Reactions of Coordinated Ligands. XX. Cobalt(III)-Promoted Hydrolysis of Glycine *t*-Butyl Ester

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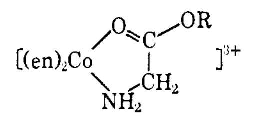
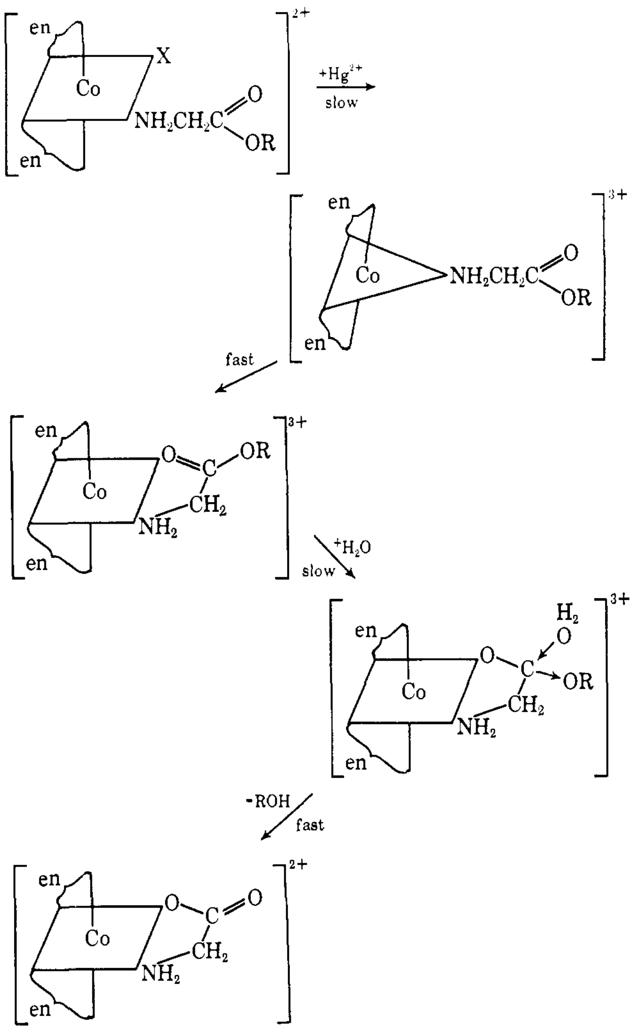
Abstract: The kinetics and mechanism of the cobalt(III)-ion-promoted hydrolysis of glycine *t*-butyl ester have been studied in water in the presence of various concentrations of sodium perchlorate, and in methanol–water mixtures. In acid solution, mercury(II) ion is used to accelerate the removal of the coordinated bromide from the complex, $[Co(en)_2\{NH_2CH_2CO_2C(CH_3)_3\}Br]^{2+}$, resulting in hydrolysis of the ester and formation of glycinatobis(ethylenediamine)cobalt(III) as the final product. The intermediate, chelated-ester complex has been observed in the course of the hydrolysis. The acceleration of the hydrolysis rate by Co(III) is less by a factor of $\sim 10^4$ for the *t*-butyl ester than for the ethyl ester. In contrast to the behavior of other glycine esters, the rupture of the glycine *t*-butyl ester takes place at the alkyl–oxygen bond. This conclusion is confirmed by oxygen-18 exchange data.

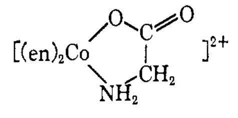
Recently the cobalt(III) promotion of the hydrolysis of amino acid esters,[1–3] amino acid amides, and small peptides[4–7] has been studied in a number of laboratories. Alexander and Busch designed compounds suitable for such studies and identified the product and reactive intermediate involved in the process. On the basis of the results obtained and from kinetic studies, they have proposed a mechanism for the promoted hydrolysis. Mercury(II) ion reacts with *cis*-$[Co(en)_2(NH_2CH_2COOR)X]^{2+}$, where R is CH_3, C_2H_5, or *i*-C_3H_7 and X is Br or Cl, in aqueous solution to yield a five-coordinate highly reactive intermediate[8] (Scheme I). The vacated position in the coordination sphere of the cobalt(III) is subsequently filled by the carbonyl oxygen of the ester to yield the chelated ester complex



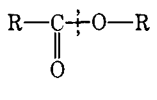
Scheme I



In the absence of other nucleophiles, water attacks the positive center, the carbonyl carbon, resulting in hydrolysis of the ester and formation of



The authors also reported that the hydrolysis of the chelated methyl, ethyl, or isopropyl ester is subject to general nucleophilic or general base catalysis,[1] and that it is the acyl–oxygen bond that breaks.



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}\vdots O{-}R}$$

Very recently, Buckingham, Foster, and Sargeson[2] have provided more evidence relevant to hydrolysis of these esters by isolation of the intermediate chelated ester complex and by use of ^{18}O-tracer techniques. The mechanism and point of cleavage in these reactions are

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(1) M. D. Alexander and D. H. Busch, *J. Amer. Chem. Soc.*, 88, 1130 (1966).

(2) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *ibid.*, **90**, 1032 (1968); **91**, 3451, 4102 (1969).

(3) R. W. Hay, M. L. Jansen, and P. I. Cropp, *Chem. Commun.*, 621 (1967).

(4) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 2772 (1967).

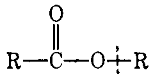
(5) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 4540 (1967).

(6) J. P. Collman and E. Kimura, *ibid.*, **89**, 6096 (1967).

(7) D. A. Buckingham, J. P. Collman, D. A. R. Happer, and L. G. Marzilli, *ibid.*, **89**, 1082 (1967).

(8) F. A. Posey and H. Taube, *ibid.*, **79**, 255 (1957).

well established. However, previous investigations have not been directed toward the metal-promoted hydrolysis of the amino acid *t*-butyl esters in acidic solution. It is to be expected that these structures may afford a different mechanism in which the alkyl–oxygen bond breaks.



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O\,\vdots\,R}$$

It has long been known that the acid hydrolyses of ordinary organic esters involves acyl–oxygen bond breakage, the activated complex in the hydrolysis involving nucleophilic attack at the carbonyl carbon of the ester.[9] From the known reactivities of saturated carbon compounds toward nucleophilic displacements, the conjugate acid of an ester might cleave to form the acid and a carbonium ion, if the carbonium ion is sufficiently stable. Cohen and Schneider presented a convincing argument for a mechanism of this sort in the acid hydrolysis of *t*-butyl benzoate, and it seems probable that the majority of the esters of tertiary alcohols behave in the same way.[10]

On the basis of the several considerations mentioned above, one might expect that the metal-ion-promoted hydrolysis of glycine *t*-butyl ester would proceed *via* a mechanism involving cleavage of the alkyl–oxygen bond.

In the present investigations, the glycine *t*-butyl ester complex, $[Co(en)_2\{NH_2CH_2CO_2C(CH_3)_3\}Br]Br_2$, has been prepared by a procedure related to that reported earlier.[11] Cobalt(III)-promoted hydrolysis has been studied kinetically and by means of oxygen-18 exchange measurements.

Experimental Section

Materials. Glycine methyl and ethyl ester hydrochlorides were obtained from Aldrich Chemical Co. These reagents were used without further purification.

Glycine isopropyl ester hydrochloride was obtained as follows. Glycine (10 g) was dissolved in an isopropyl alcohol-hydrochloric acid solution (200 ml) and refluxed for 24 hr. After evaporation to dryness at reduced pressure the process was twice repeated and the remaining syrup was induced to crystallize by repeated evaporation with isopropyl alcohol. Recrystallization from isopropyl alcohol–ether gives glycine isopropyl ester hydrochloride. *Anal.* Calcd for $NH_2CH_2CO_2CH(CH_3)_2 \cdot HCl$: C, 39.10; H, 7.88; N, 9.11. Found: C, 39.3; H, 7.65; N, 9.33.

Glycine *t*-butyl ester hydrochloride was prepared according to the method of Anderson and Callahan[12] from isobutylene. The compound was recrystallized twice from ether and dried *in vacuo* overnight at $Mg(ClO_4)_2$ at room temperature, mp 137–139°. *Anal.* Calcd for $NH_2CH_2CO_2C(CH_3)_3 \cdot HCl$: C, 43.0; H, 8.4; N, 8.4. Found: C, 43.0; H, 7.9; N, 8.4.

A mercury(II) perchlorate solution, containing 2.26 M $Hg(ClO_4)_2$ and 3.58 M $HClO_4$, was prepared by treating 21.7 g of mercury(II) oxide (yellow, reagent grade) with 37 ml of 60% perchloric acid CP grade), which had been standardized, filtering off the impurity and diluting the resulting solution to 40 ml. The solution was standardized by titrating potentiometrically with sodium hydroxide solution to determine the sum of the mercury(II) ion concentration plus the hydrogen ion concentration. The hydrogen ion concentration was determined by titrating with sodium hydroxide in the presence of sodium bromide to complex with the mercury(II) ion, The mercury(II) ion concentration was determined by difference.

A sodium perchlorate stock solution (4.97 M) was prepared by treating 417.6 g (5 M) of sodium bicarbonate (reagent grade) with an appropriate amount of 60% perchloric acid, which had been standardized, followed by boiling the solution for 20 min to drive off carbon dioxide and then diluting to a volume of 1 l. The pH of the solution was checked (pH 6.8) with a Beckman Model G pH meter.

For ^{18}O exchange, 10 atom % ^{18}O-enriched water was obtained from Bio-Rad Laboratories, Richmond, Calif.

$[Co(en)_2(NH_2CH_2CO_2R)Br]Br_2$, where R is CH_3, C_2H_5, *i*-C_3H_2, or *t*-C_4H_9, was prepared according to the method of Alexander and Busch.[11] Each compound was recrystallized twice from water and dried overnight *in vacuo* over $Mg(ClO_4)_2$ at 50°. *Anal.* Calcd for $[Co(NH_2CH_2CH_2NH_2)_2(NH_2CH_2CO_2CH_3)Br]Br_2$: C, 17.6; H, 4.87; N, 14.7. Found: C, 17.5; H, 4.75; N, 14.6. Calcd for $[Co(NH_2CH_2CH_2NH_2)_2(NH_2CH_2CO_2C_2H_5)Br]Br_2$: C, 18.4; H, 4.80; N, 13.5. Found: C, 18.7; H, 4.80; N, 14.0. Calcd for $[Co(NH_2CH_2CH_2NH_2)_2(NH_2CH_2CO_2C_3H_7)Br]Br_2$: C, 20.2; H, 5.08; N, 13.1. Found: C, 20.4; H, 5.84; N, 13.1. Calcd for $[Co(NH_2CH_2CH_2NH_2)_2(NH_2CH_2CO_2C_4H_9)Br]Br_2$: C, 21.8; H, 5.31; N, 12.7. Found: C, 21.8; H, 5.17; N, 12.4.

$[Co(en)_2(NH_2CH_2CO_2)]Cl_2 \cdot H_2O$ was prepared according to the method of Alexander and Busch,[11] recrystallized from water, and dried overnight *in vacuo* over $Mg(ClO_4)_2$ at 50°. *Anal.* Calcd for $[Co(NH_2CH_2CH_2NH_2)_2NH_2CH_2CO_2]Cl_2 \cdot H_2O$: C, 21.1; H, 6.48; N, 20.5. Found: C, 21.4; H, 6.60; N, 20.8.

Kinetic Measurements. A Cary 14 recording spectrophotometer and a Beckman DU spectrophotometer, each equipped with a thermostated cell compartment, were used for the kinetic measurements; 1-cm quartz and glass cells were used. An Eastman Kodak timer was used in all cases, Kinetic experiments were carried out at 25.0 ± 0.1°, ionic strengths from 0.2 to 1, in water or methanol–water mixtures. The pH of the solutions was controlled at 1. All aqueous solutions were made up to the desired ionic strengths with sodium perchlorate. The initial ester concentrations were in the range from 2×10^{-3} to 6×10^{-3} M. Initial $Hg(ClO_4)_2$ concentrations were in the range from 6×10^{-2} to 1×10^{-1} M. The wavelength of 487 mμ was chosen for the studies. This is the absorption maximum of the product, and at this wavelength the ratio of the molar absorbancy index of product to reactant is large. Rate constants were obtained as pseudo-first-order parameters from the slopes of plots of log $(A - A_\infty)$ *vs.* time. A is the absorbancy at time t, and A_∞ is the absorbancy of the product of the reaction.

A weighed amount of complex was dissolved in a certain volume of sodium perchlorate stock solution and equilibrated for temperature to 25.0 ± 0.1° in a constant-temperature bath. At zero time, the desired amount of $Hg(ClO_4)_2$ stock solution, also at 25.0°, was syringed into the solution. The resulting solution was rapidly mixed and transferred to the cell for spectral measurements. After measuring for 40 min, the solution in the cell compartment of the spectrophotometer was transferred back to the constant-temperature bath at 25.0° to allow the reaction to proceed for the next 2 hr (kinetic data indicate the reaction has reached completion by this time in each case). The spectra of the ultimate product solutions were obtained except for the glycine *t*-butyl ester complex. In the reaction of the glycine *t*-butyl ester complex with Hg^{2+} ion, a yellow precipitate was observed after a reaction time of 35 min. The spectra of these solutions were measured after they had stood for 2 days to allow complete precipitation and after removal of the yellow precipitate.

For studies in aqueous methanol mixtures a weighed amount of complex was dissolved in a certain volume of H_2O-CH_3OH stock solution at 25° and the solution was stirred under nitrogen. At the initiation of the reaction, the desired amount of $Hg(ClO_4)_2$ stock solution, also at 25°, was syringed into the solution. The resulting solution was rapidly transferred to the cell of the spectrophotometer for spectral measurements. The spectra of the products of the reaction were obtained as described previously. Only a single kinetic run was obtained from one stock solution because the complex is unstable in methanol.

The reaction of mercury(II) with the *t*-butyl ester complex was also observed by means of the carbonyl region of the infrared spectrum as described earlier for the other esters.[1]

Isotopic Studies. The isotopic compositions were determined on carbon dioxide with an AEI MS-10 mass spectrometer. This was accomplished by distilling a known amount of the recovered water under vacuum into a sample bulb and shaking with an appropriate amount of carbon dioxide. Cohn and Urey[13] reported

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(9) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, N. Y., 1965, p 314.

(10) S. G. Cohen and A. Schneider, *J. Amer. Chem. Soc.*, **63**, 3382 (1941).

(11) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, **5**, 602, 1590 (1966).

(12) G. W. Anderson and F. M. Callahan, *J. Amer. Chem. Soc.*, **82**, 3359 (1960).

$$C^{16}O_2 + H_2{}^{18}O \overset{K}{\rightleftharpoons} C^{16}O^{18}O + H_2{}^{16}O$$

that the time necessary to reach the complete equilibrium at room temperature is 3 hr. The value of the equilibrium constant, K, is reported by the Dostrovsky and Klein[14] to be 2.005. The isotopic composition of the water was calculated from that of the carbon dioxide using the formula of Dostrovsky and Klein.

The cobalt(III) complexes used in this investigation are $[Co(en)_2(glyOR)Br]Br_2$, where R is CH_3, t-C_4H_{19}, and $[Co(en)_2glyO]Cl_2 \cdot H_2O$.

(a) Isotopic labeling in the product of hydrolysis of $[Co(en)_2(glyOR)Br]Br_2$ was determined as follows. A weighed amount (~1.5–2 g) of the ester complex was suspended in 2 ml of oxygen-enriched water (10 atom % $H_2{}^{18}O$) which had been acidified (pH ~1) by using 70% perchloric acid. This was mixed with an appropriate amount of $AgClO_4$, where [complex]:[Ag^+] = 1:3. After the mixture had been stirred for 3 hr, the water-insoluble silver bromide was removed by filtering. The filtrate, which was collected in a sample tube, was evaporated to dryness under vacuum. The oxygen-enriched water was recovered. In order to remove the excess of oxygen-enriched water completely from the complex, the residue was redissolved in 2 ml of normal distilled water and evaporated to dryness three times. Then the orange solid was dried *in vacuo* overnight at 90°. The water-free and weighed sample of orange solid was dissolved in 1 ml of 2 M NaOH of normal isotopic composition. The solution was stirred at 50° for 10 hr, then acidified with 70% $HClO_4$ (pH ~3). The water to be analyzed was distilled into an evacuated and weighed sample bulb having a breakseal. Carbon dioxide (1 mmol) was added to the sample bulb which contained the known amount of recovered water. The mixture was then shaken vigorously at room temperature for 12 hr to permit complete equilibration.[13,14] In order to separate the carbon dioxide from water, the mixture was frozen at −78°; the carbon dioxide was sublimed into another sample bulb which was evacuated and cooled at liquid nitrogen temperature. The carbon dioxide was then introduced into the mass spectrometer at room temperature. From the ratio of the m/e peaks 44 and 46 ($C^{16}O^{16}O$ and $C^{16}O^{18}O$) and the equilibrium constant for the carbon dioxide–water exchange reaction, the atom percentage of ^{18}O in the sample was calculated.

(b) Several experiments were also performed using Hg^{2+} as the promoting halophile. This required a more cumbersome procedure. A mixture of $[Co(en)_2\{NH_2CH_2CO_2(CH_3)_3\}Br]Br_2$ (0.777 g, 1.41 mmol) and silver perchlorate (0.585 g, 2.82 mmol) was suspended in 2 ml of oxygen-enriched water (10 atom % $H_2{}^{18}O$). This is just enough Ag^+ to remove the ionic Br^-. The mixture was stirred, and after 30 min the insoluble silver bromide (yellow) was removed by filtering and washed with oxygen-enriched water (10 atom % $H_2{}^{18}O$) until the combined filtrates (red-violet) and washings totaled about 3 ml. A solution containing $HgClO_4$ (0.646 g of HgO and 0.65 ml of 60% $HClO_4$) was added with stirring. The color changed very rapidly from the red-violet of the bromo complex to the orange of the expected product. The visible spectrum of the solution was measured (λ_{max} 487 and 346 mμ) and found to correspond to the spectrum of the chelated glycine ester complex. The solution was stirred at room temperature for 2.5 hr. It was then diluted to 10 ml with normal water. Concentrated sodium hydroxide was added dropwise to precipitate a yellow solid, HgO (which changes to deep red). The final solution was at pH 4 (Beckman Model G pH meter). The insoluble mercury oxide was removed by filtering and washed with normal distilled water until the combined filtrates and washings totaled about 12 ml. The filtrate was collected in a sample tube and evaporated to dryness under vacuum. In order to remove the excess of oxygen-enriched water completely from the complex, the residue was redissolved in 4 ml of normal distilled water, undissolved solids were filtered, and the solution was evaporated to dryness. This procedure was repeated three times. The orange solid from the third cycle was dried *in vacuo* overnight at 90°. The water-free orange solid was dissolved in 1.2 ml of 2 M NaOH in solvent of normal isotopic composition. The solution was stirred at 50° for 6 hr and then acidified with 70% $HClO_4$ (pH ~3); the water was distilled into an evacuated and weighed sample bulb. CO_2 (1 mmol) was then added into the bulb. The procedure for the equilibration of the sample with carbon dioxide and the mass spectrometric determination is analogous to that described previously.

(c) $[Co(en)_2(glyO)]Cl_2$. A weighed amount of the glycinato complex was dissolved in 1 ml of 2 M oxygen-enriched alkaline solution which was prepared by dissolving solid NaOH in oxygen-enriched water (10 atom % $H_2{}^{18}O$). The resulting solution was stirred at 50° for 10 hr. After the solution was acidified with 70% $HClO_4$ (pH ~3), the water was distilled and recovered on a vacuum line. In order to remove the oxygen-enriched water completely from the complex, the residue was redissolved in 2 ml of normal distilled water and evaporated to dryness three times. The residual orange solid was dried *in vacuo* overnight at 90°. The water-free orange solid was then dissolved in 1 ml of 1 or 2 M NaOH of normal isotopic composition. The resulting solution was stirred at 50° for 10 hr. After the solution was acidified with 70% $HClO_4$ (pH ~3), the water was distilled into an evacuated and weighed sample bulb. CO_2 (1 mmol) was then added into the bulb. The procedure for the equilibration of the sample with carbon dioxide and the mass spectrometer determination is analogous to the procedure described above. One disadvantage of these methods is that highly oxygen-18 enriched water is required.

Results and Discussion

The method used for the preparation of the glycine t-butyl ester complex, $[Co(en)_2\{NH_2CH_2CO_2C(CH_3)_3\}Br]Br_2$, is identical with that reported earlier for derivatives of other esters,[11] and the visible and infrared spectra of the new complex bear very close resemblances to the spectra of the methyl-, ethyl-, and isopropyl-amino acid ester complexes. One band is observed in the visible spectrum (λ_{max} 545 mμ = 82) and a very intense charge-transfer band occurs in the ultraviolet, spilling over into the visible region where it completely obscures the high-frequency d-d band. In the infrared spectrum of the complex there appears a sharp and intense band at 1744 ± 5 cm^{-1} which is attributed to the stretching mode of the carbonyl group of the ester. The complex is stable in aqueous solution, even at a low pH, for several hours. Changes in the visible spectrum show that the complex is unstable in methanol. The stability of the complex increases with the percentage of water contained in methanol–water mixtures.

During the reaction of the bromoglycine t-butyl ester complex, $[Co(en)_2\{NH_2CH_2CO_2C(CH_3)_3\}Br]Br_2$, with mercury(II) ion in water, the visible absorption spectrum changes with time in much the same manner as has been reported for the CH_3, C_2H_5, and $CH(CH_3)_2$ ester derivatives.[1] The velocity of this Hg^{2+} promotion of the removal of the coordinated bromide is indicated by the very rapid color change from the red-violet of the bromo complex to the orange typical of the intermediate.[15] The visible spectra are very similar when the bromoglycine t-butyl ester complex reacts with Hg(II) ion in CH_3OH–H_2O mixtures.

The spectrum of the hydrolysis product in the CH_3OH–H_2O mixtures, or in H_2O, indicates that the glycinato complex is formed as the final product, in close similarity to the behavior of the methyl, ethyl, and isopropyl ester complexes. It has also been observed that the rate of reaction is insensitive to a several-fold

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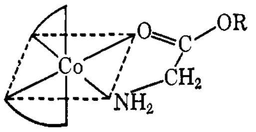
(13) M. Cohn and H. C. Urey, *J. Amer. Chem. Soc.*, **60**, 679 (1938).

(14) I. Dostrovsky and F. S. Klein, *Anal. Chem.*, **24**, 414 (1952).

(15) Difficulties were encountered because of the appearance of a yellow precipitate during the course of the hydrolysis. The infrared spectrum and the elemental analysis data of the yellow precipitate show that it contains much carbon and perchlorate, and a trace of hydrogen. The yellow precipitate is insoluble in H_2O, decomposed by nitric acid, and stable *in vacuo* at 50°. A powerful explosion occurred when the yellow precipitate was accidentally mixed with an organic liquid $[(CH_3)_2C(Br)CO_2CH_2C(CH_2OH)(CH_3)_2]$ at room temperature. It was also observed that the rate of formation of the yellow precipitate depends on the percentage of CH_3OH contained in the CH_3OH–H_2O mixture, increasing as the proportion of CH_3OH increases. Since the yellow precipitate was also obtained when mercury(II) perchlorate was mixed with aqueous t-butyl alcohol (10%) at pH 1, it was concluded that this product is not of significance to the reactions of principal interest.

change in hydrogen ion concentration, *i.e.*, in the concentration range 0.05–0.2 *N*.

The visible spectrum of the intermediate has maxima at 489 and 348 mμ with molar extinction coefficients of 91 and 96, respectively. Two bands are observed in the carbonyl stretching region, at 1640 and 1625 cm^{-1}, in the infrared spectrum in D_2O solvent during the course of reaction. The band at 1640 cm^{-1} arises from the carbonyl stretching mode of the glycinato complex which forms as the final product. A comparison of the rate at which the band at 1625 cm^{-1} first appears and then disappears with the kinetic data obtained spectrophotometrically confirms that the band is associated with the intermediate. It is concluded, therefore, that on removal of the bromide ligand, the carbonyl oxygen of the dangling ester function takes the vacated position (structure I). This is followed by hydrolysis of the chelated ester to yield the product $[Co(en)_2(NH_2CH_2CO_2)]^{2+}$, structure II.[2]



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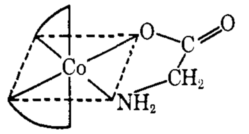

II

Table I. First-Order Rate Constants for the Reaction of *cis*-$[(Co(en)_2(NH_2CH_2CO_2R)Br]^{2+}$ with Mercury(II) Ion in Water with Various Concentrations of Sodium Perchlorate[a]

R	[Complex], $M \times 10^3$	$[Hg^{2+}]$, $M \times 10^2$	$[NaClO_4]$, M	Ionic strength (μ)	k_{obsd}, min^{-1}
C_2H_5	4.17	9.30	0	0.37	0.472 ± 0.006
	4.17	9.30	0.298	0.67	0.395 ± 0.007
	4.17	9.30	0.696	1.07	0.350 ± 0.004
i-C_3H_7	4.20	9.30	0	0.37	0.097 ± 0.012
	4.20	9.30	0.298	0.67	0.073 ± 0.006
	4.20	9.30	0.696	1.07	0.068 ± 0.001
t-C_4H_9	4.23	6.58	0	0.30	0.049
	3.81	6.58	0	0.30	0.055
	4.12	9.30	0	0.37	0.054
	3.02	6.58	0.298	0.60	0.066
	4.12	9.30	0.298	0.67	0.063
	4.12	9.30	0.298	0.67	0.078
	3.54	6.58	0.696	0.98	0.076
	3.49	6.58	0.696	0.98	0.074
	4.12	9.30	0.696	1.07	0.069
	4.12	9.30	0.696	1.07	0.081
	3.90	6.58	0	0.40	0.059[b]
	3.48	6.58	0	0.40	0.058[b]

[a] $[H^+] = 0.10$ *M*, 25°, wavelength 487 mμ. [b] In $[H^+] = 0.2$ *M*.

Table II. First-Order Rate Constants for the Reaction of *cis*-$[Co(en)_2(NH_2CH_2CO_2R)Br]^{2+}$ with Mercury(II) Ion in Various MeOH–H_2O Mixtures[a]

R	[Complex], $M \times 10^3$	% MeOH	k_{obsd}, min^{-1}
CH_3	2.34	94	0.218 ± 0.006
	2.39	89	0.393 ± 0.007
C_2H_5	2.43	94	0.142 ± 0.004
	2.42	89	0.285 ± 0.003
i-C_3H_7	2.47	94	0.038 ±0.003
	2.32	89	0.057 ± 0.001
t-C_4H_9	3.09	98	0.614
	2.87	98	0.623
	4.58	89	0.563
	3.23	89	0.568
	3.30	89	0.565

[a] $[H^+] = 0.10$ *M*, 25.0°, $[Hg^{2+}] = 6.58 \times 10^{-2}$ *M*, wavelength 487 mμ.

The rates of the cobalt(III)-promoted acid hydrolysis of glycine ester complexes have been determined in water in the presence of various concentrations of sodium perchlorate (Table I), and in methanol–water (Table II). The rate of the hydrolysis is first order with respect to complex. The data show that sodium perchlorate gives a small positive salt effect on the metal-promoted hydrolysis of *t*-butyl ester. Conversely, sodium perchlorate gives a small negative salt effect on the hydrolysis of the methyl, ethyl, and isopropyl esters. Kinetic salt effects have been observed in a number of reactions of organic *t*-butylcarboxylic acid derivatives which involve fission of the alkyl–oxide bond. For example, the acid hydrolyses of *t*-butyl acetate[16] and triphenylmethyl benzoate[17] exhibit slight positive salt effects. In the acid hydrolysis of ordinary esters and lactones,[18,19] which involves fission of the acyl–oxygen bond, both positive and the negative salt effects have been observed, depending on the particular electrolyte added.

Data on the rates of hydrolysis at 25° in CH_3OH–H_2O mixtures containing mercury(II) perchlorate and 0.1 *M* perchloric acid are given in Table II. The rates of hydrolysis of the glycine methyl, ethyl, and isopropyl ester complexes conform to the generalization that the rate of saponification of an ester decreases as the polarity of the solvent is decreased. This reflects the data obtained from the hydrolysis of ordinary esters and lactones which involve acyl–oxygen fission.[20]

A contrasting behavior is found in the hydrolysis of the glycine *t*-butyl ester complex. The rate of the saponification of this ester increases as the polarity of the solvent is decreased. This may be correlated with solvent effects on related reactions.[21–23] If the intermediate or transition state of the Co(III)-promoted hydrolysis of *t*-butyl ester is as indicated in Scheme II, the positive charge, which is localized on the cobalt complex ion before reaction, becomes dispersed over a somewhat larger area in the transition state. Since the charge density has been thus (temporarily) diminished, the transition state requires less solvation than the reactants. In this respect such a reaction is similar to that between ions of opposite charge and should therefore be more rapid in less polar solvents.[9]

In the present investigation of the cobalt(III)-promoted ester hydrolysis in media of different ionic strengths and in different solvent mixtures, the range of measurement is not sufficiently extensive to permit detailed conclusions to be drawn. However, the fact that both the salt effects and the solvent effects appear to act oppositely toward the rates of the hydrolysis of glycine *t*-butyl ester, as compared to the other glycine

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(22) E. A. Brande, *ibid.*, 443 (1944).

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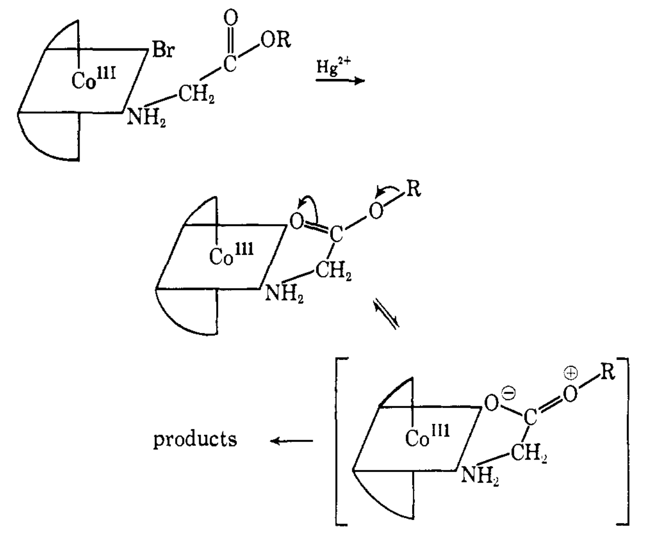
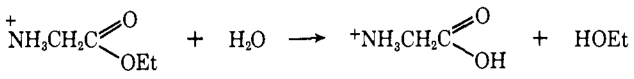
Scheme II



esters, suggests that the reaction mechanism is different in the two cases.

The extent to which the cobalt(III) ion accelerates the hydrolysis of glycine *t*-butyl ester is of interest. Although ideal data are not available, Skrabal and Hugltz[24] reported the rate of acid-catalyzed hydrolysis of *t*-butyl acetate (2.78 × 10^{-4} min^{-1} at pH 1 and 25°). This is approximately 100-fold slower than the rate of cobalt(III)-promoted hydrolysis of the glycine *t*-butyl ester (Table I). In contrast, the acceleration of the hydrolysis rate of the ethyl ester of glycine by cobalt(III) exceeds 10^6-fold. The rate of the reaction below (which is applicable at pH 1) is 3 × 10^{-9} sec^{-1} at 25°.[25]



$$\overset{+}{N}H_3CH_2C(=O)OEt + H_2O \longrightarrow {}^{+}NH_3CH_2C(=O)OH + HOEt$$

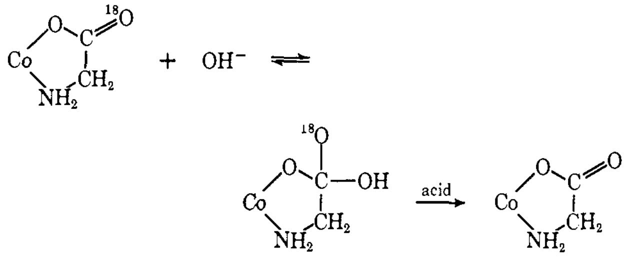
In contrast, the rate for the cobalt complex is about 8 × 10^{-3} sec^{-1} (Table I). Since the reactive intermediates for the two reactions have the same structures, the vastly different catalytic effectiveness of the metal ion may be related to different reaction pathways for the two systems.

Isotopic exchange experiments were performed with glycine methyl and *t*-butyl ester complexes in ^{18}O-enriched H_2O (10 atom %$H_2{}^{18}O$) during the cobalt(III)-ion-promoted hydrolysis. The purpose was to determine the position of C–O bond cleavage. Two kinds of systems were studied by isotopic enrichment methods: (1) ester hydrolysis, to investigate the position of the bond cleavage, with respect to the carbonyl group (most of these reactions were initiated by Ag^+ ion[26] and carried out in ^{18}O-enriched water at pH 1); (2) oxygen exchange for $[Co(en)_2(NH_2CH_2CO_2)]^{2+}$, to determine the ^{18}O isotope enrichment which appears in the carbonyl group of the reaction product. This study was required for analytical purposes. The exchange was carried out in isotopically normal alkaline solution. The solution was then acidified, and the sample of water which was recovered from the solution was equilibrated with isotopically normal CO_2. Finally, the CO_2 was introduced into the mass spectrometer.

In the case of the glycine methyl ester complex, the carbonyl group became labeled during the course of the hydrolysis reaction. The data of Table III indicate that half of the oxygen atoms of the carbonyl group have equilibrated with solvent. This is consistent with the results obtained by Buckingham, *et al.*,[2] and need not be discussed further here. However, in the glycine *t*-butyl ester case, the carbonyl group did not become labeled during hydrolysis. Oxygen exchange of the coordinated carboxyl group in $[Co(en)_2(NH_2CH_2CO_2)]^{2+}$ was determined in aqueous alkali, and this experiment deserves brief mention. Experimental results are presented, along with theoretical expectations, in Table III.

In our experiments, ^{18}O is exchanged into the carboxyl function by reaction of $[Co(en)_2(NH_2CH_2CO_2)]^{2+}$ with ^{18}O-enriched water. It is subsequently exchanged out again by reacting the sample enriched in this way with isotopically normal water, under otherwise identical conditions.

If the mechanism were to involve simple exchange by the carbonyl function of the chelated complex, then the isotope composition of the oxygen in the carboxyl group would reflect complete equilibration with the immediate residual solvent. Specifically, when the labeled complex was subjected to oxygen exchange with the alkaline solvent, more than 95% (by calculation) of the ^{18}O would be given to solvent at equilibrium. Our results show that when the glycinato complex is subjected to the full cycle of exchange, first by enriched solvent and then by normal solvent, the equivalent of 0.25 mol of ^{18}O is given up to the normal solvent. If both stages had involved complete exchange, as defined in the equation above, the equivalent of 1 mol of ^{18}O would have been liberated. Therefore simple carbonyl oxygen exchange does not occur.



Equally untenable is the other simplest theoretical behavior pattern. In base one might merely assume that the carboxyl group could be displaced by ^-OH and that the dangling CO_2^- group could then exchange with solvent. First of all, the path described above must certainly provide a faster exchange path because of the polarizing influence of Co^{3+}. Secondly, this mechanism should lead to no exchange under our conditions because of the known very slow rate of exchange of glycinate ion with base (at pH 12 and 101°, $k = 1.34 \times 10^{-8}$ l. mol^{-1} sec^{-1}).[27,28]

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[24] A. Skrabal and A. M. Hugltz, *Monatsh. Chem.*, **47**, 17 (1926).

[25] H. L. Conley, Jr., and R. B. Martin, *J. Phys. Chem.*, **69**, 2914 (1965).

[26] In most of these experiments, Ag^+ was used instead of Hg^{2+} to remove the coordinated bromide ion from the complex under conditions that are otherwise similar to those used in rate measurements. The silver ion behaves in a manner similar to Hg^{2+} in greatly accelerating the rate of release of bromide ion.[8] It was also observed that by the time the first spectrum could be obtained (conventional spectrophotometry), the removal of the coordinated bromide was complete. The hydrolysis of the resulting intermediate does not depend on the cation and the use of Ag^+ greatly facilitates the experiment.

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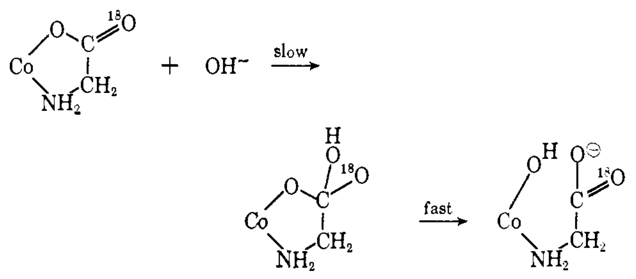
[28] C. O'Connor and D. R. Llewellyn, *ibid.*, 2669 (1965).

Table III. Mass Ratios and Isotopic Exchange Results

Compound	[Compound], mol × 10^3	$[H_2O]_T$, g	$[H_2O]$,[f] g	$[CO_2]$, mol × 10^4	Experimental ratio 44/46	Calculated ratio *a*	Calculated ratio *b*	Calculated ratio *c*	Calculated ratio *d*
H_2O		0.9601	0.9601	8.96	235				
H_2O		0.8210	0.8210	9.68	233				
H_2O[g]		0.7340	0.7340	9.20	233				
CO_2				8.64	242				
CO_2				9.66	245				
$[Co(en)_2(NH_2CH_2CO_2CH_3)Br]Br_2$	1.56	1.17	0.811	9.43	157	112	152		234
$[Co(en)_2\{NH_2CH_2CO_2C(CH_3)_3\}Br]Br_2$	1.30	1.17	0.918	9.45	229	123			233
$[Co(en)_2\{NH_2CH_2CO_2C(CH_3)_3\}Br]Br_2$	1.32	1.17	0.920	9.43	233	123			234
$[Co(en)_2\{NH_2CH_2CO_2C(CH_3)_3\}Br]Br_2$	1.38	1.17	0.800	9.43	244	120			234
$[Co(en)_2\{NH_2CH_2CO_2C(CH_3)_3\}Br]Br_2$[g]	1.41	1.17	0.991	9.20	234	118			234
$[Co(en)_2\{NH_2CH_2CO_2C(CH_3)_3\}Br]Br_2$[g]	1.41	1.17	0.994	9.09	241	136			240
$[Co(en)_2(NH_2CH_2CO_2)]Cl_2$	2.16	1.08	0.615	9.44	159	87	130	167	234
$[Co(en)_2(NH_2CH_2CO_2)]Cl_2$	1.95	1.08	0.765	9.45	155	95	135	172	235
$[Co(en)_2(NH_2CH_2CO_2)]Cl_2$[e]	1.54	1.08	0.763	9.43	210	114			235

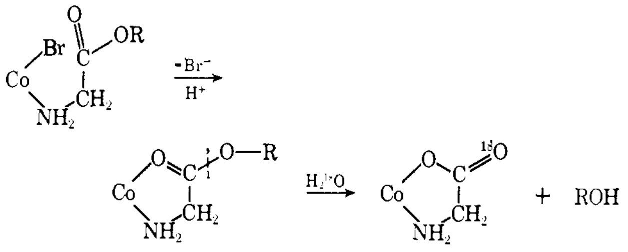
[a] ^{18}O recovered from carbonyl group is equivalent to one oxygen atom. [b] ^{18}O recovered from carbonyl group is equivalent to $^1/_2$ oxygen atom. [c] ^{18}O recovered from carbonyl group is equivalent to $^1/_4$ oxygen atom. [d] No ^{18}O in carbonyl group. [e] Exchange performed in acid solution (pH 1). [f] Amount of sample H_2O used to equilibrate with CO_2. [g] Br^- removed from Co^{3+} with Hg^{2+}. All other examples used Ag^+.

The cleavage of the C–O, rather than the Co–O bond provides the model that accounts for the observed behavior. Jordan and Taube[29] found almost complete C–O bond breaking during the base hydrolysis of $[Co(NH_3)_5(CF_3CO_2)]^{2+}$ and $[Co(NH_3)_5ox]^+$. For each complete cycle of chelate ring opening and reclosure one would expect the carbonyl oxygen atom to be replaced 50% of the time by solvent. Thus, since our conventional analytical process involves two such cycles, one expects to recover an amount of ^{18}O equivalent to one-fourth the amount of carbonyl oxygen present (*cf.* Table III).

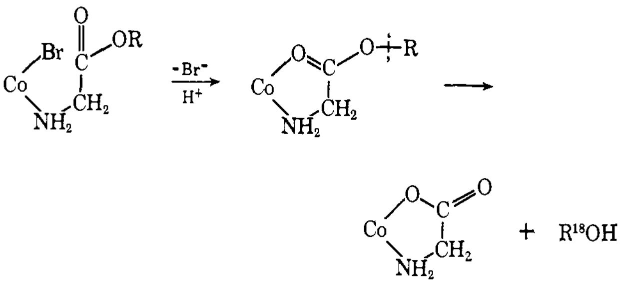


The bond cleavage and re-formation of the bidentate glycinato complex has also been observed in the visible spectrum. The bands at 487 and 344 mμ, which arise from the complex $[Co(en)_2(NH_2CH_2CO_2)]^{2+}$, are shifted to 498 and 364 mμ in 1 *M* NaOH solution. These bands are shifted back to 487 and 344 mμ when the alkaline solution is acidified. The positions of the bands in alkaline solution are also the same as in the spectra of known *cis*-chloro(methylamine)bis(ethylenediamine)cobalt(III) complexes in 1 *M* NaOH solution (λ_{max} at 498 and 364 mμ), and presumably these are band positions of *cis*-$[Co(en)_2(OH)(NH_2CH_3)]^{2+}$; however, the intensities of the bands are slightly different in these two cases.

Returning now to the major issue, both Buckingham and associates and we find that ^{18}O is exchanged during Co(III)-promoted hydrolysis of the CH_3, C_2H_5, and C_3H_7 glycine ester derivatives and conclude that the reaction pathway is essentially as shown below (though not shown, SN2 attack at carbonyl carbon is assumed).



The fact that no ^{18}O is incorporated into the carboxylate during the course of Co(III)-promoted hydrolysis of the *t*-butyl ester derivative provides final proof of a distinct point of bond cleavage for this case. The obvious and totally satisfactory model requires breaking of the alkyl C–O bond, rather than the acyl C–O bond. This conclusion is supported by the distinct salt and solvent rate dependencies and by the relatively small metal-ion promotional effect (about 10^2 rather than about 10^6).



At this point, it is appropriate to summarize the conclusions reached concerning ester hydrolysis of the cobalt(III)–glycine ester complexes, as initiated by mercury(II) ion. In the Co(III)-promoted reactions, a single mechanism operates for CH_3, C_2H_5, and *i*-C_3H_7 esters. This mechanism involves the attack of a water molecule on the carbonyl carbon of the chelated ester complexes, followed by ejection of the alkoxyl group. The mechanism was proposed by Alexander and Busch on the basis of kinetic data and the identification of the intermediate containing chelated glycine ester. Buck-

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(29) R. B. Jordan and H. Taube, *J. Amer. Chem. Soc.*, 86, 3891 (1964).

ingham, Foster, and Sargeson[2] provided elegant confirmation of the structure of the intermediate. Experiments utilizing ^{18}O support this theory (Buckingham, *et al.*,[2] and here). An alternate mechanism operates in the case of the *t*-butyl ester complex. This involves formation of the same kind of intermediate, *i.e.*, that containing chelated, carbonyl-oxygen coordinated, ester, but nucleophilic attack occurs at the carbon atom of the alkyl group and it is the alkyl group that is expelled. This mechanism is supported by the results of kinetic studies and oxygen-18 exchange data.

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Metal Isotope Effect on Metal–Ligand Vibrations. I. Phosphine Complexes[1]

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Contribution from the Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wisconsin 53233. Received December 2, 1969

Abstract: Far-infrared spectra (600–100 cm^{-1}) have been reported for $^{58}Ni(PEt_3)_2Cl_2$, $^{58}Ni(PEt_3)_2Br_2$, $^{58}Ni(PPh_3)_2Cl_2$, $^{104}Pd(PEt_3)_2Cl_2$, $^{104}Pd(PPh_3)_2Cl_2$, and their ^{62}Ni or ^{110}Pd analogs. The infrared and Raman spectra of $Pd(PPh_3)_2X_2$ and $Pd(AsPh_3)_2X_2$ (X = Cl and Br) have also been obtained. Based on the observed isotopic shifts, the Ni–P stretching vibrations have been assigned at *ca.* 274–260 cm^{-1} (one band) for *trans*-$Ni(PEt_3)_2X_2$ and at *ca.* 190–160 cm^{-1} (two bands) for tetrahedral $Ni(PPh_3)_2X_2$. Similarly, the Pd–P stretching bands have been assigned at *ca.* 235–232 cm^{-1} for *trans*-$Pd(PEt_3)_2X_2$ and at *ca.* 190 cm^{-1} for *trans*-$Pd(PPh_3)_2Cl_2$.

Recently, a number of infrared studies have been made on metal phosphine complexes.[2–8] The metal–phosphorus stretching frequencies assigned by previous investigators cover a wide frequency range from 460 to 90 cm^{-1}. This scattering of frequencies has been attributed to the differences in the nature (1) of the metals (oxidation state, electronic configuration, etc.); (2) of the phosphine ligands PR_3, where R is CH_3, C_2H_5, or C_6H_5; and (3) in the structure of the complex (stereochemistry, coordination number, etc.).[9,10] It should be noted, however, that all the metal–phosphorus stretching bands reported previously have been assigned empirically (or intuitively) without solid experimental evidence. Recently, we have found[11] that the metal isotope technique provides a unique method of assigning the metal–ligand vibrations of a variety of coordination compounds. The purpose of this work is to apply this new technique to the vibrational spectra of metal phosphine complexes and to examine the validity of previous band assignments. In this paper, we report the results obtained for *trans*-$Ni(PEt_3)_2X_2$ (X = Cl and Br), tetrahedral $Ni(PPh_3)_2Cl_2$, *trans*-$Pd(PEt_3)_2Cl_2$, *trans*-$Pd(PPh_3)_2Cl_2$, and related compounds.

Experimental Section

Preparation of Compounds. All the Ni(II) phosphine complexes were prepared according to the methods of Jensen.[12] All the Pd(II) phosphine complexes were prepared according to the methods reported in literature.[13] Metal phosphine complexes containing metal isotopes were prepared on a milligram scale. In each case, metallic nickel or palladium (10–15 mg each) was converted into $NiCl_2 \cdot 6H_2O$ or $Na_2[PdCl_4] \cdot 4H_2O$, respectively, and these salts were treated with the ligands. The purity of each metal isotope was: ^{58}Ni (99.98%), ^{62}Ni (99.02%), ^{104}Pd (89.75%), and ^{110}Pd (96.98%). All the metal isotopes were purchased from Oak Ridge National Laboratory. Triethylphosphine (PEt_3) was purchased from Strem Chemicals, Inc., Danvers, Mass. Triphenylphosphine (PPh_3) and triphenylarsine ($AsPh_3$) were purchased from Aldrich Chemical Co., Milwaukee, Wis. The purity of each metal phosphine complex was checked by comparing the spectrum with that reported in literature.

Spectral Measurements. Infrared spectra of all the complexes except $Ni(PPh_3)_2Cl_2$ (^{58}Ni and ^{62}Ni) were measured on a Beckman IR-12 (650–200 cm^{-1}) and a Hitachi Perkin-Elmer FIS-3 (400–100 cm^{-1}) infrared spectrophotometer. The spectra of the remaining complexes were measured on a Beckman IR-11 (600–100 cm^{-1}) infrared spectrophotometer. The Nujol mull technique with polyethylene plates was employed in obtaining the spectra of solids. Calibration of the frequency readings was made with 1,2,4-trichlorobenzene and water vapor.

The spectra were run with a scanning speed of 1–2 cm^{-1}/min. Reproducibility of the spectra was checked by running the spectra three to five times. The average error in frequency reading was 0.5 cm^{-1}.

The Raman spectra of $Pd(PPh_3)_2X_2$ and $Pd(AsPh_3)_2X_2$ (X = Cl or Br) were measured by using a Cary Model 81 Raman spectrophotometer equipped with a He–Ne gas laser source.

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(1) Supported by a Petroleum Research Fund unrestricted research grant (3318-C3,5) administered by the American Chemical Society. Part of this work was carried out at the Department of Chemistry, Illinois Institute of Technology, Technology Center, Chicago, Ill.

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