allyl derivative is known in which a substituent is present in the *anti* position of the terminal carbon while the metal also is bonded to *four* other ligands. It is apparent from the reported structural work[18] that a fully formed methyl group in the *anti* position on the π-allyl group would seriously interfere with the "axial" ligand (see position 3 in structure I, above). A minor structural adjustment in the cyclohexenyl complexes could be responsible for the difference. In these protonated derivatives, the second proton becomes sufficiently tightly bound to the carbon adjacent to the allyl moiety to give rise to a resonance typical of a methylene proton of the cyclohexyl ring, as observed. The solvent (SO_2) might also play a role in these systems. Studies on this and related systems are in progress to provide further elucidation of these phenomena.

Acknowledgment. We are indebted to Professors F. A. L. Anet and S. Winstein of this department for stimulating discussions, and to the following sources for support of departmental instruments used in this work: NSF GP-8223 (Varian HA-100 nmr spectrometer); Du Pont donation and NSF G-20207 (Varian A-60 nmr spectrometer); and NSF GP-3672 (AEI-MS9 mass spectrometer).

Chemistry of Macrocyclic Complexes of Cobalt(III). Acid Hydrolysis of Bidentate Carbonate and *cis–trans* Isomerization of Macrocyclic Complexes[1a,b]

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Abstract: Rates have been determined for the relatively slow acid hydrolyses of $CoLCO_3^+$ complexes containing a macrocyclic tetracoordinate ligand L and bidentate carbonate. In the case that L is a cyclic tetramine (hexamethylcyclam = Curtis' tet*b*), the hydrolysis rate is slower by a factor of about 10^5 than the hydrolysis rate of the analogous $Co(en)_2CO_3^+$. This great disparity in rates most likely has its source in steric crowding of the fifth and sixth coordination positions by methyl groups of the ligand L. The immediate product of hydrolysis of Co(tet*b*)CO_3^+ appears to be *cis*-Co(tet*b*)$(OH_2)_2^{3+}$, but the kinetics are complicated by a chloride-catalyzed *cis* → *trans* isomerization reaction. The acid hydrolysis of Co(*trans*[14]diene)CO_3 (where *trans*[14]diene is Curtis' Schiff base amine) is intermediate in rate and gives *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ as the first isolable product. It appears that the *cis* → *trans* isomerization for the latter complex is unusually fast. It is suggested that the presence of Co(III)–N(imine) groups in the macrocyclic ligand may stabilize the five-coordinated intermediate in the isomerization reaction.

Bidentate carbonate complexes have been reported recently for cobalt(III) complexes containing the tetradentate macrocyclic ligands 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane[2,3] and 5,7,-7,12,14,14-hexamethyl-1,4,8,11-azacyclotetradeca-4,11-diene[5,6] (see Figure 1). The Co(*trans*[14]diene)CO_3^+ complex is one of the very few known complexes containing the *trans*[14]diene ligand in a folded (or *cis*) configuration; it is the only such cobalt(III) complex yet reported. In fact all reported complexes of Co^{III}(*trans*-[14]diene)X_2 and Co^{III}(tet*b*)X_2 for monodentate ligands X have a *trans* geometry despite the fact that many of these complexes have been prepared from Co(*trans*[14]-diene)CO_3^+ and Co(tet*b*)CO_3^+, respectively. Since *cis*-Co^{III}(cyclam)X_2 complexes seem to be easily prepared and isomerize only slowly,[7,8] the relative difficulty in preparing *cis*-Co^{III}(*trans*[14]diene)X_2 and *cis*-Co^{III}(tet*b*)X_2 complexes might well be attributed to rather great steric strains (possibly between some of the six methyl groups and the fifth and sixth coordination positions) which result when the *trans*[14]diene and tet*b* ligands are folded.

We have found Co(*trans*[14]diene)CO_3^+ and Co(tet*b*)CO_3^+ to be very rugged complexes in aqueous solution. Their general inertness is particularly surprising when it is realized that the *trans*-Co^{III}(tet*b*)X_2 complexes are generally quite labile with respect to aquation of the ligand X.[9] In fact, Co(tet*b*)CO_3^+ is a most remarkable substance for its stability for hours in dilute acid solutions at room temperature and for its ready formation from *trans*-Co(tet*b*)$(OH_2)OH^{2+}$ in neutral solution.

In this paper we report our studies of the acid hydrolysis of Co(*trans*[14]diene)CO_3^+ and Co(tet*b*)CO_3^+. Several features of these macrocyclic ligand systems permit the examination of simple chemical reactions from an unusual point of view. The significance of steric interactions has been alluded to above and the manifestations of steric interactions are an important part of the

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[1] (a) Taken in part from the dissertation submitted by J. A. Kernohan to Boston University in partial fulfillment of the requirements of the Ph.D. (b) Supported in part by the Public Health Service (Grant AM 08737) and in part by a grant in aid from Boston University. (c) Correspondence may be addressed to J. F. E., Department of Chemistry, Wayne State University, Detroit, Mich. 48202.

[2] P. W. Whimp and N. F. Curtis, *J. Chem. Soc., A*, 1827 (1966).

[3] For the C-*dl* isomer of the ligand which Curtis[4] designates tet*b*.

[4] N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

[5] N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 6, 770 (1967).

[6] Following Curtis' suggestion[4] this ligand will hereafter be referred to as *trans*[14]diene.

[7] C. K. Poon and M. L. Tobe, *J. Chem. Soc., A*, 1549 (1968).

[8] C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 7, 2398 (1968).

[9] J. A. Kernohan, Ph.D. Dissertation, Boston University, 1969.

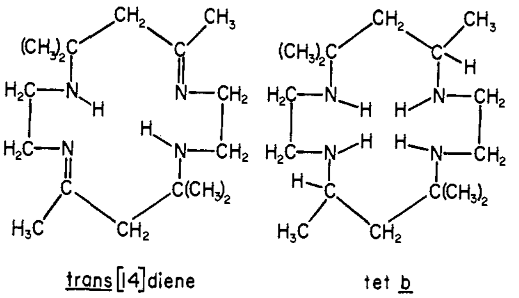

Figure 1. Macrocyclic ligands: *trans*[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; tet*b* = C-*dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

chemistry reported here. One major difference between the *trans*[14]diene and the tet*b* ligands is the presence of two azomethine groups in the former. It is of interest to discover how the presence of Co(III)–N(imine) bonds affects the chemistry of the macrocyclic complex. Our investigation of the acid hydrolysis of bidentate carbonate in these complexes has resulted in some unexpected observations concerning the *cis* → *trans* isomerizations of macrocyclic complexes.

Experimental Section

Preparation of Complexes. The preparations of [Co(tet*b*)CO_3]$(ClO_4)_2$, [Co(tet*b*)CO_3]Cl_2, and [Co(*trans*[14]diene)CO_3]$(ClO_4)_2$ have been described.[2,5] For some experiments, the perchlorate salt of the latter was metathesized to the chloride in methanolic KCl essentially as described for the preparations of [Co(*trans*[14]diene)Cl]Cl_2.[5] The identification of species and the determination of equilibria in aqueous solutions containing *trans*-Co(tet*b*)$(OH_2)_2^{3+}$ or *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ in the presence of chloride have been reported briefly[10] and are described in detail elsewhere.[9]

Preparation of Solutions and Procedure for Kinetic Determinations. Stock solutions were prepared by dissolving perchlorate salts of the complexes in distilled water. Samples of stock solutions, thermostated at the reaction temperature, were mixed with acid in a 5-cm thermostated spectrophotometer cell. Thermostating of the cell was accomplished by circulating water from a constant temperature bath through a glass water jacket around the cell. The progress of reactions was followed by measuring absorbance changes at the low energy absorption maxima of the carbonato complexes. The ionic strength in kinetic runs was maintained at 0.25 (with $NaClO_4$) except as indicated. Absorbance changes and spectra were determined with Cary 14 or Unicam SP 800 spectrophotometers.

^{1}H Nmr Studies. Sufficiently concentrated (≥ 0.1 *M*) solutions of the carbonato complexes were prepared by dissolving the chloride salts in acidic solutions at room temperature. In these experiments the temperature of the nmr probe was 40° and this was the effective temperature of these reactions. Spectra were determined using a Varian A-60 spectrometer.

Miscellaneous Procedures. Analytical grade AG 50-W × 4 (200–400 mesh) cation-exchange resin was obtained from Bio-Rad Laboratories. For cation-exchange studies the resin was used in the acid form.

Results

Identification of Reaction Products and Some Qualitative Observations. The reactions of Co(tet*b*)CO_3^+ and Co(*trans*[14]diene)CO_3^+ with acid appear to differ from analogous reactions of $Co(NH_3)_4CO_3^+$ and $Co(en)_2CO_3^+$. The Co(tet*b*)CO_3^+ is a most incredible substance which generally precipitates as the chloride or perchlorate salt when HCl or $HClO_4$ is added in excess at room temperature. This limited solubility of the carbonato complex coupled with the extraordinarily slow decarboxylation reaction have contributed greatly to frustrate our attempts to isolate *cis*-CO(tet*b*)Cl_2^+ or *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ complexes. However, in relatively concentrated nitric acid (>1 *M*) the decarboxylation proceeds readily (to completion in less than 2 hr) at room temperature. The intensely absorbing (λ_{max} 535 nm, $\epsilon_{max} \geq 76$) product of this reaction has been tentatively identified as the *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ complex. Acidic (HNO_3) solutions of *cis*-Co(tet*b*)$(OH_2)_2^{2+}$ are stable at room temperature for a day or more but readily isomerize to *trans*-Co(tet*b*)$(OH_2)_2^{3+}$ when heated. The reaction of Co(tet*b*)CO_3^+ with HBr (~0.1 *M* at 25°) appears to give a mixture of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ and *trans*-Co(tet*b*)OH_2Br^{2+}.

The reaction of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ with Cl^- is complete in 30 min at 25° with $[Cl^-] \simeq 0.1$ *M* ($[H^+] \sim 2$ *M*). This reaction proceeds with well-defined isosbestic points at 477 and 697 nm. These isosbestic points correspond to the formation of *trans*-Co(tet*b*)OH_2Cl^{2+} as the first detectable reaction product; *trans*-Co(tet*b*)Cl^{2+} forms late in the reaction in the presence of excess Cl^-. Since *trans*-Co(tet*b*)$(OH_2)_2^{3+}$ anates at a similar rate ($t_{1/2} \simeq 15$ min in 0.1 *M* HCl at 25°), it appears that *trans*-Co(tet*b*) $(OH_2)_2^{3+}$ is not formed as an intermediate in reaction 1.

$$cis\text{-Co(tet}b\text{)}(OH_2)_2^{3+} + Cl^- \longrightarrow trans\text{-Co(tet}b\text{)}OH_2Cl^{2+} + H_2O \quad (1)$$

Further examination of the substitution chemistry of cyclic complexes will be left to a later communication. For the present we should note that the reaction of Co(tet*b*)CO_3^+ with HNO_3 does not necessarily yield 100% *cis*-CO(tet*b*)$(OH_2)_2^{3+}$ (hence the lower limit on the molar absorptivity). There is frequently a fine blue dispersion in these reactions which may be due to a small amount of [Co(tet*b*)NO_3]$(NO_3)_2^2$, but is more likely to be [Co(tet*b*)CO_3]NO_3. When solutions of Co(tet*b*)CO_3^+ stand in HNO_3 (~3 *M*) for several weeks, a blue crystalline precipitate which appears to be [Co(tet*b*)NO_3]$(NO_3)_2$ does form.

Complete characterization of species in solution resulting from mixing Co(tet*b*)CO_3^+ with HNO_3 has not been possible since (1) the *trans*-Co(tet*b*)XY complexes are weakly absorbing compared to the corresponding *cis* complexes and cannot be unambiguously identified from examination of visible spectra,[9] (2) ^{1}H nmr spectra of Co^{III}(tet*b*)XY complexes are complex and chemical-shift differences from complex to complex are small,[9] and (3) when the reddish solutions (apparently containing largely *cis*-Co(tet*b*)$(OH_2)_2^{3+}$) are added to a cation-exchange resin the initial reddish band turns first blue (in a few minutes) and finally green (after standing a day).

Spectral changes which occur during the acid hydrolysis of Co(*trans*[14]diene)CO_3^+ appear to be simple and are nearly independent of the kind of acid used. Thus, isosbestic points at 25° are observed at 580 and 451 nm for the hydrolysis in HCl and at 581 and 451 nm in HBr; in both of these cases the initial hydrolysis product (λ_{max} ~580 nm) undergoes further reaction, forming species with absorption maxima at longer wavelengths. Hydrolyses in $HClO_4$ or HNO_3 at 25° also give a product with an absorption maximum at about 580 nm (isosbestic points similar to those listed above). ^{1}H nmr spectra of the hydrolysis products in $HClO_4$ (Figure 2)

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[10] R. E. Ball, J. A. Kernohan, and J. F. Endicott in "Coordination Chemistry," Paper No. C8, M. Cais, Ed., Elsevier Publishing Co., New York, N. Y., 1968.

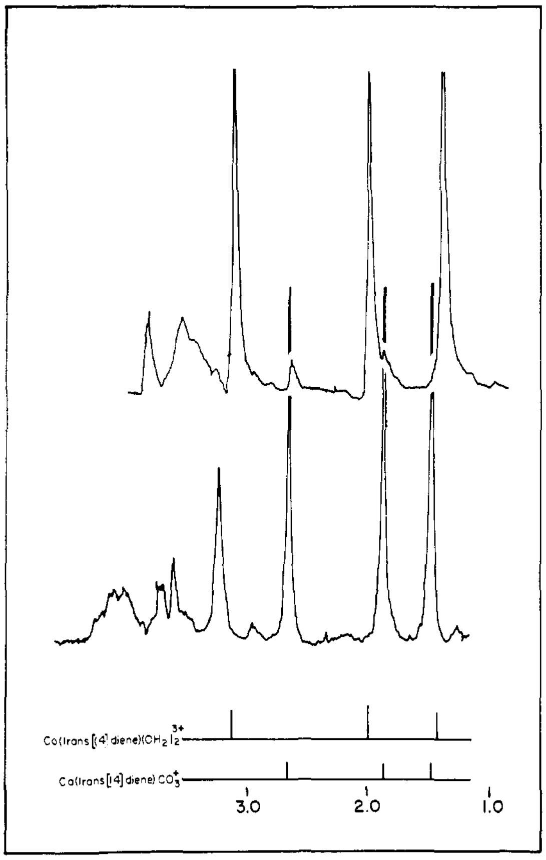

Figure 2. Methyl proton nmr of the product of hydrolysis of Co(*trans*[14]diene)CO_3^+ in $HClO_4$: upper spectrum, hydrolysis product; lower spectrum, Co(*trans*[14]diene)CO_3^+ in D_2O. The three methyl bands of each complex are assigned at the bottom of the figure. Chemical shift (ppm) relative to external TMS is indicated.

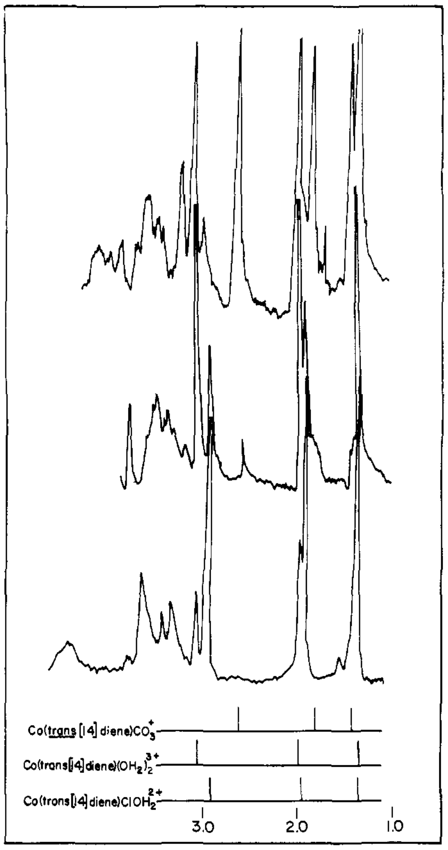

Figure 3. The proton nmr spectra of products and intermediates in the hydrolysis of Co(*trans*[14]diene)CO_3^+ in HCl: upper spectrum, approximately 1 min after mixing; middle spectrum, 20 min after mixing; bottom spectrum, 15 hr later. The three methyl bands of each complex are assigned and a scale of reference for chemical shifts (relative to external TMS) is indicated at the bottom of the figure.

are identical with the spectra of *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$.[9,10] Furthermore, when Co(*trans*[14]diene)CO_3^+ is mixed with HCl, the initial hydrolysis product (at ~40°) appears to be *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ which slowly equilibrates with Cl^- in solution (Figure 3).

Some kinetic evidence is cited below for the intermediate formation of *cis*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ at low temperatures. This evidence led us to attempt to prepare solutions of *cis*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ at about 0° from the hydrolysis of Co(*trans*[14]diene)CO_3^+ in $HClO_4$. These attempts have been unsuccessful and, in marked contrast to the behavior of Co(tet*b*)CO_3^+, solutions formed from the low-temperature hydrolysis of Co(*trans*[14]diene)CO_3^+ are green.

The kinetic studies reported below for Co(tet*b*)CO_3^+ were performed at relatively high temperatures (75°). Table I is a summary of the spectral characteristics of the products which result from the acid hydrolyses of Co(tet*b*)CO_3^+ and Co(*trans*[14]diene)CO_3^+ under the conditions of the kinetic runs reported below.

Some Preliminary Observations on the Base Hydrolysis of $CoLCO_3^+$. Detailed kinetic studies of the base hydrolysis of the $CoLCO_3^+$ complexes will be reported elsewhere.[11] However, some of our preliminary qualitative observations bear on the mechanistic issues raised by the acid hydrolyses. These pertinent preliminary observations are reported here. Both Co(*trans*[14]diene)CO_3^+ and Co(tet*b*)CO_3^+ undergo hydrolytic reactions in strongly basic solution. The initial reaction of Co(*trans*-[14]diene)CO_3^+ with 0.06 *M* NaOH at 25° is complete in about 30 min. The final product of this reaction is indistinguishable from *trans*-Co(*trans*[14]diene)$(OH)_2^+$ (λ_{max} 520 nm with a shoulder at λ ~585 nm). Examination of spectra of the carbonato and dihydroxy complexes shows that a simple decarboxylation reaction to form *trans*-Co(*trans*[14]diene)$(OH)_2^+$ should result in isosbestic points at about 410, 460, and 580 nm. In the above reaction a rather poor isosbestic point was ob-

Table I. Products for *trans*-$Co^{III}LX_2$

L	λ_{max},[a] cm^{-1} × 10^3 (ϵ)	λ_{max}, cm^{-1} × 10^3 (ϵ)
trans[14]diene	17.3 (24)	17.3 (23)[b]
	16.8 (41)[c]	16.8 (38)[d,e]
tet*b*	17.0 (28)[d]	17.0 (34)[b]
	18.1 (32)[c,d]	18.1 (~31)[e]

[a] Lowest energy-band maximum, determined at 25° in $HClO_4$ except as indicated. [b] Reference 9 for *trans*-$CoL(OH_2)_2^{3+}$. [c] In HCl (0.1 *M*). [d] Hydrolyses performed at 73°; spectral determinations at 25°. [e] Calculated for the equilibrium distribution of *trans*-$CoL(OH_2)^{3+}$, *trans*-$CoLClOH_2^{2+}$, and *trans*-$CoLCl_2^+$ in 0.1 *M* HCl using equilibrium constants and molar absorptivities reported elsewhere.[9]

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(11) N. A. P. Kane-Maguire and J. F. Endicott, work in progress.

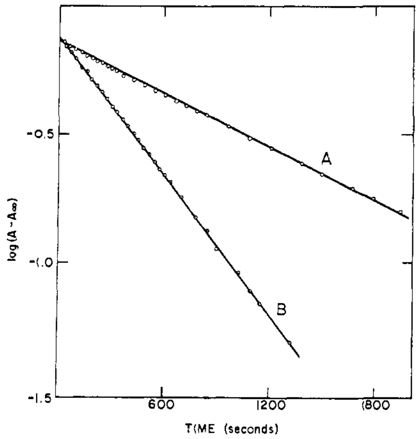

Figure 4. Acid hydrolysis of Co(*trans*[14]diene)CO_3^+: perchlorate medium ($NaClO_4$, $HClO_4$), 24.8°, ionic strength = 0.25. Complex concentration = 4.5×10^{-4} *M*. A = 0.1 *M* H^+; B = 0.25 *M* H^+.

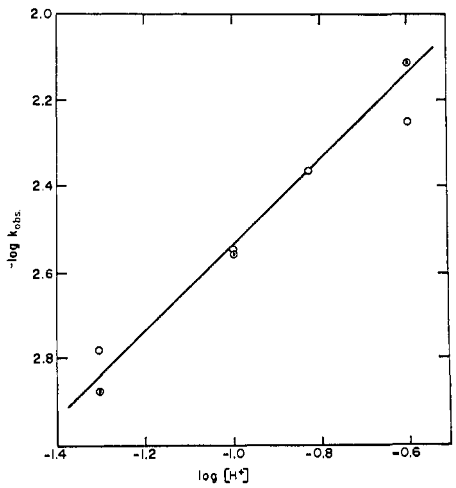

Figure 5. Acid dependence of the hydrolysis of Co(*trans*[14]diene)-CO_3^+ at 40.8°: open circles, $HClO_4$; dotted circles, HCl.

served at about 455 nm, but the absorbance appeared to change in a systematic manner in the other two wavelength regions. Systematic absorbance changes continued to occur in these wavelength regions for some time (about 2 hr) after the large absorbance change at 525 nm was complete.

The base hydrolysis of Co(tet*b*)CO_3^+ appears to be about one-tenth as fast as the corresponding reaction of Co(*trans*[14]diene)CO_3^+. The final reaction product in this case appears to be *trans*-Co(tet*b*)$(OH)_2^+$ (λ_{max} ~520 nm). This decarboxylation reaction gives no indication of the preliminary ring-opening reaction reported[12,13] for Co$(en)_2CO_3^+$ and exhibits excellent isosbestic points at appropriate wavelengths (432 and 483 nm).

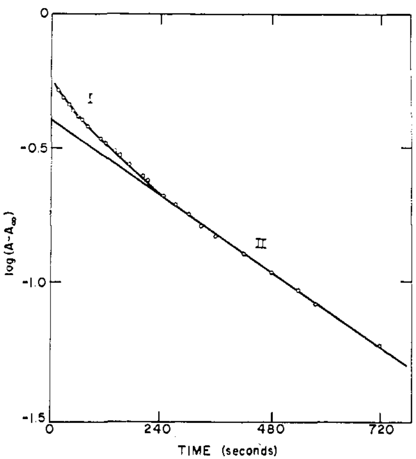

Figure 6. Acid hydrolysis of Co(*trans*[14]diene)CO_3^+ at 9.8°, 3.0 *M* $HClO_4$.

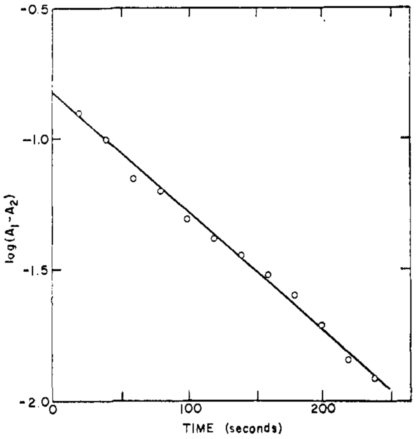

Figure 7. Difference plot for step I of Figure 6.

Kinetics of the Acid Hydrolyses of CoLCO_3^+. The measured rate of change of absorbance for Co(*trans*[14]-diene)CO_3^+ follows the expected first-order rate law under most experimental conditions (Figure 4). The apparent first-order rate constants, k_a, are proportional to $[H^+]$ (Figure 5). This $[H^+]$ dependence of k_a was observed at 24.8, 40.8, and 72.5° and seems independent of $[Cl^-]$ within reasonable limits of experimental error. The apparent activation energy for k_a was found to be E_a = 24.3 kcal/mol ($[H^+]$ = 0.1 *M*).

At 9.8° in 3 *M* $HClO_4$, the kinetic behavior of Co-(*trans*[14]diene)CO_3^+ is more complex (Figure 6), exhibiting curvature which suggests consecutive first-order processes involving change in absorbance. The observed decay kinetics have been treated in a manner analogous to the treatment of radioactive decay where a daughter species is generated whose decay half-life is longer than that of the parent.[14] Thus, the final decay constant, k'', is determined from the slope in region II, Figure 6. The initial decay rate, k', is determined from the difference between the observed absorbance (at any time, *t*) in region I and the absorbance calculated (at time *t*) from the final rate of absorbance change. Such a difference plot of data for the acid hydrolysis of Co-(*trans*[14]diene)CO_3^+ at 9.8° is shown in Figure 7.

The absorbance changes in $HClO_4$ solutions of Co-(tet*b*)CO_3^+ implied consecutive first-order processes under all conditions employed in this study (*e.g.*, see Figure 8). Because the acid hydrolysis of Co(tet*b*)CO_3^+ is so slow we have only examined this reaction at 73.5°. Values of k' and k'' have been obtained for the initial

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[12] D. J. Francis and R. B. Jordan, submitted for publication.

[13] G. Hargis, Ph.D. Dissertation, Ohio University, 1966, University Microfilms, Inc., 66–8804; we wish to thank Dr. T. P. Dasgupta for bringing this reference to our attention.

[14] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 1962.

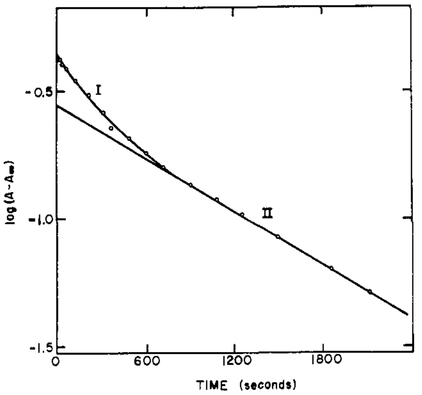

Figure 8. Acid hydrolysis of Co(tet*b*)CO_3^+ at 73.6°. Ionic strength = 0.25, [$HClO_4$] = 0.15 *M*, complex concentration = 3.9×10^{-4} *M*.

and final decay-rate constants in the same way as described above for Co(*trans*[14]diene)CO_3^+ at 9.8°. In the case of the Co(tet*b*)CO_3^+ we have observed that both step I and step II are acid dependent (*e.g.*, Figure 9) with $k' = k_I[H^+]^{0.99}$ and $k'' = k_{II}[H^+]^{0.57}$.[15] When [Cl^-] > 0.1 *M*, the change in absorbance is simply first order with a decay-rate constant indistinguishable from k' in $HClO_4$ (Figure 9). Rate constants for the acid hydrolyses are summarized in Table II.

Table II. Summary of Kinetic Data for Acid Hydrolysis of $CoLCO_3^{+}$[a]

L	Acid	Temp, °C	$k'/[H^+] \times 10^2$ mol^{-1} sec^{-1}	$k'' \times 10^2$ sec^{-1}
tet*b*	$HClO_4$	73.5	2.6 ± 0.3[b]	0.26[c]
	HCl	73.5	3.1 ± 0.6[b,d]	*e*
trans[14]diene	$HClO_4$	9.8	0.35 ± 0.05[f]	0.28 ± 0.02[f]
		24.8	0.79 ± 0.02[g]	*e*
		40.8	7.7 ± 0.7[h]	*e*
	HCl	40.8	6.3 ± 0.7[b]	*e*
	$HClO_4$	72.5	260 ± 20[i]	*e*
	HCl	72.5	133 ± 5[j]	*e*

[a] Ionic strength = 0.25 ($NaClO_4$) except as indicated. No corrections have been made for activity effects. Errors are average deviations from the mean. [b] For 0.25 *M* ≤ [H^+] ≤ 0.05 *M*. [c] For [H^+] = 0.10 *M*. [d] $k'/[H^+]$ was 30% higher than the mean in 0.25 *M* HCl. [e] No reaction observed. [f] For [H^+] = 3.0 *M*. [g] For [H^+] = 0.25 *M* and 0.10 *M*. [h] For 2.2×10^{-3} *M* ≤ [H^+] ≤ 0.25 *M*. [i] For 0.01 *M* ≤ [H^+] ≤ 0.10 *M*. [j] For [H^+] = 0.10 *M* and 0.05 *M*. $k'/[H^+]$ = 0.8 mol^{-1} sec^{-1} when [HCl] = 0.25 *M*.

Discussion

Stoichiometry of the Acid Hydrolyses. It appears that acid hydrolysis of Co(tet*b*)CO_3^+ is stoichiometrically similar to acid hydrolysis of $Co(en)_2CO_3^+$ [16] and $Co(NH_3)_4CO_3^+$;[17] *i.e.*, in all cases it appears that the immediate product of reaction is *cis*-$Co(AM)_4(OH_2)_2^{3+}$. The different behavior of Co(tet*b*)CO_3^+ in HCl can clearly be ascribed to the rapidity of reaction 1.

In the case of Co(*trans*[14]diene)CO_3^+ our evidence is that the first detectable product of acid hydrolysis (at or above room temperature) is *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ independent of the acid used. The two possible implications of this are either that reaction 2 is fast

$$cis\text{-}Co(trans[14]diene)(OH_2)_2^{3+} \longrightarrow trans\text{-}Co(trans[14]diene)(OH_2)_2^{3+} \quad (2)$$

compared to the over-all hydrolysis reaction or that *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ can be the immediate product of reaction. At the present we cannot rule out either alternative, although the former is simpler.

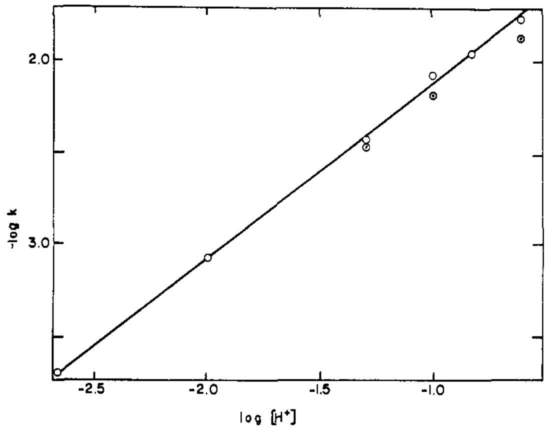

Figure 9. Acid dependence of the hydrolysis of Co(tet*b*)CO_3^+ (step I, perchlorate medium, 73.6°): open circles, $HClO_4$; dotted circles, HCl.

Mechanism of Decarboxylation. Acid-catalyzed hydrolysis reactions of bidentate carbonate have been described by a multistep mechanism.[12,16-18]

$$CoLCO_3^+ + H_3O^+ \longrightarrow cis\text{-}CoL(HCO_3)(H_2O)^{2+} \quad (3)$$

$$cis\text{-}CoL(HCO_3)(H_2O)^{2+} \longrightarrow CoL(CO_3)(H_2O)^+ + H^+ \quad (4)$$

$$cis\text{-}CoL(HCO_3)(H_2O)^{2+} \longrightarrow cis\text{-}CoL(OH)(H_2O)^{2+} + CO_3 \quad (5)$$

$$cis\text{-}CoL(OH)(H_2O)^{2+} + H^+ \longrightarrow cis\text{-}CoL(OH_2)_2^{3+} \quad (6)$$

In the present systems the kinetics are apparently complicated by eq 7 (*i.e.*, $k'' \equiv k_7$).

$$cis\text{-}CoL(OH_2)_2^{3+} \longrightarrow trans\text{-}CoL(OH_2)_2^{3+} \quad (7)$$

The observations of Dasgupta and Harris on the acid hydrolysis of $Co(NH_3)_5CO_3^+$ suggest that step 5 is fast,[19] at least insofar as decarboxylation of *cis*-$CoL(HCO_3)(H_2O)^{2+}$ is similar to decarboxylation of $Co(NH_3)_5$-

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(15) Note that the fractional order in [H^+] is consistent with a faster isomerization rate for *cis*-$CoLOHOH_2^{2+}$ than for *cis*-$CoL(OH_2)_2^{3+}$. Similar behavior is observed for other aquo complexes; *e.g.*, see ref 7 and 8.

(16) G. M. Harris and V. S. Sastri, *Inorg. Chem.*, 4, 263 (1965).

(17) T. P. Dasgupta and G. M. Harris in ref 10, Paper No. C 29.

(18) A referee has suggested that a reasonable alternative to the mechanism discussed below would involve a rapid preequilibrium to form $CoLCO_3H^{2+}$ followed by a rate-determining ring-opening step. This model would attribute the observed differences in hydrolysis rates to the differences in pK_a of the $CoLCO_3H^{2+}$ complexes. This suggestion has some merit as the *trans*-$CoL(OH_2)_2^{3+}$ complexes are more acidic (by 1–2 pH units) for L, a macrocyclic ligand, than for the corresponding ammonia or ethylenediamine complexes.[9] We have no direct evidence bearing on the acidity of the $CoLCO_3^+$ complexes; however, owing to the following points we find the steric argument presented in the text more satisfying: (1) if acidity differences between Co(tet*b*)CO_3H^{2+}, Co(*trans*[14]diene)CO_3H^{2+}, and $Co(en)_2CO_3H^{2+}$ are similar to the acidity differences of corresponding *trans*-$CoL(OH_2)_2^{3+}$ complexes, then differences in acidity could only account for relative reactivities of about 10^2:10:1 out of the observed variation of 10^5:10^3:1 (Table III), respectively; (2) the most sterically strained complex, Co(tet*b*)CO_3^+, undergoes a reasonably rapid base hydrolysis but without forming detectable amounts of the *cis* complexes which seem so characteristic of the base hydrolyses of the other carbonato complexes; (3) the spectral comparisons mentioned below are indicative of significant steric crowding in the first coordination sphere of Co(tet*b*)CO_3^+. It might also be noted here that there should be two geometrical isomers each of Co(tet*b*)CO_3^+ and Co(*trans*[14]diene)CO_3^+ depending on which nitrogen atoms are in the carbonate plane. We have so far been unable to find either spectral or kinetic evidence for more than one isomer of each complex.

(19) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **90**, 6360 (1968).

$(HCO_3)^{2+}$. Step 6 is, of course, very fast and reaction 4 does not appear important in the acidic solutions to which this study has been confined. A steady-state treatment of steps 3 and 5 gives for the observed hydrolysis constant, $k' = \{k_3k_5/(k_{-3} + k_5)\}[H^+]$. Of the two limiting cases which must be considered, $k' \rightarrow k_3[H^+]$ when $k_5 \gg k_{-3}$. That is, in this limit ring opening is rate determining and this process must be extraordinarily slow to account for the inertness of $Co(tet\textit{b})CO_3^+$. In the other limit $k_{-3} \gg k_5$ and $k' \rightarrow k_5K_3[H^+]$. That is, ring closing is unusually rapid and the relative inertness of these complexes is to be attributed to the instability of the *cis* geometry for monodentate ligands (*i.e.*, to unusually small values of K_3). Our present information does not allow an unambiguous choice between these alternatives.

One unique feature of the *cis* → *trans* isomerization of a six-coordinate complex containing a tetracoordinate macrocyclic ligand is that the activated complex necessarily involves bond breaking to the fifth and sixth ligand. A carbonate ring-opening process which involves breaking of a Co–O bond rather than a C–O bond would generate a five-coordinate species. Such a five-coordinate species should isomerize readily.[20] Our evidence concerning the decarboxylation of Co(*trans*-[14]diene)CO_3^+ suggests that reactions 3 and 4 must be important at low temperatures ($\leq 10°$) in strongly acidic solutions; the evidence does not rule out the possibility that for this complex, at higher temperatures, reactions 3 to 7 compete with a mechanism involving a five-coordinate intermediate.

Under similar conditions, in acidic solution, hydrolyses of bidentate carbonate increase in rate in the order Co(tet*b*)CO_3^+ $\ll$ Co(*trans*[14]diene)CO_3^+ $\ll$ $Co(en)_2CO_3^+$ (see Table III).

Table III. Rates of Acid Hydrolysis of Bidentate Carbonate Coordinated in Cobalt(III) Complexes (at 73°, 0.10 *M* $HClO_4$)

Complex	k, sec^{-1}
Co(tet*b*)CO_3^+	0.00282
Co(*trans*[14]diene)CO_3^+	0.235[b]
$Co(en)_2CO_3^+$	200[a]

[a] Estimated from the value at 25° ($k = 5.63 \times 10^{-7}$ sec^{-1}) for $Co(en)_2CO_3^+$ [14] using the activation energy for Co(*trans*[14]diene)-CO_3^+; see footnote *b*. [b] E_a = 24.3 kcal/mol.

Despite the mechanistic ambiguities noted above, this increasing order of reactivity is consistent with the decreasing steric constraints expected on a preequilibrium (or rate-determining) step 3. That is, there should be greater steric (or nonbonding) repulsive interactions between ligand methyl groups and the fifth and sixth coordination positions for Co(tet*b*)CO_3^+ than for Co(*trans*[14]diene)CO_3^+. A limited amount of support for this interpretation of the relative reactivities may be inferred from a comparison of the visible spectra of these complexes. The visible spectra of $Co(en)_2CO_3^+$ and Co(*trans*[14]diene)CO_3^+ are very nearly identical.[4,9] Furthermore, the values of the apparent crystal field splitting parameters, Δ_{amine}, of the ligands en and *trans*-[14]diene ($\Delta_{amine} \simeq 25.3 \times 10^3$ and 24.7×10^3 cm^{-1}, respectively) do not appear to depend on ligand geometry, *i.e.*, whether calculated $CoLCO_3^+$ or *trans*-$CoLX_2^+$.[4,9] On the other hand, Co(tet*b*)CO_3^+ absorbs at significantly longer wavelengths than does $Co(en)_2CO_3^+$.[2,4,9,21] Furthermore, Δ_{amine} has been found to be smaller in Co(tet*b*)CO_3^+ [4] (22.9×10^3 cm^{-1}) than in *trans*-Co(tet*b*)Cl_2^+ (24.1×10^3 cm^{-1}).[4,9] These related observations suggest that folding the tet*b* ligand increases steric interactions (about 2 kcal/mol more in the *cis* than in the *trans* complexes) between coordinated ligands. That a similar effect is not observed for the Co^{III}(*trans*[14]diene)X_2 complexes implies that *trans*-(14)diene can be folded without changing steric interactions between coordinated ligands.

cis → *trans* **Isomerizations in Complexes Containing Macrocyclic Ligands.** Unanticipated but intriguing results of this study are our observations concerning *cis* → *trans* isomerization in complexes containing macrocyclic ligands. It appears that a *trans* geometry is the favored one for complexes containing either tet*b* or *trans*[14]diene;[2,4,5,22] thus the *cis* → *trans* isomerization reactions proceed to completion with none of the *cis* complex detected at equilibrium (see Table I).

It has been found that *cis* → *trans* isomerization reactions of cobalt(III) generally have large activation energies (of the order of 25 kcal/mol).[23] Thus our estimates of $k_7 = 1.0 \times 10^{-3}$ sec^{-1} for Co(tet*b*)$(OH_2)_2^{3+}$ (in 0.3 *M* H^+ at 74°) and $k_7 = 2.8 \times 10^{-3}$ sec^{-1} for Co(*trans*[14]diene)$(OH_2)_2^{3+}$ (in 3 *M* H^+ at 10°) imply over a 10^5-fold difference in isomerization rates. This difference in reactivity has been qualitatively confirmed at room temperature by the apparent stability of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ and our failure to find any evidence for the existence of *cis*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$.[24]

This range of reactivity is even more remarkable when these macrocyclic systems are compared to simpler tetramine complexes which have been studied in detail. The information available[7,8,23,25–27] indicates that the rates of *cis* → *trans* isomerization reactions increase in the order Co(cyclam)$(OH_2)_2^{3+}$ $\leq$ Co(tet*b*)$(OH_2)_2^{3+}$ $<$ $Co(en)_2(OH_2)_2^{3+}$ $<$ $Co(NH_3)_4(OH_2)_2^{3+}$ $<$ Co(*trans*[14]diene)$(OH_2)_2^{3+}$. It is of interest that it is the extreme members of this series for which the *trans* complex is most favored thermodynamically.[4,8,23,25–28] *cis* → *trans* isomerization in each of these same macrocyclic complexes necessarily involves Co–O bond breaking and readjustment of the conformations of at least two chelate rings. In view of these considerations the slowness of the isomerization of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ is very reasonable regardless of steric interactions. The exceedingly rapid isomerization of *cis*-Co(*trans*[14]diene)-

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(20) Evidence has recently been cited[6] for a faster water exchange than isomerization in *cis*-Co(cyclam)$(OH_2)_2^{3+}$. Clearly for L, a macrocyclic ligand, each *cis* or *trans* isomerization of $CoL(OH_2)_2^{3+}$ must involve water exchange; however, each Co–OH_2 bond-breaking event need not result in isomerization, especially if large conformational changes in the ligand L are involved.[7,8] The probability of isomerization of a Co-LOH_2^{3+} species clearly depends on its lifetime.

(21) It should also be noted that the energy of the visible absorption maximum is $\sim 18.2 \times 10^3$ cm^{-1} both in solution and in the solid state.

(22) P. O. Whimp and N. F. Curtis, *J. Chem. Soc.*, *A*, 867 (1966).

(23) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 4.

(24) Note that the qualitative observations of the kinetic stability of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ in HNO_3 at 25°, reported above, implies the half-lives for *cis* → *trans* isomerizations of these complexes at 25° stand in a ratio of less than 1 :10^{-4}, respectively.

(25) W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1280 (1961).

(26) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *ibid.*, **85**, 1215 (1963).

(27) R. G. Yalman and T. Kuwana, *J. Phys. Chem.*, **59**, 298 (1955).

(28) R. C. Henney, *Inorg. Chem.*, **8**, 389 (1969).

$(OH_2)_2^{3+}$ seems very much out of order. Despite the presence of the azomethine groups the *trans*[14]diene ligand seems quite flexible; certainly the steric differences between the macrocyclic ligands are too small to be obvious from examination of molecular models of *cis*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ and *cis*-Co(tet*b*)$(OH_2)_2^{3+}$. A more likely hypothesis is that the presence of Co–N-(imine) bonds in the *trans*[14]diene complex stabilizes a $CoLOH_2^{3+}$ intermediate.

The kinetic stability of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ is to be contrasted with the rapidity of reaction 1. A further and even more remarkable contrast is that Cl^- *inhibits* the *cis* → *trans* isomerization of Co(cyclam)$(OH_2)_2^{3+}$.[8] It should also be noted (1) that Co–O bond breaking should lead to *cis* → *trans* isomerization (even in the absence of Cl^-); (2) that *cis*-Co(tet*b*)$ClOH_2^{2+}$ cannot be detected as a transient in reaction 1 and has not been prepared by other methods; (3) that Co–Cl bonds are generally about as labile as Co–OH_2 bonds;[29] and (4) that *trans*-Co(tet*b*)$(OH_2)_2^{3+}$ does not seem to be an important product of reaction 1. These considerations suggest that reaction 1 may proceed by means of a nucleophilic attack of Cl^- at the organic backside of *cis*-Co-(tet*b*)$(OH_2)_2^{3+}$.

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(29) Reference 23, Chapter 3.

Chlorotris(triphenylphosphine)iridium(I) and Related Complexes. Oxidative Addition Reactions and Hydrogen Abstraction from the Coordinated Ligand[1]

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Abstract: The preparation, properties, and reactions of a series of complexes of general formula $IrClL_3$ are described, where L is $(C_6H_5)_3P$, $(C_6D_5)_3P$, $(o\text{-}DC_6H_4)_3P$, $(p\text{-}FC_6H_4)_3P$, $(p\text{-}CH_3OC_6H_4)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, $(C_6H_5)_3As$, and $(C_6H_5)_3Sb$. The complex $IrCl(Ph_3P)_3$ differs from the analogous rhodium compound in two principal ways: (i) triphenylphosphine is not so readily lost in solution; (ii) the reaction with hydrogen is irreversible and occurs without displacement of triphenylphosphine, so that $IrCl(Ph_3P)_3$ does not function as a homogeneous hydrogenation catalyst. Reactions with CO, PF_3, NO, and HCl are described. Reaction of $IrCl(Ph_3P)_3$ with chlorine gives initially an iridium(III) complex $IrCl_3(Ph_3P)_2$, which appears to be five-coordinate in solution, and with excess chlorine or nitrosyl chloride the iridium(IV) complex $IrCl_4(Ph_3P)_2$ is formed. This and the analogous triphenylarsine complex are characterized by far-infrared, magnetic susceptibility, and esr measurements. Metal–chlorine stretching frequencies are reported for the new compounds and used where possible to assign stereochemistries. Unlike their rhodium analogs, the iridium(I) complexes $IrClL_3$ isomerize on heating in solvents to octahedral hydrido aryls of iridium(III), the stereochemistry of which is inferred from infrared and proton nmr measurements. It is shown that the isomerization arises by transfer of one hydrogen atom from the *ortho* position of an aromatic ring of the coordinated ligand to the metal, with the formation of a metal–carbon σ bond at the *ortho* position. In the triarylphosphine series, the rate of isomerization depends on the substituent *para* to phosphorus in the order $F < H < OCH_3 < CH_3$. On the basis of the small kinetic isotope effect, a three-center mechanism is suggested for the hydrogen transfer. The reactions of the hydrides are generally similar to but slower than those of the parent iridium(I) complexes. Some of these reactions apparently proceed *via* the iridium(I) complex formed by return of the hydrogen to the ligand. The iridium(I)–iridium(III) tautomerism is compared with similar situations involving Fe(0)–Fe(II) and Ru(0)–Ru(II), and a brief analogy is drawn with metal-catalyzed H–D exchanges in aromatic hydrocarbons.

The ability to undergo oxidative addition reactions with a variety of simple molecules and to catalyze the homogeneous hydrogenation of olefins and acetylenes are features of a number of d^8 metal complexes, notably $IrCl(CO)(Ph_3P)_2$[3] and $RhCl(Ph_3P)_3$.[4,5] On the basis of the limited data presently available, it appears that (a) iridium(I) complexes undergo oxidative addition more readily than rhodium(I) complexes, and (b) oxidative addition is assisted by the presence of good σ-donor ligands on the metal. We therefore decided to attempt the preparation of $IrCl(Ph_3P)_3$, expecting

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(1) Preliminary communication: M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967); presented in part at the Symposium on Transition Metal Complexes of Hydrogen, Oxygen, and Nitrogen and Homogeneous Catalysis, Osaka, Japan, Sept 22, 1967.

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(3) L. Vaska and J. W. Di Luzio, *J. Amer. Chem. Soc.*, 83, 2784 (1961).

(4) M. A. Bennett and P. A. Longstaff, *Chem. Ind.* (London), 846 (1965).

(5) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).