

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 $Co_2(CO)_8$ was investigated⁴ 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 $\text{Co}_2(\text{CO})_9$.

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^{1,2}

By Andrew Wojcicki³ and Fred Basolo Received June 9, 1960

Kinetic studies on the exchange of ¹⁴CO with metal carbonyl halides in solution are reported. The exchange of $Mn(CO)_{\delta}X$ proceeds by an S_N1 path whereas that of $Fe(CO)_4I_2$ involves an S_N2 mechanism. The relative rates of exchange of the $Mn(CO)_{\delta}X$ compounds decrease in the order: $Mn(CO)_{\delta}Cl > Mn(CO)_{\delta}Br > Mn(CO)_{\delta}I$. This same order was found for $C_{\delta}H_{\delta}Fe(CO)_2X$; moreover, $C_{\delta}H_{\delta}Fe(CO)_2I > C_{\delta}H_{\delta}Fe(CO)_2CN$. The exchange for some square planar compounds was too fast to measure.

The kinetics and mechanism of carbon monoxide exchange with metal carbonyls^{4,5} and with cyclopentadienyl metal carbonyls¹ were reported recently. This paper describes the investigation of ¹⁴CO exchange with solutions of Mn(CO)₅X, C₅H₅Fe(CO)₂X, Fe(CO)₄I₂, Rh₂(CO)₄Cl₂, Rh(P-(C₆H₅)₃)₂COCl and Pt₂(CO)₂Cl₄.

- (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.⁶ We also wish to acknowledge the gift of a sample of $C_5H_5Fe(CO)_2Br$ by Professor E. O. Fischer and of a sample of $Rh_2(CO)_4Cl_2$ by Dr. H. W. Sternberg. The solvents used were all puri-

⁽⁶⁾ $Mn(CO)_{5}C1$ and $Mn(CO)_{5}Br$, E. W. Abel and G. Wilkinson, J. Chem. Soc., 1501 (1959); $Mn(CO)_{5}I$, E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, THIS JOURNAL, **76**, 3831 (1954); $C_{5}H_{5}Fe(CO)_{2}X$ (where X = C1, CN), T. S. Piper, F. A. Cotton and G. Wilkinson, J. Inorg. Nuclear Chem., **1**, 165 (1955); $C_{5}H_{5}Fe(CO)_{2}I$, T. S. Piper and G. Wilkinson, *ibid.*, **2**, 38 (1956); $Fe(CO)_{4}I_{2}$, W. Hieber and G. Bader, Ber., **61B**, 1717 (1928); $Rh(P(C_{4}H_{5})_{3})_{2}COCl$, L. Vallarino, J. Chem. Soc., 2287 (1957); $Pt_{2}(CO)_{2}Cl_{4}$, F. Mylius and F. Foerster, Ber., **24**, 2424 (1891).

Carbon monoxide of C.P. grade, obtained from Matheson Co., was passed through concentrated H_2SO_4 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_2SO_4 .

also bubbled through concentrated H_2SO_4 . 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.⁵ 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 McKay⁸ 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 $k_{\rm apparent}/2.303$, which is related to $k_{\rm true}$ by the equation

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

where a is the concentration of metal carbonyl halide, α is the order in a, b is the concentration of carbon monoxide in solution, β 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 $Mn(CO)_5X$, the experimental infinite time radioactivity corresponds to the value cal-culated on the basis that all CO's in the metal carbonyl halide exchange. For $Mn(CO)_5X$, as shown in Fig. 1, one CO exchanges much more slowly than do the other four. Therefore the values of k_{true} reported in Table I are calculated on the basis of four CO's undergoing exchange. Data for the exchange of $Fe(CO)_4I_2$ are given in Table I. Under the exchange conditions, there is some decomposition of the compounds $C_5H_5Fe(CO)_2X$. 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 $Mn(CO)_5X$ and Fe- $(CO)_4I_2$ are octahedra, $C_5H_5Fe(CO)_2X$ 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. 304.

Table I

RATES OF CO EXCHANGE WITH SOME METAL CARBONVL HALIDES IN TOLUENE AT 31.8°

(Conen. (mmole/	1.)		
Com- pound	(CO),g	(CO).b	kappar. (sec. ⁻¹)	(sec1)
12.6	6.2	2.4	$1.3 imes10$ T $^{-2}$	$3.0 \times 10^{-3^{\circ}}$
13.3	6.6	3.1	3.6×10^{-1}	$1.1 imes10^{-4}$
16.6	6.2	2.6	4.8×10^{-1}	1.1×10^{-4}
15.2	0.85	0.32	2.8×10^{-4}	1.5×10^{-4}
16.6	6.2	2.7	5.2×10^{-1}	1.3 × 10 - 5
16.6	2.2	0.84	1.6×10^{-1}	$1.7 imes 10^{-5}$
23.7	6.6	2.8	4.1×10^{-1}	$1.4 imes 10^{-2'}$
18.1	6.2	2.7	3.3×10^{-1}	1.3×10^{-24}
15.8	0.32	0.13	$2.3 imes10$ $^{-1}$	$1.8 imes10^{-24}$
33.3	.28	.12	1 × 10 ⁻⁴	
3 3.3	.28	.12	5×10^{-1}	
33.3	.28	.12	2×10^{-1}	
33.3	.28	.12	1 imes 10 -1	
	Com- pound 12.6 13.3 16.6 15.2 16.6 23.7 18.1 15.8 33.3 33.3 33.3 33.3	$\begin{array}{c} C \text{oren}, \\ (\text{mmole}/ \\ \text{Com}, \\ \text{pound} \ (\text{CO}), \\ \text{se} \\ 12, 6 \ 6, 2 \\ 13, 3 \ 6, 6 \\ 16, 6 \ 6, 2 \\ 15, 2 \ 0, 85 \\ 16, 6 \ 6, 2 \\ 16, 6 \ 6, 2 \\ 16, 6 \ 6, 2 \\ 16, 6 \ 6, 2 \\ 16, 6 \ 6, 2 \\ 16, 6 \ 6, 2 \\ 16, 8 \ 1 \ 6, 2 \\ 15, 8 \ 0, 32 \\ 33, 3 \ .28 \\ 33, 3 \ .28 \\ 33, 3 \ .28 \end{array}$	$\begin{array}{c} \text{Corren.}\\ (\text{mmole}/1.)\\ \hline \text{Com}\\ \text{pound} (\text{CO})_{*} (\text{CO})_{*}^{b}\\ 12.6 & 6.2 & 2.4\\ 13.3 & 6.6 & 3.1\\ 16.6 & 6.2 & 2.6\\ 15.2 & 0.85 & 0.32\\ 16.6 & 6.2 & 2.7\\ 16.6 & 2.2 & 0.84\\ 23.7 & 6.6 & 2.8\\ 18.1 & 6.2 & 2.7\\ 15.8 & 0.32 & 0.13\\ 33.3 & .28 & .12\\ 33.3 & .28 & .12\\ 33.3 & .28 & .12\\ 33.3 & .28 & .12\\ \end{array}$	$\begin{array}{c} \text{Conen,} \\ (\text{mmole/L}) \\ \hline \\ \text{Com-} \\ \text{pound} \ (\text{CO})_{*} \ (\text{CO})_{*} \ (\text{sec.}^{-1}) \\ 12.6 \ 6.2 \ 2.4 \ 1.3 \times 10^{-2} \\ 13.3 \ 6.6 \ 3.1 \ 3.6 \times 10^{-1} \\ 16.6 \ 6.2 \ 2.6 \ 4.8 \times 10^{-1} \\ 15.2 \ 0.85 \ 0.32 \ 2.8 \times 10^{-4} \\ 16.6 \ 6.2 \ 2.7 \ 5.2 \times 10^{-1} \\ 16.6 \ 2.2 \ 0.84 \ 1.6 \times 10^{-1} \\ 23.7 \ 6.6 \ 2.8 \ 4.1 \times 10^{-1} \\ 18.1 \ 6.2 \ 2.7 \ 3.3 \times 10^{-1} \\ 18.1 \ 6.2 \ 2.7 \ 3.3 \times 10^{-1} \\ 15.8 \ 0.32 \ 0.13 \ 2.3 \times 10^{-1} \\ 13.3 \ .28 \ .12 \ 1 \times 10^{-1} \\ 33.3 \ .28 \ .12 \ 1 \times 10^{-1} \\ 33.3 \ .28 \ .12 \ 1 \times 10^{-1} \\ 33.3 \ .28 \ .12 \ 1 \times 10^{-1} \end{array}$

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

Γ	`AB	LE	II	

Rates	OF	CO	Exchange	WITH	Some	Square	Planar	
METAL CARBONYL HALIDES								

	Concer	ntration	(mmol	e/1.)		
Compound	Car- bonyl	(CO) ₃ °	(CO) ₁ b	Solvent	°C.	Exchange rate¢
$Rh_2(CO)_4Cl_2$	16.7	2.4	2.1	Toluene	0.0	Instanta- neous
	14.2	1.1	0.90	Chloro- form	0.0	Instanta- neous
Rh(P(C6H5)2)2- COC1	15.9	0.75	. 55	Chloro- form	- 20	Instanta- neous
Pt ₂ (CO) ₂ Cl ₄	18.0	1.2	. 54	Benzene	25	Instanta-

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

>> Fe(CO)₄X₂> Mn(CO)₅X > C₅H₅Fe(CO)₂X (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 C₅H₅Fe-(CO)₂X may indicate that these compounds behave more like six-coördinated systems than sterically accessible distorted tetrahedra.

Octahedral Metal Carbonyl Halides.—Three definite conclusions can be drawn from the exchange studies on $Mn(CO)_5X$: (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 π -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 π -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

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

with X and as a result is more π -bonded than it would be if in competition with CO for the dorbital electrons.

That there are four reactive CO's in these systems is in agreement with the recent observations of Abel and Wilkinson.9 They find that the reaction between $Mn(CO)_5X$ and excess L (where L = amines, phosphines and arsines) takes place as



The cis structures were assigned to Mn(CO)₃L₂X on the basis of the similarity of the infrared spectra of $Mn(CO)_3(py)_2X$ and $Mn(CO)_3(bipy)X$ (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 π -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-coördinated 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 $Mn(CO)_5X$ 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 π -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 I- has the greatest polarizability and smallest electronegativity, it renders the Mn least positive and promotes Mn = C = O bonding. Thus, in agreement with experiment, the CO exchange of Mn(CO)₅I is the slowest and that of $Mn(CO)_{5}Cl$ the fastest.





Fig. 1.-Rate of CO (6.6 mmole/l.) exchange with Mn-(CO)₅Br (13.3 mmole/l,) in toluene solution at 31.8°.

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" $Cr(CO)_6$, with zerovalent Cr, does indeed exchange CO very slowly.⁵

In order to further determine the effect of oxidation state of the metal on the rate of CO exchange in isoelectronic systems, the compound $Fe(CO)_4I_2$ was investigated. This compound is assigned a cis structure on the basis of dipole moment measurements.¹⁰ It is also known¹¹ to react with phosphines, arsines and stibines to yield $Fe(CO)_{3}LI_{2}$. In view of the findings with $Mn(CO)_5X$, 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 Fe- $(CO)_4I_2$ 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

$$Fe(CO)_4I_2 + CO \longrightarrow Fe(CO)_5I_2$$
 (5)

The SN2 exchange for $Fe(CO)_4I_2$, compared to SN1 for $Mn(CO)_{5}I$, may result from the greater positive charge on Fe tending to promote nucleophilic attack. It is significant that $Fe(CO)_{5}I_{2}$ has been isolated from the reaction of iodine with iron pentacarbonyl at moderately low temperatures.12

"Tetrahedral" Metal Carbonyl Halides .- The compounds C5H5Fe(CO)2X are somewhat analogous to $Mn(CO)_5X$ and $Fe(CO)_4X_2$. These are essentially "isoelectronic" d^6 systems according to the Fischer¹³ concept of bonding. However according to the Piper, et al.,14 concept of bonding, $C_5H_5Fe(CO)_2X$ 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 Cotton¹⁵ 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.

membered that perhaps neither extreme, three bonds or one bond between the ring and the metal, is entirely correct.

The CO exchange data for $C_5H_5Fe(CO)_2X$ compounds are given in Table I. Because of some decomposition only approximate apparent rate constants are reported. No attempt was made to determine the dependence of rate on the CO concentration. Therefore nothing can be said as to the mechanism of exchange.

Since the concentrations of $C_5H_5Fe(CO)_2X$ and of CO were kept constant, it is possible to compare the relative rates of exchange. The data show that the ratio of rates for $C_5H_5Fe(CO)_2X$ is 1:2:50:1000 for X = CN, I, Br and Cl, respectively. This is the same rate order as that observed for the Mn(CO)₅X compounds, but it need not mean that the mechanisms of exchange are the same. A decrease in positive charge on M due to the polarizabilities of X is expected to result in a decrease in rate of CO exchange by either SN1 or SN2 mechanism. Since the compounds $C_5H_5Fe-(CO)_2X$ are more like $Fe(CO)_4I_2$ than $Mn(CO)_5X$, there is some reason to favor a bimolecular displacement process. Furthermore, the CO exchange of some other cyclopentadienyl metal carbonyls has been found to involve an SN2 process.1

Square Planar Metal Carbonyl Halides .--- The data in Table II show that the CO exchange in the three square planar compounds investigated is much too fast to study by the technique used. Two of these compounds are dimeric with chloro-bridged structures. The presence of one or more such bridges in a molecule seems to provide a reactive site.¹⁶ Therefore a possible exchange process may involve the scheme

$$\begin{array}{c} OC\\OC\\OC\\OC\\OC\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl\\Rh\\Cl_Rh\\Cl\\Rh\\Cl_Rh\\Cl\\Rh\\Cl_Rh\\Cl$$

Depending on which reaction step is rate determining, the rate of exchange may or may not depend on the CO concentration.

Since $Rh(P(C_6H_5)_3)_2(CO)Cl$ also undergoes exchange very rapidly, it is clear that a bridged structure is not required for fast reaction in square planar compounds. In keeping with current theories on substitution reactions in square complexes,¹⁷ it would appear that the rapid rate in this system is due to extensive π -bonding which greatly stabilizes the five-coördinated transition state. Recent observations¹⁸ show that chloride exchange is also very rapid. Since the compound $Rh(P(\tilde{C}_{6}$ - $H_{5}_{3}_{2}(CO)(Cl)$ is known to be extremely stable,¹⁹ these results provide an excellent example of a very labile but thermodynamically extremely stable system.

Acknowledgment.-We wish to thank the Eastman Kodak Company for providing a fellowship to A. W.

(16) J. Chatt, J. Chem. Soc., 652 (1951).
(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Ch. 4.

(18) H. B. Gray and A. Wojcicki, Proc. Chem. Soc., 358 (1960).

(19) L. Vallarino, J. Chem. Soc., 2287 (1957).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

Reactions of Coördinated Ligands.¹ Acylation of the Coördinated Oxime Group

BY RONALD A. KRAUSE, DONALD C. JICHA AND DARYLE H. BUSCH

RECEIVED AUGUST 1, 1960

The reactions of the nickel(II), palladium(II) and platinum(II) complexes of dimethylglyoxime and 2-pyridinaldoxime with acetyl chloride have been studied and are reported here. Recent publications indicate that the nickel dimethylglyoxime complex, $[Ni(DMG)_2]$, reacts with acetyl chloride to form a complex containing acylated ligand. The present investigation shows that this is not the case; the nickel(II), palladium(II) and platinum(II) complexes of dimethylglyoxime on reaction with acetyl chloride yield $[M^{II}(HDMG)Cl_2]$ and free, diacylated ligand. The results with the 2-pyridinaldoxime system are somewhat different. While the nickel(II) complex decomposes on treatment with acetyl chloride, the palladium(II) complex gives a monoacylated compound, $[Pd(POX-COCH_3)Cl_2]$, in which one mole of ligand has been replaced by two chloride ions. When this compound is hydrolyzed in aqueous sodium hydroxide a new complex, $[Pd(POX)-COCH_2)Cl_2]$, results. results. Reaction of the platinum(II) complex with acetyl chloride gives a diacylated complex, [Pt(POX-COCH₃)₂]Cl₂.

Introduction

The reactions of coördination compounds may be classified as belonging to four different categories. These categories are substitution of one ligand by another, intramolecular isomerization, reactions of the central metal atom only (i.e., oxidation or reduction) and reactions involving coördinated ligands. The first three types of reaction have received a great deal of attention in the literature; the last one, reactions of coördinated ligands, has been the subject of relatively few investigations. This paper deals with the reactions of the nickel(II)

(1) Presented at the 137th American Chemical Society Meeting at Cleveland, Ohio, April, 1960.

palladium(II) and platinum(II) complexes of dimethylglyoxime (I) and 2-pyridinaldoxime (II)^2 $\,$ with acetyl chloride.



One might expect an oxime oxygen to be readily attacked by an acyl halide to form the correspond-

(2) (HDMG) will be used to denote dimethylglyoxime, and (DMG) its monovalent anion, formed by ionization of an oxime proton. Likewise, (HPOX) will denote 2-pyridinaldoxime and (POX) its monovalent anion.