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Electron Transfer Through Organic Structural Units. XII. Reductions of Alkenecarboxylatopentaamminecobalt(III) Complexes with Chromium(II)[1]

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The reductions, with Cr^{2+}, of carboxylatopentaamminecobalt(III) complexes in which a conjugated double bond lies between an aromatic ring and $-COOCo(NH_3)_5$ are retarded at high acidities. A number of these reductions, and that of the sorbato complex (III) as well, conform to the rate law rate = $[Cr^{II}][Co^{III}](k + k'K_B[H^+])(1 + K_B[H^+])^{-1}$, where k and k' are the specific reduction rates of the deprotonated and protonated forms of the complex and K_B is the equilibrium constant for the protonation. Comparable quantities of the tripositive forms (for which k' values lie in the range 0.4–0.8 M^{-1} sec^{-1}) and the dipositive forms (for which k exceeds 1.1 M^{-1} sec^{-1}) are present in 0.1–0.3 M $HClO_4$. It is suggested that conjugative stabilization of a binuclear transition state having radical cation character enhances rates beyond those observed with aliphatic or aromatic carboxylato complexes and that protonation of the double bond at high acidities diminishes conjugation but does not eliminate it.

Early studies[2] of the kinetics of Cr(II) reductions of carboxylatopentaamminecobalt(III) complexes indicated that the rates of such reactions varied with (H^+) in a number of cases where the oxidant featured a chelating site or an additional unsaturated donor center separated from bound cobalt(III) by an extended conjugated system but implied that rates should be independent of acidity in the absence of such groups. Reservations as to the latter point were expressed in the mid 1960's,[3] and these have been substantiated by reports[4] that reduction of the acetatopentaammine complex (which is sometimes taken as a prototype reaction in this series) is approximately 25% more rapid in 0.1 M $HClO_4$ (25°, μ = 1.0) than in 1.0 M $HClO_4$.[5] The present contribution, which deals with $(NH_3)_5Co^{III}$ complexes of α,β-unsaturated carboxylic acids, describes additional instances in which Cr(II) reductions are retarded at high acidities. The effects we observe are more marked than those associated with reductions of the acetato complex,[4] and our treatment differs, in some of its details, from those presented previously.

Experimental Section

Materials. Carboxylatopentaamminecobalt(III) perchlorates not available from previous studies[3,6a] were prepared in water from aquopentaamminecobalt(III) perchlorate[2c] or in diethylene glycol,[6b] either from carbonatopentaamminecobalt(III) nitrate[6c] or from the corresponding carbonato chloride.[6d,7] The principal impurity in these complexes was the parent carboxylic acid. In stubborn cases, it could be removed neigher by repeated recrystallization nor by prolonged extraction with ether, but the presence of such carboxylic acids has been shown, here and in previous studies,[2c,3] to have no measurable effect on the specific rates of reduction by excess Cr^{2+}. Our preparations of the complexes of cinnamic, *m*-hydroxycinnamic, 2-furanacrylic, 2-thiopheneacrylic, and 3-pyridineacrylic acids were found to contain from 5 to 20% of the parent acids, whereas cobalt analyses[2c] of the remaining complexes in this study indicated the presence of less than 3% by weight of parent acid. Single-component kinetic curves in each of the reductions studied ruled out the presence of measurable quantities of reducible Co(III)-containing impurities (including the aquopentaammine complex which sometimes contaminates carboxylato preparations).

Chromous solutions and lithium perchlorate were prepared as described.[2c,8]

Kinetics Experiments. Reductions were first order both in Co(III) and in Cr(II) but were carried out under pseudo-first-order conditions and were monitored spectrophotometrically as described.[8] Rate constants obtained from successive half-life measurements within a single run agreed to better than 3%, whereas those obtained from different runs agreed to about 5%.

Stoichiometry Experiments. Competition experiments, in which a deficiency of Cr(II) was treated with a number of the carboxylato complexes, were carried out as described.[2c] Results are presented in Table I. Stoichiometry was found to be erratic for complexes prepared from the carbonatopentaammine nitrate *via* the aquopentaammine perchlorate, due almost certainly to contamination of these complexes by traces of nitrate. Satisfactory results were obtained from complexes prepared from the carbonatopentaammine chloride.

Table I. Yields of Co(II) from Reduction of Carboxylatopentaamminecobalt(III) Complexes[a]

Ligand	Yield of Co(II), %
Aquo	99
	100[b]
Sorbato	100
	100[b]
o-Hydroxycinnamato	100
p-Hydroxycinnamato	100
m-Methoxycinnamato	100
Phenylpropiolato	99
Acetylenecarboxylato	87[c]

[a] $[H^+]$ = 1.2 M; [Co(III)] = 0.02 M; [Cr(II)] = 0.014 M; Cr(II) added to Co(III). [b] $[H^+]$ = 0.1 M. [c] See ref 3.

Results and Discussion

Rate data are summarized in Table II. Reductions of the *o*-hydroxycinnamato and acetylenecarboxylato complexes have been shown[3] to give carboxylatochromium(III) products, confirming the expected inner-sphere paths for these

(1) From the Ph. D. thesis of A. Liang, Kent State University, 1972. This work was sponsored by the Petroleum Research Fund of the American Chemical Society under Grant 2878-A3; this support is gratefully acknowledged.

(2) See, for example, (a) D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1785 (1961); (b) R. T. M. Fraser, *ibid.*, **84**, 3436 (1962); (c) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

(3) See, for example, E. S. Gould, *J. Amer. Chem. Soc.*, **87**, 4730 (1965).

(4) (a) E. A. Deutsch, Ph.D. Thesis, Stanford University, 1967; (b) M. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10** 1983 (1971).

(5) For description of related acid dependencies in the reductions of dicarboxylatocobalt(III) complexes, see (a) J. R. Ward and A. Haim, *J. Amer. Chem. Soc.*, **92**, 475 (1970); (b) T. J. Przystas and A. Haim, *Inorg. Chem.*, **11**, 1016 (1972).

(6) (a) E. S. Gould, *J. Amer. Chem. Soc.*, **88**, 2983 (1966); (b) E. R. Dockal, E. T. Everhart, and E. S. Gould, *ibid.*, **93**, 5661 (1971); (c) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1946); (d) J. Kranig, *Bull Soc. Chim. Fr.*, [4] **43**, 992 (1928).

(7) The parent carboxylic acids (Aldrich products) used in the preparation of the *o*-, *m*-, and *p*-hydroxycinnamato, the *m*-methoxycinnamato, the furanacrylato, and the thiopheneacrylato complexes had melting points above 140°. In analogy to cinnamic acid, they are taken to be trans acids.

(8) A. Liang and E. S. Gould, *J. Amer. Chem. Soc.*, **92**, 6791 (1970).

Table II. Kinetic Data for Chromium(II) Reduction of Carboxylatopentaamminecobalt(III) Complexes, $RCo(NH_3)_5^{2+}$

Organic ligand, R	$[H^+]$, M	k[a]
Benzoato	0.020	0.15[b]
	1.20	0.15[b]
	0.10	0.153[c]
p-Hydroxybenzoato	0.019	0.18[b]
	1.20	0.20[b]
Acrylato (I)	0.010	0.62
	1.18	0.43
Acetylenecarboxylato	0.010	1.46
	1.18	1.16
trans-Cinnamato (II)	0.010	1.15
	1.18	0.70
Sorbato (III)	0.010	1.25
	0.10	0.94
	0.20	0.86
	0.49	0.69
	1.18	0.52
2-Furanacrylato (IV)	0.010	1.36
	0.10	1.28
	0.20	0.99
	0.49	0.95
	1.18	0.89
o-Hydroxycinnamato	0.010	1.30
	0.10	1.13
	0.20	0.86
	1.18	0.55
m-Methoxycinnamato	0.010	1.26
	0.10	1.09
	0.20	0.97
	0.30	0.88
	0.49	0.82
	1.18	0.74
p-Hydroxycinnamato	0.010	1.12
	0.20	0.92
	1.18	0.60
Phenylpropiolato (V)	0.010	1.40
m-Hydroxycinnamato	0.010	1.14
	1.18	0.78
2-Thiopheneacrylato	0.010	1.36
	1.18	0.84
3-Pyridineacrylato(IV)	0.010	1.2
	1.18	1.03

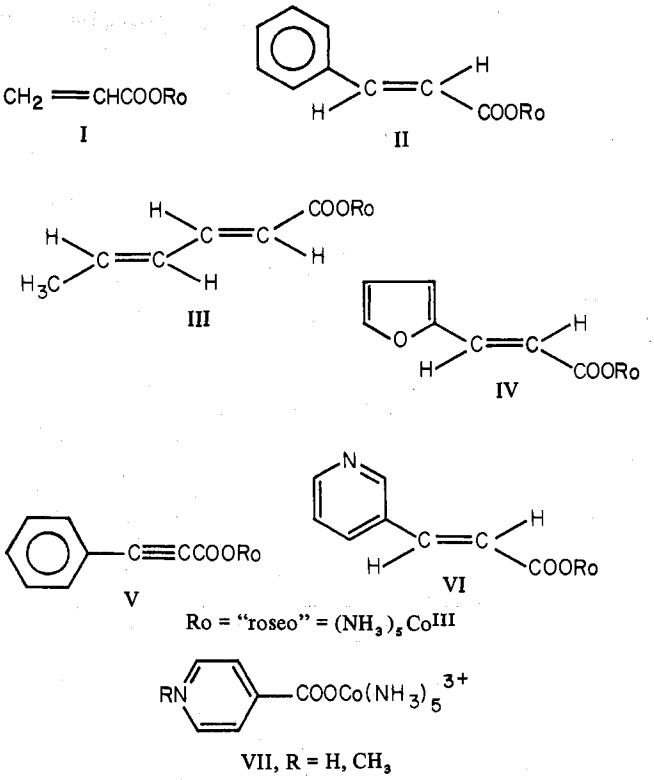
[a] Specific rates in M^{-1} sec^{-1} at 25°; $[Co^{III}]_0 = 0.0002$–0.0015 M; $[Cr^{II}]/[Co^{III}] = 10$; supporting electrolyte $LiClO_4$; $\mu = 1.20$. [b] See ref 8. [c] $\mu = 1.00$. See ref 4b.

complexes. From the correspondingly high specific rates observed for other members of the series, we may safely infer a bridged mechanism for these derivatives as well. The absence of suitable "lead-in groups"[9] other than bound carboxylate in the ligands here chosen rules out remote attack. Moreover, these ligands do not have sites which permit chelation during reduction.[7] The quantitative yields of Co(II) (Table I) eliminate reduction of organic ligands as a significant factor in these reactions, although, in a number of cases, Cr^{2+} has been observed to reduce α,β-unsaturated carboxyl systems in the absence of bound Co(III).[3,6a,10,11]

Specific rates for the reduction of α,β-unsaturated carboxylato complexes are seen to be significantly higher than those observed for straight-chain and aromatic derivatives (which, in the absence of complicating effects, tend to cluster in the range 0.1–0.3 M^{-1} sec^{-1} at 25° and unit ionic strength[2c,9]). Moreover, the decrease in rate at high acidity appears to be general for complexes of this type. The differences are, for the most part, far too great to be attributed reasonably to differences in media[12] and therefore are taken as indicating the existence of (at least) two forms of Co^{III}, differing in their degree of protonation and being reduced at different specific rates. The rate law[4b,8] describing reduction in a system having a protonated and a deprotonated Co(III) species, between which interconversion is rapid, is

$$\text{rate} = [Cr^{II}][Co^{III}]\frac{k + k'K_B[H^+]}{1 + K_B[H^+]} \quad (1)$$

where k and k' are the specific reduction rates of the deprotonated and protonated forms and K_B is the equilibrium constant for the protonation. Although adherence to this expression cannot be tested for all complexes in Table II, agreement is satisfactory for each case in which measurements were made at four or more acidities.[13] In particular, if the specific rate, k_{lim}, at the lowest measured acidity is



(9) See, for example, H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).

(10) (a) A. Lalliaris and D. Katakis, *J. Amer. Chem. Soc.*, **87**, 3077 (1965); (b) C. E. Castro, R. D. Stevens, and S. Moje, *ibid.*, **88**, 4969 (1966).

(11) Although the acetylenecarboxylato complex gives slightly less than the stoichiometric quantity of Co(II) when treated with a deficiency of Cr^{2+}, the good pseudo-first-order kinetic curves obtained for reduction of this complex with excess Cr(II) indicate that reduction of Co(III)-bound ligand is not seriously competing with reduction of Co(III). It seems likely that some ligand reduction occurs after the carboxylato group has been transferred to chromium.

(12) Ionic medium effects in the redox reactions involving cationic species in perchlorate media have been treated by D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971).

(13) The reductions of complexes for which measurements were made at four or more acidities did not conform to either of two more familiar rate laws, (a) or (b), which have been observed for other

$$k_{obsd} = k' + \frac{k}{K_B[H^+]} \quad (a)$$

$$k_{obsd} = k/(1 + K_B[H^+]) \quad (b)$$

Nonadherance to (a) is expected, for this expression describes situations in which the (very small) concentration of a very reactive basic form of the oxidant is inversely proportional to (H^+), and this proportionality is reflected in sharp rate increases at low acidities. Equation b, which has been found to describe the Cr(II) reduction of the acetato complex[4b] and the Cu(I) reduction of several pyridinedicarboxylato complexes,[6b] is similar to (1), but the reactivity of the protonated form of the oxidant, which is represented by the second term in the numerator of the fraction, is considered to be negligible, and observed rate becomes inversely proportional to (H^+) at high acidities.

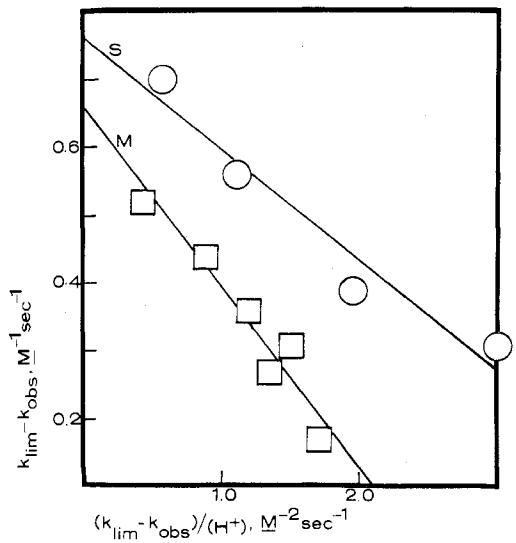


Figure 1. Hofstee-like treatment of rate data for Cr(II) reductions of the sorbato (S) and *m*-methoxycinnamato (M) complexes (rate constants in M^{-1} sec^{-1}, 25°, $\mu = 1.20$). The differences $k_{lim} - k_{obsd}$ are plotted against $(k_{lim} - k_{obsd})[H^+]^{-1}$. Values of k_{lim} (1.25 for the sorbato complex, 1.26 for the methoxycinnamato complex) are taken as the specific rates in 0.010 M $HClO_4$, the lowest acidity studied. Intercepts of the least-squares lines shown lead to k' values (specific rates at very high acidity) of 0.49 and 0.60 M^{-1} sec^{-1} for the sorbato and methoxycinnamato complexes, whereas the slopes correspond to pK_A values of 0.79 and 0.58 for the protonated (tripositive) forms of these complexes (see text).

taken as k, characteristic of the nonprotonated form, both k' (for the protonated form) and K_B may be conveniently obtained by plotting $(k_{lim} - k_{obsd})/[H^+]$ *vs.* $(k_{lim} - k_{obsd})$.[14] Representative graphs in which the data for the sorbato and *m*-methoxycinnamato complexes are treated in this fashion are shown in Figure 1. Values of k', the specific rates for reduction of the protonated complexes (obtained from intercepts of such plots) and acidity constants (obtained from the slopes), are listed in Table III. Data for the derivatives in this table thus indicate the partition of each complex into a protonated (tripositive) form, reduced at specific rate greater than 0.45, and a nonprotonated (dipositive) form, reduced at specific rate greater than 1.0 M^{-1} sec^{-1}, with comparable quantities of the two forms present in 0.1–0.3 M $HClO_4$. For the other complexes having both α,β unsaturation and an aromatic system in conjugation with carboxyl, too few data are at hand to allow estimates of pK values or specific rates of reduction of the protonated forms, but the measured rates, taken at those high- and low-acid ends of the scale practical in this work, are consistent with the same picture.

The rate-enhancing effect associated with the conjugated systems brings to mind an earlier report[2c] of the Cr^{2+} reductions of the protonated and N-methylated derivatives of the 4-pyridinecarboxylato complex VII, both of which react at rates very near to the low-acid limits for the unsaturated complexes here described. Acceleration in the case of such pyridine complexes was ascribed to conjugative stabilization of a binuclear transition state having radical cation character, and a similar description appears appropriate, despite some misgivings,[15] for the conjugated derivatives in the present study. Instances are becoming more numerous in which conjugation is found to enhance inner-sphere reduction although the conjugated system does not lie in the line of electron

(14) This is a modification of the Hofstee treatment described in an earlier communication.[6b] See also B. H. J. Hofstee, *Nature (London)*, **184**, 1296 (1959).

Table III. Specific Rates for Reduction, by Cr(II), and Acidity Constants for Protonated Forms of Carboxylatopentaaminecobalt(III) Complexes, $RCo(NH_3)_5$[a]

R	k'[b]	pK_A[c]
Sorbato (III)	0.49	0.79
2-Furanacrylato (IV)	0.78	0.78
o-Hydroxycinnamato	0.44	0.55
m-Methoxycinnamato	0.60	0.58

[a] At 25°; $\mu = 1.20$. [b] Specific rates, in M^{-1} sec^{-1}, obtained by extrapolation of Hofstee-like plots (see text) to high acidities. [c] Values refer to protonated (tripositive) forms of the complexes. These were obtained from slopes of Hofstee-like plots.

transfer.[9] Indeed, it now appears[16] that the high rates of reduction of coordinated fumarato derivatives (which complexes figured importantly in formulation of the concept of remote attack[2a,17]) arise, at least in part, from such pendant group effects. The extension of these effects to the systems at hand is not completely expected, for, aside from the two acetylenic acids, the ligands in the present study are reduced by Cr^{2+} with much greater difficulty than are fumaric or pyridinecarboxylic acids.[3,6a,10b]

Note that whereas the reductions described here are retarded by increasing acidity, Cr^{2+} reductions of pentaammine-fumarato derivatives are accelerated at high (H^+).[16a] This difference is in keeping with the suggested[16b] duality of paths for reduction of fumarato complexes—an acid-independent path involving adjacent attack at low acidities, supplemented by a first-order acid path featuring protonation of the bound carboxyl and remote at high acidities. The absence of the second carboxyl rules out the rapid high-acid path for the complexes in Table II.

The manner in which protonation facilitates electron transfer in fumarato and related systems has not yet been precisely defined, and the retarding action associated with protonation in our own systems is no more clear. If it is assumed that a single carboxyl group can serve as a bridge only when its carbonyl is free,[18] the substantial rates of reduction of the unsaturated monocarboxylato complexes at the highest acidities studied implies that the protonation, for which kinetic evidence is here presented, takes place elsewhere in the complex, almost certainly at the olefinic or acetylenic linkage. Since the rates observed at high acidities indicate that such protonation diminishes conjugation but does not eliminate it, we suggest that the extra proton is held loosely to the double or triple bond in a π complex, rather than being σ bonded to C_α or C_β.

The pK_A's in Table III are estimated to be 5–7 units more positive than the corresponding values for α,β-unsaturated carboxylic esters,[19] from which the present complexes may

(15) In earlier work[6a] E. S. G. noted that α,β-unsaturated carboxylato complexes were reduced more rapidly than were their saturated analogs but attributed this difference to the circumstance that each doubly bonded carbon has one less interfering substituent than a singly bonded one. Although such a steric factor cannot be ruled out in the present group of reactions, the further accelerations resulting from incorporating a conjugated aromatic system into the ligand indicate the operation of an additional effect.

(16) (a) J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1178 (1968); (b) H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970).

(17) R. T. M. Fraser, D. K. Sebera, and H. Taube, *J. Amer. Chem. Soc.*, **81**, 2906 (1959).

(18) In support of this view, Barrett, Swinehart, and Taube[4b] found the reduction of the protonated form of the acetato complex to be immeasurably slow in solutions containing comparable quantities of the protonated and nonprotonated forms. Note also that Cr(II) reductions of carbonyl-bound carboxamidopentaaminecobalt(III) complexes proceed slowly and through outer-sphere paths. See E. S. Gould, *J. Amer. Chem. Soc.*, **90**, 1740 (1968); R. J. Balahura and R. B. Jordan, *ibid.*, **92**, 1533 (1970).

be derived (in thought) by substituting $(NH_3)_5Co^{III}$ for an alkyl group. A similarly large gap separates the reported pK_A for the protonated acetato complex (−0.60 at μ = 1.0[4b]) from the acidities of protonated acetate esters. The aquo complex H_2O-$Co(NH_3)_5^{3+}$ (pK_A = 6.21[20]) and the protonated alcohols H_2O^+-R (for which pK_A's lie between −2 and −4[19]) are functionally interrelated in an analogous fashion, and here an even greater acidity difference exists. If, as we suspect, the acetato complex is protonated at the carbonyl oxygen whereas the unsaturated complexes are protonated at the double or triple bond, the acid dependencies observed in this series suggest that the strong base-strengthening action of $(NH_3)_5Co^{III}$ (when substituted for hydrogen or alkyl) is transmitted remarkably effectively through conjugated systems. Why such action is not observed also with the formato, benzoato, or trimethylacetato[4b] complexes remains a puzzling point.[21]

Registry No. Table II I, 21035-07-4; II, 36191-54-5; III, 15558-13-1; IV, 36191-56-7; V, 36191-57-8; VI, 36191-58-9; acetylenecarboxalato, 15603-19-7; *o*-hydroxycinnamato, 36191-60-3; *m*-methoxycinnamato, 36191-61-4; *p*-hydroxycinnamato, 36191-62-5; *m*-hydroxycinnamato, 36245-47-3; 2-thiopheneacrylato, 36191-63-6. Cr, 7440-47-3.

(19) Since pK_A's for such unsaturated esters have not yet been reported, it is assumed that interposition of a -CH=CH- linkage between an aromatic ring and a carboxylate group increases the pK_A of an ester by about 1 unit, as has been observed for the protonated (monopositive) forms of the corresponding carboxylic acids. Appropriate data have been compiled by E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 223-402 (1963). This author also emphasizes the conceptual and experimental obstacles associated with fixing a meaningful pK_A value for water. Arguments here are presented in terms of esters and alcohols, rather than carboxylic acids, to avoid this difficulty.

(20) R. C. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, 7, 901 (1968).

(21) An additional unexpected item in the report of Barrett and coworkers[4b] is the marked decrease in K_A of the acetato complex from 4.0 *M* at μ = 1.0 to 0.45 *M* at μ = 4.0, implying that reduction rates should vary more drastically, in the range 0.1-1.0 *M* $HClO_4$, at the higher ionic strength than at the lower. Since a tenfold change in K_A with only a fourfold change in μ appeared unusually large and because one of Barrett's values was obtained spectrophotometrically whereas the other was obtained kinetically, a confirmation of K_A at high μ was undertaken. Rate measurements at μ = 4.0 by J. R. Barber, Jr., Kent State University, 1971, yield a K_A value of 0.44 for the acetato complex, in excellent agreement with the spectrophotometric value. Moreover, in accord with Barrett's findings, no evidence for protonation of the formato complex is obtained, even on extending measurements to μ = 4.0.

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Equilibrium Energetics of Cis-Trans Isomerization for two Square-Planar Palladium(II)-Phosphine Complexes

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Equilibrium thermodynamics for the cis-trans isomerization of the compounds $[PhP(CH_3)_2]_2PdCl_2$ and $(Ph_2PCH_3)_2PdCl_2$ in a series of 11 solvents as determined by variable-temperature proton nuclear magnetic resonance are reported. It is found that for both complexes in most solvents the cis isomer is thermodynamically more stable than the trans isomer, that polar solvents favor the cis isomer, and that the isomerization process is entropy controlled and probably occurs *via* a solvent association mechanism.

Introduction

It has long been known that the cis isomers of square-planar platinum(II)-phosphine complexes are thermodynamically more stable than the trans isomers.[1,2] The trans isomers have, however, been isolated in several cases and the ability to isolate both isomers has been attributed to a kinetic phenomenon (*viz.*, the robust nature of these complexes).[3]

Electronic spectral studies, X-ray crystallography, and dipole moment measurements have shown that in general for the platinum complexes, the trans isomers are yellow and the cis isomers are colorless.[4] By analogy with these results, the palladium complexes $(R_3P)_2PdX_2$, which are nearly always various shades of yellow and possess low dipole moments in benzene solution, have been assigned the trans configuration.[4] In only three cases have both isomers been isolated for palladium.[3] The tendency for isomerization of the relatively labile palladium complexes makes these assignments tenuous since the less polar trans complexes are favored in solvents such as benzene.[5] In fact, more recent studies using infrared and nmr methods have shown that the cis complexes of palladium are indeed more common than originally believed.[6-12]

In addition, it has recently been shown by X-ray crystallography that the yellow complex $[PhP(CH_3)_2]_2PdCl_2$, originally believed to be trans, is cis in the solid state.[13] Jenkins and Shaw[12] found that this complex existed as a mixture of 67% cis and 33% trans in deuteriochloroform

(1) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 273, 4300 (1952).
(2) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 525 (1956).
(3) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 3833 (1971).
(4) G. Booth, *Advan. Inorg. Chem. Radiochem.*, 6, 1 (1964).
(5) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. 1, Academic Press, New York, N. Y., 1971, p 42.
(6) G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).
(7) A. Pidcock, *Chem. Commun.*, 92 (1968).
(8) R. G. Goodfellow, *Chem. Commun.*, 114 (1968).
(9) S. O. Grim and R. L. Keiter, *Inorg. Chim. Acta*, 4, 56 (1970).
(10) R. L. Keiter, Ph.D. Thesis, University of Maryland, 1967.
(11) R. G. Goodfellow, J. G. Evans, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc. A*, 1604 (1968).
(12) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).
(13) L. L. Martin and R. A. Jacobsen, *Inorg. Chem.*, 10, 1795 (1971).