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 S_N1 or S_N2 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 S_N2 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

$$(CO)_2Rh–Cl–Rh(CO)_2Cl \underset{-CO}{\overset{+CO}{\rightleftarrows}} (OC)_3Rh–Cl–Rh(CO)_2Cl \quad (6)$$
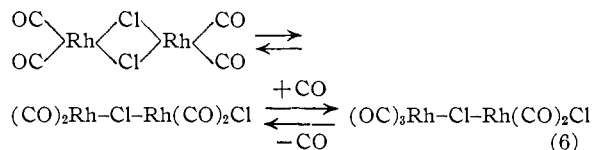
Depending on which reaction step is rate determining, the rate of exchange may or may not depend on the CO concentration.

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 observations[18] show that chloride exchange is also very rapid. Since the compound $Rh(P(C_6H_5)_3)_2(CO)(Cl)$ is known to be extremely stable,[19] these results provide an excellent example of a very labile but thermodynamically extremely stable system.

(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).

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

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

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)Cl]$_2$, results. Reaction of the platinum(II) complex with acetyl chloride gives a diacylated complex, [Pt(POX–COCH$_3$)$_2$]Cl$_2$.

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.
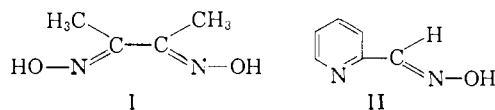

One might expect an oxime oxygen to be readily attacked by an acyl halide to form the correspond-

(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.

ing oxime ester (III) and (IV). When the oxime nitrogen is coördinated to a metal it is difficult to
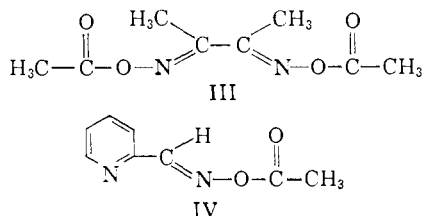
predict the reaction products; a stable complex may be formed by the oxime ester, a mixture of metal salt and oxime ester may be obtained, or a much more complex mixture may result.

In 1925 Barker[3] reported a reaction between [Ni(DMG)$_2$] and CH$_3$I in alcohol yielding alkylated products containing coördinated nickel(II). A few years later, in 1929, Thilo and Friedrich[4] studied a similar reaction. Their results indicate, however, that methyl iodide does not react with [Ni(DMG)$_2$] to give a compound containing the coördinated oxime ether. Only by starting with the ether and using alcohol as the solvent could they obtain a complex of the oxime ether.

Sharpe and Wakefield have studied the reaction of [Ni(HDMG)$_2$Cl$_2$] and of [Ni(DMG)$_2$] with acetyl chloride,[5] and claim to have obtained a complex containing acylated ligand, [Ni(DMG–CO–CH$_3$)$_2$Cl$_2$]. They also report that, in the presence of hydrogen chloride, [Pd(DMG)$_2$] yields [Pd(HDMG)$_2$Cl$_2$] which acylates to form [Pd(DMG–COCH$_3$)$_2$Cl$_2$]. The reaction with the palladium compound was refuted a short time later by the same authors,[6] but they retained their opinion on the nickel system.

Experimental

Dimethylglyoxime Complexes.—The complexes [Ni(DMG)$_2$], [Pd(DMG)$_2$] and [Pt(DMG)$_2$] were prepared by standard procedures.

[Ni(HDMG)Cl$_2$]·H$_2$O.—This compound was first prepared by Paneth and Thilo[7] and also by Dubsky and Brychta[8]; a somewhat different procedure was employed in the present work.

Dimethylglyoxime, 2.32 g., was dissolved in 75 ml. of absolute ethanol with heating. This solution slowly was added to a solution of 4.75 g. of nickel chloride 6-hydrate dissolved in 50 ml. of absolute ethanol containing three drops of concentrated hydrochloric acid. The mixture was stirred for an additional 15 minutes and then concentrated to 20 ml. under a stream of dry nitrogen. The bright green crystals were separated by filtration and dried *in vacuo* over Ascarite; yield: 2.92 g.

Anal. Calcd. for [Ni(C$_4$H$_8$N$_2$O$_2$)Cl$_2$](H$_2$O): C, 18.19; H, 3.81; N, 10.61; Cl, 26.94. Found: C, 18.55; H, 3.86; N, 10.41; Cl, 26.74.

Preparation of [Ni(HDMG)Cl$_2$].—Dimethylglyoxime, 1.16 g., was dissolved in a small amount of hot glacial acetic acid and added to a hot solution of 1.30 g. of anhydrous nickel chloride in the same solvent. After refluxing for 1 hr. the solution was allowed to cool; the flocculent green solid was filtered under dry nitrogen and dried *in vacuo* at 78° over Ascarite; yield: 2.06 g.

(3) M. F. Barker, *Chem. News,* **130**, 99 (1925).

(4) E. Thilo and K. Friedrich, *Chem. Ber.,* **62B**, 2990 (1929).

(5) A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.,* 496 (1957).

(6) A. G. Sharpe and D. B. Wakefield, *ibid.,* 3323 (1957).

(7) F. Paneth and E. Thilo, *Z. anorg. u. allgem. Chem.,* **147**, 196 (1925).

(8) J. V. Dubsky and Fr. Brychta, *Czechoslov. Chem. Comm.,* **1**, 137 (1929); *C. A.,* **23**, 3417 (1929).

Anal. Calcd. for [Ni(C$_4$H$_8$N$_2$O$_2$)Cl$_2$]: C, 19.53; H, 3.29; N, 11.39; Cl, 28.89. Found: C, 19.29; H, 3.50; N, 11.27; Cl, 28.44.

The infrared spectrum of this sample was in good agreement with that obtained for the monohydrate.

Preparation of [Pd(POX)$_2$] and [Pt(POX)$_2$].—These compounds were prepared as described earlier.[9]

Reaction of [Ni(DMG)$_2$] with Acetyl Chloride.—One gram of [Ni(DMG)$_2$] was treated with 50 ml. of freshly distilled acetyl chloride and stirred continuously for 15 hours. During this treatment, precautions were taken to exclude atmospheric moisture. The solid, which displayed low solubility in the acylating agent, changed color from deep red to green-blue within a few minutes. After separating the product from the solution by filtration under dry N$_2$, it was immediately transferred to a desiccator, still wet with acetyl chloride, and dried *in vacuo* over Ascarite.

The infrared spectrum of this solid corresponds to that of [Ni(HDMG)Cl$_2$].

The filtrate from the above reaction was allowed to evaporate in the atmosphere. A white solid was isolated, washed with petroleum ether and dried over Ascarite *in vacuo*. This material was identified by its infrared spectrum and by analysis as the diacylated ligand.

Anal. Calcd. for (CH$_3$C:NOCOCH$_3$)$_2$: C, 47.99; H, 6.04; N, 14.00. Found: C, 47.68; H, 6.08; N, 13.83.

The above experiment was repeated by refluxing [Ni(DMG)$_2$] in acetyl chloride for 4 hr., separating the green solid by filtration and adding fresh acetyl chloride. After refluxing for an additional 19 hr. the solid was pale yellow and consisted principally of anhydrous nickel(II) chloride. Evaporation of the acetyl chloride filtrates gave a 90% yield of the diacylated ligand.

Similar results were obtained when the reaction was conducted using glacial acetic acid as the solvent, while the use of pyridine as a solvent resulted in the formation of the tetra-(pyridine)-nickel(II) complex.

Reaction of [Pd(DMG)$_2$] with Acetyl Chloride.—Solid [Pd(DMG)$_2$] and acetyl chloride were allowed to react as described for the case of [Ni(DMG)$_2$] (above). The infrared spectrum of the thoroughly dry product showed no acylation.

Anal. Calcd. for [Pd(HDMG)Cl$_2$]: C, 16.35; H, 2.75; N, 9.54. Found: C, 16.76, 17.02; H, 2.79, 3.02; N, 9.59, 9.50.

Reaction of [Pt(DMG)$_2$] with Acetyl Chloride.—Five tenths gram of [Pt(DMG)$_2$] was mixed with 300 ml. of chloroform and 20 ml. of acetyl chloride (a hundred fold excess) was added. The mixture was boiled for 30 minutes, and allowed to stand overnight. The yellow-brown solid was collected by filtration, washed thoroughly with chloroform and dried *in vacuo* over P$_2$O$_5$; yield: 0.44 g. (theoretical, 0.45 g.).

Anal. Calcd. for [Pt(HDMG)Cl$_2$]: C, 12.57; H, 2.11; N, 7.33; Cl, 18.55; Pt, 51.07. Found: C, 12.57; H, 2.16; N, 7.49; Cl, 18.38; Pt, 50.95.

Reaction of Mono-acylated Dimethylglyoxime with NiCl$_2$·6H$_2$O and NiCl$_2$.—Eight-tenths gram of mono-acylated dimethylglyoxime[10] was dissolved in 20 ml. of absolute ethanol and added to a stirred solution of 1.20 g. of nickel chloride 6-hydrate in 125 ml. of absolute ethanol containing three drops of concentrated hydrochloric acid. The solution was stirred for 15 minutes and then concentrated to 20 ml. by means of a stream of dry nitrogen. The blue-green solid was separated by filtration and dried *in vacuo* over Ascarite for 3 hr.

No evidence of acylation could be detected in the infrared spectrum of this compound. The spectrum is very similar to that of [Ni(HDMG)$_2$Cl$_2$] or [Ni(HDMG)Cl$_2$], and the product of this reaction appears to be a mixture of these last mentioned compounds. Replacement of nickel chloride 6-hydrate by anhydrous nickel chloride in this reaction leads to the same products.

Reaction of Di-acylated Dimethylglyoxime with Anhydrous NiCl$_2$.—A sample weighing 0.53 g. of di-acylated dimethylglyoxime (prepared in the reactions described above) was dissolved in 25 ml. of absolute ethanol. This solution was added to a cool solution of 0.35 g. of anhydrous nickel

(9) R. A. Krause and D. H. Busch, THIS JOURNAL, **82**, 4830 (1960).

(10) Private communication from G. Coraor and L. G. Donaruma. E. I. du Pont de Nemours, Explosives Department.

chloride in 125 ml. of the same solvent containing three drops of concentrated hydrochloric acid. Treatment of the solution in the same manner as described for mono-acylated dimethylglyoxime yielded a similar green-blue solid which also showed no evidence of acylation in its infrared spectrum. Again, the solid appeared to be [Ni(HDMG)₂Cl₂] or [Ni-(HDMG)Cl₂].

Reaction of [Pd(POX)₂] with Acetyl Chloride.—A 1.07 g. sample of [Pd(POX)₂] (0.003 mole) was dissolved in 250 ml. of hot chloroform, filtered to remove any undissolved material, and one ml. of acetyl chloride (a two fold excess over 0.0061 mole) was added, with stirring, to the warm solution. The color of the solution immediately changed from yellow to orange. Precipitation started within 30 seconds and, after five minutes, the yellow solid was collected by filtration, washed thoroughly with chloroform and dried *in vacuo* over P₂O₅; yield: 0.91 g.

This solid was recrystallized from hot nitrobenzene and dried *in vacuo* over P₂O₅ at 78°; yield on recrystallization, 84%.

Anal. Calcd. for [Pd(C₆H₅N₂O-CH₃CO)Cl₂]: C, 28.11; H, 2.36; N, 8.20; Cl, 20.75. Found: C, 28.09, 28.16, 27.83; H, 2.37, 2.48, 2.54; N, 8.10, 8.98, 8.24; Cl, 20.55, 20.71, 20.70. (Analyses performed on three different preparations.)

Reaction of [Pt(POX)₂] with Acetyl Chloride.—One gram of [Pt(POX)₂] (0.0023 mole) was dissolved in 150 ml. of boiling chloroform; 0.4 ml. of acetyl chloride (a slight excess over 0.0045 mole) was added. At this point the brown solution immediately turned yellow. The solution was placed in the freezer compartment of a refrigerator overnight. It then was filtered and the solid was washed several times with chloroform and dried *in vacuo* over P₂O₅; yield: 0.50 g. The solid appears to be a mixture of yellow and orange solids. A sample was mixed with warm dimethylformamide and filtered to give a yellow solid (yield: 45.7%) and an orange filtrate.

Anal. of solid. Calcd. for [Pt(C₆H₅N₂O-CH₃CO)₂]Cl₂: C, 32.32; H, 2.71; N, 9.43; Cl, 11.92; Pt, 32.84. Found: C, 32.98; H, 3.40; N, 8.89; Cl, 11.90; Pt, 31.59.

The Hydrolysis of [Pd(POX-COCH₃)Cl₂].—A sample weighing 0.25 g. of [Pd(POX-COCH₃)Cl₂] was mixed with 20 ml. of warm water. Dilute sodium hydroxide was added in small portions until all the solid was dissolved and apparently hydrolyzed as indicated by a constant value pH 8. The solution was filtered and dilute hydrochloric acid added to the filtrate until it was strongly acid. On lowering the pH, a flocculent yellow precipitate formed. After 3 hr., the product was collected by filtration, washed twice with water and dried *in vacuo* over P₂O₅; yield: 0.20 g. (theoretical, 0.19 g.).

Anal. Calcd. for [Pd(C₆H₅N₂O)Cl]: C, 27.37; H, 1.91; N, 10.64; Cl, 13.47. Found: C, 27.07; H, 2.50; N, 10.14; Cl, 13.27.

Infrared Spectra.—Infrared absorption spectra were obtained on a Perkin–Elmer Model 21 recording spectrophotometer, with a sodium chloride prism, using the KBr pellet technique.

Analyses.—Microanalyses were performed by Schwarzkopf Microanalytical Laboratories and by Galbraith Microanalytical Laboratories.
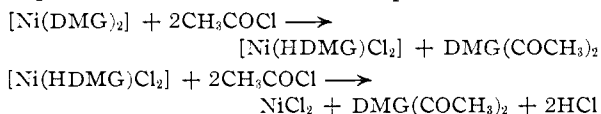
Discussion

The reactions of [Ni(DMG)₂], [Pb(DMG)₂] and [Pt(DMG)₂] with acetyl chloride have been found to yield similar products in all three instances. These are [Mᴵᴵ(HDMG)Cl₂] and free diacylated ligand. No evidence was found for the presence of stable, acylated complexes. The complexes [Pd(POX)₂] and [Pt(POX)₂], however, have been treated with acetyl chloride to yield relatively stable complexes containing acylated ligand. To our knowledge this is the first example to appear in the literature of the acylation of an oxime complex without complete removal of the oxime ester from the coördination sphere.

Stirring [Ni(DMG)₂] with acetyl chloride gives a green-blue solid which has been identified as [Ni-

(HDMG)Cl₂] by comparing its infrared spectrum with that of a known sample of this compound.[11] The spectrum shows no evidence of acylation of the coördinated dimethylglyoxime. On evaporation of the acetyl chloride solvent a white solid was isolated and identified as free, diacylated ligand. If the acetyl chloride solvent is replaced with fresh acetyl chloride and the mixture refluxed for 19 hr., the formation of diacylated ligand and anhydrous nickel chloride is complete.

From these considerations, it is apparent that the acetylation process proceeds stepwise, the first step completely destroying the starting material, [Ni-(DMG)₂], producing only [Ni(HDMG)Cl₂] and DMG(COCH₃)₂. The second step appears to involve acetylation and removal from the complex of the remaining molecule of dimethylglyoxime. This sequence is summarized in the equations

$$[Ni(DMG)_2] + 2CH_3COCl \longrightarrow$$
$$[Ni(HDMG)Cl_2] + DMG(COCH_3)_2$$
$$[Ni(HDMG)Cl_2] + 2CH_3COCl \longrightarrow$$
$$NiCl_2 + DMG(COCH_3)_2 + 2HCl$$

The analogous palladium(II) and platinum(II) complexes, [Pd(DMG)₂] and [Pt(DMG)₂], react with acetyl chloride in a manner similar to that observed with [Ni(DMG)₂], giving [Pd(HDMG)-Cl₂] and [Pt(HDMG)Cl₂]. These compounds have been identified by analysis and their infrared spectra are quite similar and compare favorably with that of [Ni(HDMG)Cl₂]. The preparation of [Pt(HDMG)Cl₂] has not previously been reported. The reaction of [Pt(DMG)₂] with acetyl chloride serves as a very convenient method for the preparation of this complex.

In an effort to prepare acylated dimethylglyoxime complexes, nickel chloride was treated with mono- and diacylated dimethylglyoxime in absolute alcohol containing a trace of concentrated hydrochloric acid. In all cases, the acetyl group was removed from the oxime ester and the only complexes formed were [Ni(HDMG)₂Cl₂] and [Ni-(HDMG)Cl₂]. In the complete absence of hydrochloric acid, [Ni(DMG)₂] also was found among the products. This stands in contrast to the results of Thilo and Friedrich.[4] Those workers were able to prepare nickel(II) complexes of the methyl ether of dimethylglyoxime by using alcohol as the solvent.

In view of the evidence presented above, it may be concluded that the complexes of nickel(II), palladium(II) and platinum(II) with acetylated dimethylglyoxime are unstable. They tend greatly to decompose either by cleavage of the coördinate bond or by solvolytic loss of the acetyl group.

Experiments designed to acylate the coördinated oxime group were much more successful with the palladium(II) and platinum(II) complexes of 2-pyridinaldoxime, [Pd(POX)₂] and [Pt(POX)₂]. The palladium complex reacts with acetyl chloride in chloroform solution to give a monoacylated complex in which one mole of the organic ligand, HPOX, has been replaced by two chloride ions, [Pd(POX-COCH₃)Cl₂]. This compound has been identified

(11) It is interesting to note that the compound [Ni(HDMG)Cl₂] is strongly paramagnetic (μ_eff = 3.2 Bohr Magnetons). The compound is probably polymeric consisting of octahedra joined by chloride bridges.

by analysis and by its infrared spectrum, which exhibits a strong sharp carbonyl band[12] near 1790 cm.$^{-1}$.

When this acylated palladium(II) complex is treated with dilute, aqueous sodium hydroxide the ester is cleaved and the resulting compound appears to be [Pd(POX)Cl]. This compound probably is dimeric (V).

(V)
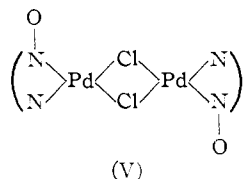
The reaction of [Pt(POX)$_2$] with acetyl chloride in chloroform solution produces a substance conforming approximately to the formulation [Pt-(POX–COCH$_3$)$_2$]Cl$_2$. This compound is not so easily purified as [Pd(POX–COCH$_3$)Cl$_2$], and the analyses are not ideal. The infrared spectrum of the product shows the band (at 1780 cm.$^{-1}$) characteristic of the oxime ester, and there seems to be little question that acylation has taken place.

On treatment with acetyl chloride the nickel(II) complex, [Ni(POX)$_2$], undergoes decomposition.

Insofar as the studies reported here reveal, the effect of coördination of an oxime group to a metal ion on the ease of formation and solvolysis of oxime esters and, conversely, the effect of acylation on the

stability and ease of dissociation of the oxime–metal ion bond are in keeping with expectations based on modern concepts of chemistry. Since both the metal ion and the acetyl group are electrophilic toward the oxime function, it is not surprising to find the effects mutually deleterious.

The apparent catalysis of the solvolysis of the oxime ester by metal ions provides an additional example of a type of observation which is rapidly approaching the status of a generalization of *ligand reactions.* At this time, there exist no broadly established generalizations in this realm, despite the fact that certain seemingly obvious generalizations may soon find experimental justification. In the case at hand, the acetyl group represents an uncoördinated bulky function adjacent to a coördinated function. Further, this *dangling* group is attached to the coördinated group by a link which is normally susceptible to solvolytic cleavage. In such circumstances, the lability toward solvolytic cleavage is expected to be enhanced by metal ion coördination so long as the bond undergoing cleavage is not a part of a chelate ring. Eichhorn and Bailar[13] first pointed out an example of this kind among Schiff base complexes.

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(12) O. Exner and M. Horak, *Collection Czechoslov. Chem. Comms.,* **24**, 2992 (1959).

(13) G. L. Eichhorn and J. C. Bailar, Jr., THIS JOURNAL, **75**, 2905 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA]

The Reaction of Metal Chelates. I. Halogenation of Metal Chelates of 1,3-Diketones[1,2]

BY JAMES P. COLLMAN, ROBERT A. MOSS,[3a] HENRY MALTZ[3b] AND CLIFFORD C. HEINDEL

Chlorine, bromine and iodine have been substituted directly on the chelate rings of metal chelates of 1,3-diketones. Bromine, iodine monochloride, and the N-halosuccinimides have been used as halogenating agents. Halogenated chelates containing chromium, cobalt, aluminum, iron and copper have been prepared by these direct substitution processes.

The chemical literature reveals many studies of metal acetylacetonates; however, these researches have focused on the physical properties, stereochemistry, bonding and synthesis of these chelates.[4] Very few reports record the chemical reactions of metal acetylacetonates.

Of the scattered reports concerning the chemical reactions of metal chelates, only a few describe processes in which the chelate molecule was altered, but the chelate rings were not destroyed. Chlorination of copper phthalocyanine yielded a hexadeca-

chlorinated copper phthalocyanine.[5] The copper chelate of 2-hydroxy-1-naphthaldehyde reacted with aqueous methylamine to form *cis* and *trans* isomers of the chelate of the N-methylimine.[6]

The first example of the direct substitution of a metal acetylacetonate is the reported bromination of chromium(III) acetylacetonate (I) by the action of bromine in chloroform.[7] The product of this reaction was reported to be tris-(3-bromo-2,4-pentanediono)-chromium(III) (II), but this substance was not fully characterized. Another isolated example of this type of reaction was reported recently.[8] Treatment of copper acetylacetonate (XIII) with N$_2$O$_4$ yielded a complex which was

(4) A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952.

(5) M. Shigemitsu, *J. Chem. Soc. Japan, Ind. Chem. Soc.,* **62**, 112 (1959).

(6) P. Pfeiffer and H. Glaser, *J. prakt. Chem.,* **153**, 265 (1939).

(7) H. Reihlen, R. Illig and R. Wittig, *Ber.,* **58B**, 12 (1925).

(8) C. Djoidjeric, J. Lewis and R. S. Nyholm, *Chem. and Ind. (London),* 122 (1959).