

fit to the experimental data, but approximate fits are provided with $k_{13} \approx 3 \times 10^5 M^{-1} \text{sec}^{-1}$, $k_{-13}/k_0K_{14} \approx 10^5 M^{-2}$, and $k_{0H}/k_0K_{14} \approx 10^3 M^{-1}$ for the Co(*trans*-[14]diene)(OH₂)₂³⁺-Cr²⁺ reaction, and $k_{13} \approx 5 \times 10^6 M^{-1} \text{sec}^{-1}$, $k_{-13}/k_0K_{14} \approx 10^6 M^{-2}$, and $k_{0H}/k_0K_{14} \approx 3 \times 10^3 M^{-1}$ for the Co(*teta*)(OH₂)₂³⁺-Cr²⁺ reaction. Thus physically possible rate parameters can be assigned (note that "estimates" are not possible) for this mechanism so that K_{13} is $\sim 10^{-4}$ for the former and $\sim 10^{-3}$ for the latter reaction. Therefore the maximum amount of reactants in the form of precursor complexes need be not more than 1 or 10%, respectively, even at pH 4.

Mechanism II.—Consider reactions 7, 12, 14, and 15. The appropriate steady-state approximations and some algebraic manipulation lead to

$$k_{\text{obsd}} = \frac{K_1}{[\text{H}^+]} \left\{ \frac{1 + a[\text{H}^+]}{b + c[\text{H}^+]} \right\} \quad (17)$$

where

$$a = \frac{k_{0H}k_{-14}}{(k_{0H} + k_{14})k_0}$$

$$b = \frac{(k_{-12} + k_{0H})}{k_{12}k_0(k_{0H} + k_{14})}$$

$$c = \frac{k_{-12} + k_{0H} + k_{14}}{k_{12}(k_{0H} + k_{14})}$$

Equation 17 is also consistent with (10). Using values of K_1 from Table I we find $a/c = 3.6 \times 10^6 M^{-1} \text{sec}^{-1}$ and $b = 8 \times 10^{-7} M^{-1} \text{sec}^{-1}$ for the Co(*trans*[14]diene)-(OH₂)₂³⁺-Cr²⁺ reactions and $a/c = 0.65 \times 10^7 M^{-1} \text{sec}^{-1}$ and $b = 1.2 \times 10^{-6} M^{-1} \text{sec}^{-1}$ for the Co(*teta*)-(OH₂)₂³⁺-Cr²⁺ reaction. For this mechanism assignment of possible rate parameters (again "estimates" are not possible) can result in $K_{12} \approx 10^{-2} M^{-1}$ for both reactions. Thus under our reaction conditions (*i.e.*, [reactants] $\leq 10^{-4} M$) this mechanism does not require more than 1% of the reactants be in the form of precursor complexes even at a pH of 4.

As noted above these two mechanisms are only marginally distinguishable by our experimental data with mechanism II being slightly preferred. Either mechanism is adequate to illustrate the significant features of our study. Other mechanisms can be proposed. However our work indicates that any proposed mechanism must involve precursor complex formation and some acid-base chemistry of the precursor intermediates.

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Phenylacetyl-Benzyl(carbonyl) Rearrangement at Iridium. A Kinetic Study

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The oxidative additions of variously substituted phenylacetyl chlorides to *trans*-chlorobis(triphenylphosphine)dinitrogeniridium(I) give five-coordinated phenylacetyliridium complexes, 1. These complexes rearrange in solution to six-coordinated benzyl(carbonyl) complexes, 2. The kinetics of this rearrangement have been investigated and mechanistic implications of the kinetic data are discussed.

Insertion or ligand migration processes are important in reactions which are homogeneously catalyzed by complexes of transition metals.² Information presently available on migration reactions is predominantly comprised of stereochemical and kinetic studies of the methyl- or acetylpentacarbonylmanganese and related systems.^{2,3} Considerable attention has been directed to determine whether these reactions proceed by CO insertion or methyl migration, but information on the actual migration step has been elusive. Since the rate-determining step in the conversion of acetylmanganese complexes to methyl(carbonyl)manganese complexes involves the loss of CO or another ligand and not the migration of the methyl moiety to manganese,² intimate details of the actual migration step have not been obtained from studies of the decarbonylation of acetylmanganese complexes. The rate-determining step in the decarbonylation of CH₃COMn(CO)₅ and in

the carbonylation of CH₃Mn(CO)₅ is presumably the formation of five-coordinated intermediates of manganese (d⁶ electronic configuration).² Such intermediates have not been detected or isolated for the manganese system. Herein, we report isolation of five-coordinated phenylacetyliridium(III) complexes (d⁶ electronic configuration) and kinetic studies of the rearrangement of these five-coordinated complexes to six-coordinated benzyl(carbonyl)iridium(III) complexes. Five-coordinated acyl complexes have been recently proposed⁴ as intermediates in the decarbonylation of complexes such as Ir(CO)₂Cl₂(CH₃)As(C₆H₅)₃.

Results and Discussion

The addition of various substituted phenylacetyl chlorides to suspensions of *trans*-chlorobis(triphenylphosphine)dinitrogeniridium(I)⁵ in benzene results in evolution of nitrogen and formation of red solutions from which fibrous orange crystals of the five-coordinated acyl complexes 1 are precipitated. These five-coordinated complexes which have been isolated and

(1) National Science Foundation Undergraduate Research Participant.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 578-609.

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(4) R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, **4**, 331 (1970).

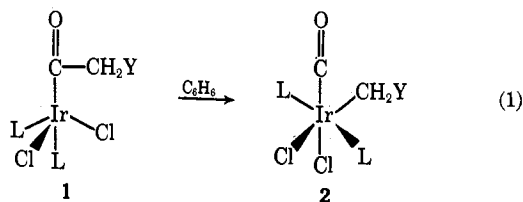
(5) J. P. Collman, M. Kubota, F. D. Vastine, J.-Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, **90**, 5430 (1968).

TABLE I
ANALYTICAL DATA

Compd	% C		% H		% Cl		Mol wt		Mp, °C
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found ^a	
IrCl ₂ (C(O)CH ₂ C ₆ H ₅)(P(C ₆ H ₅) ₃) ₂	58.2	58.4	4.22	4.21	7.81	7.74	907.85	872	138
IrCl ₂ (C(O)CH ₂ C ₆ H ₄ CH ₃)(P(C ₆ H ₅) ₃) ₂	58.69	60.12	4.27	4.50	7.70	7.68	920.87	930	134
IrCl ₂ (C(O)CH ₂ C ₆ H ₄ NO ₂)(P(C ₆ H ₅) ₃) ₂	55.52	57.44	3.81	3.95	7.45	7.26	951.85	775	153-154
IrCl ₂ (C(O)CH ₂ C ₆ F ₅)(P(C ₆ H ₅) ₃) ₂	53.02	53.64	3.24	3.34	7.11	7.09	996.79	700	162-163
IrCl ₂ (C(O)CH ₂ C ₆ H ₄ OCH ₃)(P(C ₆ H ₅) ₃) ₂	57.7	55.4	4.19	4.01	7.57	7.64			132 dec
IrCl ₂ (CH ₂ C ₆ H ₅)(CO)(P(C ₆ H ₅) ₃) ₂	58.2	59.0	4.22	4.32	7.81	7.72			200 dec
IrCl ₂ (CH ₂ C ₆ H ₄ CH ₃)(CO)(P(C ₆ H ₅) ₃) ₂	58.69	58.76	4.27	4.37	7.70	7.48			264 dec
IrCl ₂ (CH ₂ C ₆ H ₄ NO ₂)(CO)(P(C ₆ H ₅) ₃) ₂	55.52	56.36	3.81	3.96	7.45	7.51			220 dec
IrCl ₂ (CH ₂ C ₆ F ₅)(CO)(P(C ₆ H ₅) ₃) ₂	53.02	54.90	3.24	3.46	7.11	7.23			237-240 dec
		54.54		3.69					

^a Osmometric in benzene solution.

characterized are monomeric in benzene solution (see Table I). They undergo rearrangement in benzene and other solvents, presumably by migration of the benzyl group from CO to Ir, to give the *cis*-dichloro-benzyl(carbonyl) complexes **2**. This rearrangement



(L = P(C₆H₅)₃; Y = C₆F₅, *p*-O₂NC₆H₄, C₆H₅, *p*-CH₃-C₆H₄, *p*-CH₃OC₆H₄) is characterized by diminution of the acyl $\nu(\text{CO})$ band at 1670 cm⁻¹ with concomitant growth of $\nu(\text{CO})$ at 2040 cm⁻¹ (Table II). The assign-

TABLE II
INFRARED FREQUENCIES (CM⁻¹, NUJOL)

	$\nu(>\text{C}=\text{O})$	$\nu(\text{CO})$	$\nu(\text{Ir}-\text{Cl})$
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (C(O)CH ₂ C ₆ F ₅)	1662 (1668) ^a	320	
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (C(O)CH ₂ C ₆ H ₄ NO ₂)	1664 (1667)	319	
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (C(O)CH ₂ C ₆ H ₅)	1672 (1669)	316	
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (C(O)CH ₂ C ₆ H ₄ CH ₃)	1671 (1674)	316	
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (C(O)CH ₂ C ₆ H ₄ OCH ₃)	1672 (1674)	318	
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (CO)CH ₂ C ₆ F ₅	2053 (2052) ^a	300, 261	
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (CO)CH ₂ C ₆ H ₄ NO ₂	2051 (2044)	301, 260	
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (CO)CH ₂ C ₆ H ₅	2048 (2044)	302, 249	
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (CO)CH ₂ C ₆ H ₄ CH ₃	2044 (2043)	302, 258	
IrCl ₂ (P(C ₆ H ₅) ₃) ₂ (CO)CH ₂ C ₆ H ₄ OCH ₃	2044 (2043)	301, 253	

^a Spectra in dichloromethane solution.

ment of the *cis*-dichloro structure **2** is based on the far-ir data: $\nu(\text{Ir}-\text{Cl})$ 302 cm⁻¹ (Cl trans to CO) and 249-261 cm⁻¹ (Cl trans to benzyl).⁶ Compounds with structures having Cl trans to P would be expected to have $\nu(\text{Ir}-\text{Cl})$ in the 270-280-cm⁻¹ region. The facile spontaneous migration of the benzyl group in the five-coordinated complexes is attributed to the existence of the vacant sixth coordination site in **1**. Migration of the benzyl group from CO to Ir(III) has not been observed in six-coordinated phenylacetyliridium(III) complexes.⁷

Kinetic measurements using visible spectra show that the rates of reaction 1 are first order with respect to the iridium complex. Values of rate constants illustrating the effects of several variables are given in Table III. By observing the relative rates of migration of substituted benzyl derivatives, it is possible to examine the influence of electronic effects. The rate data clearly

(6) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969), and references therein.(7) M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, **93**, 1368 (1971).TABLE III
FIRST-ORDER RATE CONSTANTS FOR REARRANGEMENT OF PHENYLACETYL YCH₂C(O)Ir COMPLEXES TO BENZYL(CARBONYL) YCH₂Ir(CO) COMPLEXES

Y	Solvent	10 ⁴ k ₁ , sec ⁻¹	Temp, °C
C ₆ H ₅	Benzene	4.40	25.15
		7.09	30.05
		11.9	35.05
		18.8	40.20
		51.2	35.05
	Dimethylformamide	11.4	35.05
	Chlorobenzene	7.25	35.05
	Chloroform	4.54	35.05
	Tetrahydrofuran	9.32	35.05
	Benzene-triphenylphosphine (8.8 × 10 ⁻³ M)	7.07	35.05
Benzene-pyridine (8.7 × 10 ⁻³ M)			
<i>p</i> -CH ₃ OC ₆ H ₄	Benzene	9.19	30.00
		14.1	35.00
		21.0	40.00
		8.35	30.00
<i>p</i> -CH ₃ C ₆ H ₄	Benzene	14.8	35.00
		20.4	40.00
		3.90	30.00
<i>p</i> -O ₂ NC ₆ H ₄	Benzene	6.32	35.00
		11.7	40.00
		0.68	40.00
C ₆ F ₅	Benzene		

indicate that electron-releasing substituents promote migration and electron-withdrawing substituents retard it; *viz.*, rates decrease as Y is varied: *p*-CH₃-OC₆H₄ > *p*-CH₃C₆H₄ > C₆H₅ > *p*-O₂NC₆H₄ >> C₆F₅. The effect of para substituents on the rates can be described by a Hammett equation with a small negative regression constant, $\rho = -0.30$. There is a mild solvent effect, namely, a fivefold enhancement of rate in dimethylformamide compared to benzene.

The conversion of methyl(carbonyl)manganese to the acetylmanganese complex is 10,000 times faster in dimethylformamide than in mesitylene. This observation has been taken as evidence that the role of the solvent is to ease charge separation which occurs during the rearrangement. The possibility that the coordinating ability of the solvent may also be important has led to the concept of the "solvent-assisted migration."^{8,9}

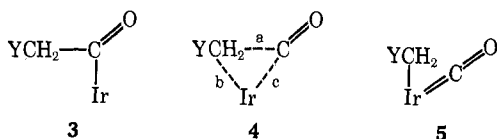
The retardation of the rates of migration of benzyl groups in the presence of triphenylphosphine or pyridine (Table III) may reflect competition by these ligands for the sixth site on **1**. Reversible additions of ligands to a site trans to the acyl group have been observed.⁷

(8) I. S. Butler, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **6**, 2074 (1967).(9) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **86**, 3994 (1964).

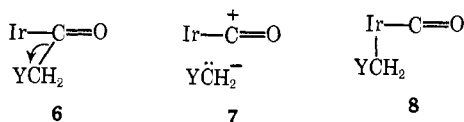
TABLE IV
ACTIVATION PARAMETERS FOR REARRANGEMENT OF PHENYLACETYL $YCH_2(O)Ir$ TO
BENZYL(CARBONYL) $YCH_2Ir(CO)$ COMPLEXES IN BENZENE

Y	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	Y	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
<i>p</i> -O ₂ NC ₆ H ₄	20.2 ± 1.6	-7.5 ± 4.0	<i>p</i> -CH ₃ C ₆ H ₄	16.3 ± 2.0	-18.9 ± 6.0
C ₆ H ₅	17.5 ± 0.5	-15.2 ± 1.5	<i>p</i> -CH ₃ OC ₆ H ₄	15.0 ± 0.5	-22.9 ± 1.5

The transition state for reaction 1 can be represented by **4** and its structure along the reaction coordinate between **3** and **5** may be governed by the extent of bond

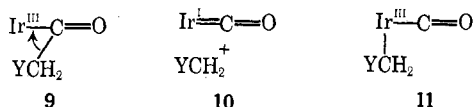


breaking a, bond making b, and π -bond formation c. As the five-coordinated acyl complexes **1** may be solvated, the formation of bond b may be preceded by or be simultaneous with a desolvation process. The present study which illustrates acceleration of the migration rate with increased electron density at the migrating carbon atom might suggest that the bond-making step b can be viewed as an electrophilic attack by the metal atom on the migrating carbon atom. While there is evidence indicating that the migrating group does not become free,² it is worthwhile to give consideration as to whether the migrating group moves with carbanionic or carbonium ion character. If electrophilic attack by the metal atom on the migrating carbon atom is important, examination of factors contributing to the process **6**–**8** may be considered. Elec-



tron-withdrawing substituents Y which favor formation of a carbanionic migrating group should lead to faster reactions. In the present study electron-withdrawing substituents were observed to cause retardation of the migration rate. However, this observation by itself cannot be taken as evidence against a pathway which involves electrophilic substitution.¹⁰ Electrophilic attack by the metal atom would be favored by a higher charge on the metal atom. The more facile acyl to alkyl conversions recently observed with iridium(I) complexes¹¹ compared with the iridium(II) complexes reported herein lend further support to arguments against the importance of the carbanionic character of the migrating group.

The alternative path **9**–**11** can account for the observed acceleration of rates by electron-releasing sub-



stituents. Such substituents may accelerate the rate by their stabilization of the migrating carbonium ion **10**. This carbonium ion may oxidatively add to the iridium(I) species to form **11**. A similar oxidative addi-

tion of a carbonium ion to a more reactive d¹⁰ species to form a d⁸ iridium(I)-alkyl species might account for the facile acyl-alkyl conversion at iridium(I) mentioned above.

The large variation of activation entropies (Table IV) with various benzylic substituents is of considerable interest. Since the kinetic studies have been conducted in benzene solution, contributions to the activation entropies due to differences in solvation of the reactants **1** are expected to be minimal. The variation of the entropies thus might reflect the position of the transition state along the reaction coordinate. The more negative entropies for reactions with the complexes with electron-releasing substituents which favor formation of a transition state with carbonium ion character as in **10** may be attributed to the greater ordering of solvent by charged species.

It has previously been noted¹² that the rate of migration of R from Mn to CO in $RMn(CO)_5$ decreases as $CH_3CH_2 > C_6H_5 > CH_3 > C_6H_5CH_2 \sim CF_3$. This trend in decreasing rates may be related to increasing Mn–R bond strengths.² If metal–R bond strengths are important in affecting the rates of migration of R from CO to the metal atom, the rate of migration of $C_6H_5CH_2$ from CO might be expected to be faster than the migration of CH_3 or C_6H_5 . The addition of acetyl chloride or benzoyl chloride to *trans*-dichlorobis(triphenylphosphine)dinitrogeniridium(I) leads directly to the methyl(carbonyl)- and phenyl(carbonyl)iridium complexes.⁷ There was no evidence of long-lived acetyl or benzoyl intermediates analogous to **1**. The reasons for the apparent rapid methyl and phenyl migrations in comparison to the slow benzyl migrations reported herein remain to be explored.

While the present study provides details of the migration step in the decarbonylation of a series of acyl complexes, it should be noted that the rate-determining step of homogeneously catalyzed decarbonylation reactions may be some step other than the migration step. The observation¹³ that electron-releasing groups on acyl halides tend to decrease the rate of homogeneously catalyzed decarbonylation thus may be attributed to the retardation of the formation of the acyl-metal intermediate.

Experimental Section

Chlorodinitrogenbis(triphenylphosphine)iridium(I) was prepared by standard methods.⁵ Para-substituted phenylacetyl chlorides were prepared from commercial samples of the corresponding carboxylic acids by reaction with thionyl chloride and were recrystallized or vacuum distilled as appropriate. Pentafluorophenylacetyl chloride was from Peninsular Chem-Research, Inc. Acyl halides were stored and handled in a Vacuum Atmospheres drybox. Solvents, except chloroform, were distilled and stored over molecular sieves. Infrared spectra were recorded on a Perkin-Elmer 621 instrument. Molecular weights were determined on a Mechrolab vapor-phase osmometer. Melting points were obtained on a Mel Temp apparatus and are uncorrected. Visible spectra and kinetic data were obtained on a

(10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1967, pp 563–571.

(11) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

(12) F. Calderazzo and F. A. Cotton, *Proc. Int. Conf. Coord. Chem.*, 7th, 1962, 296 (1962).

(13) K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, **90**, 99 (1968).

Cary 16 spectrometer fitted with a water-jacketed cell holder using 1-cm quartz cells. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., and Dr. F. Pascher, Bonn, Germany.

Five-Coordinated Substituted Phenylacetyliridium(III) Complexes (1).—To a suspension of 300 mg of chlorodinitrogenbis(triphenylphosphine)iridium(I) in 3 ml of benzene was added 0.5 ml (or 0.5 g) of the acyl halide. There was vigorous nitrogen evolution and a deep red solution formed. Within 3 min, the complexes 1 precipitated as fibrous, orange solids. The pentafluorophenyl complex was precipitated from the red solution by slow addition of ether. The products were washed with small amounts of cool benzene followed by about 20 ml of ether. The solids were then dried for at least 24 hr *in vacuo* and stored under nitrogen (yield about 80–90%). Infrared spectra showed the products thus obtained contained very little or none of the six-coordinated carbonyl complexes 2. Molecular weights were determined in benzene solution. The preparation of the unsubstituted phenyl complex was as previously described.⁷

***cis*-Dichloro(substituted benzyl)bis(triphenylphosphine)-carbonyliridium(III).**—To a suspension of 300 mg of the dinitrogen complex in 4 ml of benzene was added 0.5 ml (or 500 mg) of the acyl halide and the resulting orange mixture was stirred for 24 hr at room temperature. In the case of the pentafluorophenyl complex it was necessary to reflux the orange mixture for 2 hr.

Filtration gave the colorless products (about 90% yield) which were recrystallized from benzene-*n*-hexane.

Kinetic Studies.—The reactions of the five-coordinate acyl complexes were followed by monitoring the decay of the absorption band at 480 nm for all the compounds. Plots of $\ln(A - A_\infty)$ vs. time were linear with correlation coefficients in the range -0.997 to -0.999 . The rate constants in Table III are in each case the average of three or four separate determinations. Temperatures were held constant within $\pm 0.05^\circ$. Exposure of the reaction solutions to air was found to have no effect on the results. Changes in concentration of the acyl complex in the range 4–12 mg/10 ml of solvent had no effect on the rate constant. Kinetic runs for the phenylacetyl complex in the presence of an excess of phenylacetyl chloride (50:1 phenylacetyl chloride to complex) or of an excess of triphenylphosphine (20:1 $P(CrH_3)_3$ to complex) also gave linear $\ln(A - A_\infty)$ vs. time plots.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
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Studies on Coordination Compounds of Silver(II). V.¹ The Preparation and Characterization of New Pyrazine and Pyrazine Carboxylate Complexes and Some Related Silver (I), Copper(II), Cobalt(II), and Nickel(II) Derivatives

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Pyrazine and several pyrazine carboxylic acids have been found to stabilize silver(II). Whereas bis(pyrazine-2-carboxylato)-silver(II) is magnetically dilute and isostructural with square-planar bis(pyridine-2-carboxylato)silver(II), the pyrazine complex $[Ag(pyzo)_2]_2S_2O_8$ contains polymeric square-planar cations and has magnetic properties (300–80°K) which can be interpreted in terms of an antiferromagnetic exchange interaction. Pyrazine-2,3-dicarboxylic acid forms an unusual silver complex which contains both silver(I) and silver(II) species. It is formulated as $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$ with an Ag(I):Ag(II) ratio of 2:1. The versatile complexing properties of this ligand are demonstrated by the preparation and structural elucidation of the related cobalt(II), nickel(II), copper(II), and silver(I) derivatives. Related studies on the silver(II)-pyrazine-2,3,5-tricarboxylic acid system are also described.

Introduction

From our studies on pyridine carboxylates of silver(II),^{1,4–6} we established the stereochemistry of these derivatives in the hope of better understanding this relatively rare oxidation state and enabling a meaningful comparison to be made with the more common and stable copper(II) species. This oxidation state is usually unstable with respect to reduction to silver(I), and, indeed, silver(II) compounds can be important oxidants in organic chemistry. Also silver(II) species

have been postulated as intermediates in kinetic studies involving silver(I)-catalyzed oxidations.⁷

Although most silver(II) complexes which are known are essentially insoluble in polar and nonpolar solvents, a fact which aids their isolation, some solubility in aqueous media is sometimes observed although such solutions are only stable for short periods of time. Thus the partial solubilities of silver(II) bis(pyridine-2,6-dicarboxylate) monohydrate and silver(II) bis(pyridine-2,3-dicarboxylate) dihydrate in water enabled us to isolate single crystals of these compounds. X-Ray analyses have now been completed^{1,5,8} and provide a basis for interpreting the properties of other derivatives of silver(II).

Since pyrazine⁸ and the pyrazinecarboxylic acids

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