I <sup>a,b</sup>	16.6	6.2	2.7	$5.2 \times 10^{-1}$	$1.3 \times 10^{-3}$
	16.6	2.2	0.84	$1.6 \times 10^{-1}$	$1.7 \times 10^{-5}$
Fe(CO) <sub>4</sub> I <sub>2</sub>	23.7	6.6	2.8	$4.1 \times 10^{-1}$	$1.4 \times 10^{-2}$
	18.1	6.2	2.7	$3.3 \times 10^{-1}$	$1.3 \times 10^{-2}$
	15.8	0.32	0.13	$2.3 \times 10^{-1}$	$1.8 \times 10^{-2}$
C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> Cl <sup>c</sup>	33.3	.28	.12	$1 \times 10^{-4}$	...
C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> Br <sup>c</sup>	33.3	.28	.12	$5 \times 10^{-4}$	...
C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> I <sup>c</sup>	33.3	.28	.12	$2 \times 10^{-1}$	...
C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> CN <sup>c</sup>	33.3	.28	.12	$1 \times 10^{-1}$	...

<sup>a</sup> Calculated on the basis of the exchange of 4 CO's (Fig. 1). <sup>b</sup> After exchange of the 4 labile CO's, the 5th CO equilibrated in about 3 hr. at 50°. <sup>c</sup> Calculated assuming a dissociative process. <sup>d</sup> Reaction is second order so  $k_{\text{true}}$  is in l. mole<sup>-1</sup>, sec<sup>-1</sup>. <sup>e</sup> Appreciable decomposition noted. <sup>f</sup> Some decomposition noted. <sup>g</sup> Mmoles/l. of dissolved CO. <sup>h</sup> Total mmoles of CO in enclosed system.

TABLE II  
RATES OF CO EXCHANGE WITH SOME SQUARE PLANAR METAL CARBONYL HALIDES

Compound	Concentration (mmole/l.)			Temp., °C.	Exchange rate <sup>c</sup>
	Carbonyl (CO) <sub>a</sub>	(CO) <sub>b</sub>	Solvent		
Rh <sub>2</sub> (CO) <sub>4</sub> Cl <sub>2</sub>	16.7	2.4	2.1	Toluene	0.0 Instantaneous
	14.2	1.1	0.90	Chloroform	0.0 Instantaneous
Rh(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> -COCl	15.9	0.75	.55	Chloroform	-20 Instantaneous
Pt <sub>2</sub> (CO) <sub>2</sub> Cl <sub>4</sub>	18.0	1.2	.54	Benzene	25 Instantaneous

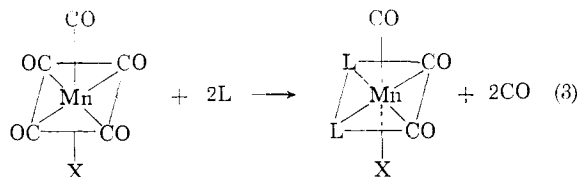
<sup>a</sup> Mmoles/l. of dissolved CO. <sup>b</sup> Total mmoles of CO in enclosed system. <sup>c</sup> Exchange complete in less than 2 min.

$\gg \text{Fe}(\text{CO})_4\text{X}_2 > \text{Mn}(\text{CO})_5\text{X} > \text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$  (2). The rapid rate of exchange for the square complexes may suggest a low energy bimolecular displacement path. Unfortunately, the exchange was much too fast to permit kinetic studies by this technique, so that there is no information on the reaction process. The slow exchange of C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>X may indicate that these compounds behave more like six-coordinated systems than sterically accessible distorted tetrahedra.

**Octahedral Metal Carbonyl Halides.**—Three definite conclusions can be drawn from the exchange studies on Mn(CO)<sub>5</sub>X: (1) one CO exchanges more slowly than do the other four, (2) the rate of CO exchange does not depend on the concentration of CO and (3) the rate of CO exchange does depend on ligand X. That four CO's exchange more rapidly than does the fifth is clearly shown in Fig. 1. One possible explanation for this is that the Mn-C bond *trans* to X is stronger than the M-C bond *trans* to CO. This may result from the greater amount of  $\pi$ -bonding of CO compared to X. In  $d^6$  octahedral systems of this type, there is back donation of the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  pairs of electrons *via*  $\pi$ -bonding into vacated  $p$  orbitals of the carbonyl carbons, *e.g.* M=C=O. Because of the geometry of these orbitals, ligands *trans* to each other compete for the same sets of  $d$  orbitals. Therefore, the CO *trans* to X is in competition

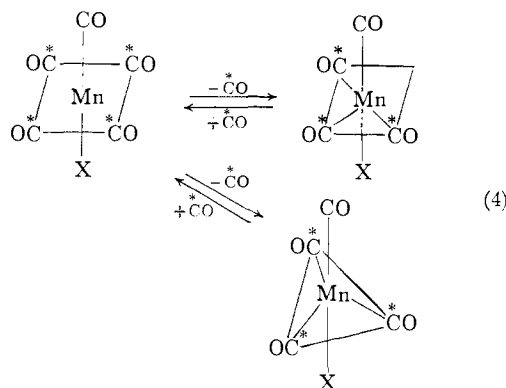
with X and as a result is more  $\pi$ -bonded than it would be if in competition with CO for the  $d$ -orbital electrons.

That there are four reactive CO's in these systems is in agreement with the recent observations of Abel and Wilkinson.<sup>9</sup> They find that the reaction between  $\text{Mn}(\text{CO})_5\text{X}$  and excess L (where L = amines, phosphines and arsines) takes place as



The *cis* structures were assigned to  $\text{Mn}(\text{CO})_3\text{L}_2\text{X}$  on the basis of the similarity of the infrared spectra of  $\text{Mn}(\text{CO})_3(\text{py})_2\text{X}$  and  $\text{Mn}(\text{CO})_3(\text{bipy})\text{X}$  (where py = pyridine and bipy = 2,2'-bipyridine). That only two CO's are replaced by L is said to be due to the weaker  $\pi$ -bonding tendency of L compared to CO. Thus the *cis* structure results in which the CO's *trans* to L are now more strongly bonded and not readily replaced.

The second point, as shown by the data in Table I, is that the rate of CO exchange does not depend on the concentration of CO. This then means that a dissociation or SN1 mechanism is involved. The configuration of the five-coordinated active intermediate is not known, but whatever its structure, the inactive CO retains its identity and does not become identical with the other three COs. This can happen with either a tetragonal pyramid or a trigonal bipyramid intermediate



The final point to make on these systems is that the ratio of rates of CO exchange for  $\text{Mn}(\text{CO})_5\text{X}$  for I:Br:Cl is 1:8:200. This reactivity order may be explained on the basis of the polarizability and/or electronegativity of the halide ions. The bond strength of Mn-C is greater, the greater the  $\pi$ -bonding by back donation of Mn  $d$  electrons into vacated  $p$  orbitals of C. This flow of electron density away from Mn is enhanced by a smaller effective positive charge on Mn. Since  $\text{I}^-$  has the greatest polarizability and smallest electronegativity, it renders the Mn least positive and promotes  $\text{Mn}=\text{C}=\text{O}$  bonding. Thus, in agreement with experiment, the CO exchange of  $\text{Mn}(\text{CO})_5\text{I}$  is the slowest and that of  $\text{Mn}(\text{CO})_5\text{Cl}$  the fastest.

(9) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

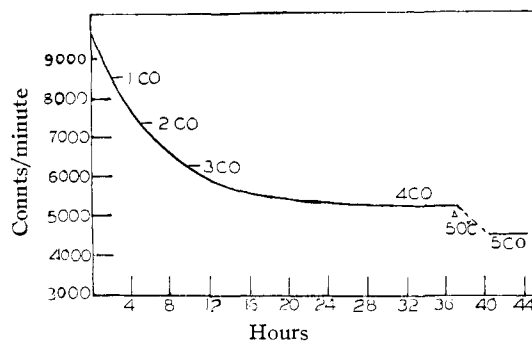
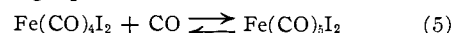


Fig. 1.—Rate of CO (6.6 mmole/l.) exchange with  $\text{Mn}(\text{CO})_5\text{Br}$  (13.3 mmole/l.) in toluene solution at  $31.8^\circ$ .

Were it possible to decrease the charge on Mn to zero while maintaining a  $d^6$  octahedral system, the exchange would be expected to be markedly slower. It is of interest to note that the "isoelectronic"  $\text{Cr}(\text{CO})_6$ , with zerovalent Cr, does indeed exchange CO very slowly.<sup>5</sup>

In order to further determine the effect of oxidation state of the metal on the rate of CO exchange in isoelectronic systems, the compound  $\text{Fe}(\text{CO})_4\text{I}_2$  was investigated. This compound is assigned a *cis* structure on the basis of dipole moment measurements.<sup>10</sup> It is also known<sup>11</sup> to react with phosphines, arsines and stibines to yield  $\text{Fe}(\text{CO})_3\text{LI}_2$ . In view of the findings with  $\text{Mn}(\text{CO})_5\text{X}$ , these results tentatively suggest that the two COs *trans* to each other will exchange more rapidly than the two *trans* to I.

Instead it was found that all four CO's in  $\text{Fe}(\text{CO})_4\text{I}_2$  exchange at the same rate and that the rate of exchange depends on the CO concentration (Table I). These results support a bimolecular, SN2, exchange process



The SN2 exchange for  $\text{Fe}(\text{CO})_4\text{I}_2$ , compared to SN1 for  $\text{Mn}(\text{CO})_5\text{I}$ , may result from the greater positive charge on Fe tending to promote nucleophilic attack. It is significant that  $\text{Fe}(\text{CO})_5\text{I}_2$  has been isolated from the reaction of iodine with iron pentacarbonyl at moderately low temperatures.<sup>12</sup>

**"Tetrahedral" Metal Carbonyl Halides.**—The compounds  $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$  are somewhat analogous to  $\text{Mn}(\text{CO})_5\text{X}$  and  $\text{Fe}(\text{CO})_4\text{X}_2$ . These are essentially "isoelectronic"  $d^6$  systems according to the Fischer<sup>13</sup> concept of bonding. However according to the Piper, *et al.*,<sup>14</sup> concept of bonding,  $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$  may be considered a four-coordinated system. On this basis it is discussed under the heading of "tetrahedral" rather than octahedral structure. However, as Wilkinson and Cotton<sup>15</sup> have recently suggested, it should be re-

(10) E. Weiss, *Z. anorg. allg. Chem.*, **287**, 223 (1956).

(11) W. Hieber and A. Thalhofer, *Angew. Chem.*, **68**, 679 (1956).

(12) W. Hieber and G. Bader, *Ber.*, **61B**, 1717 (1928).

(13) E. O. Fischer and H. P. Fritz, "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, H. J. Emeleus and A. G. Sharpe, Editors, Academic Press, Inc., New York, N. Y., 1959, Ch. 2.

(14) T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nuclear Chem.*, **1**, 165 (1955).

(15) G. Wilkinson and F. A. Cotton, "Progress in Inorganic Chemistry," Vol. I, F. A. Cotton, Editor, Interscience Publishers, Inc., New York, N. Y., 1959, Ch. 1.

