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Registry No. $CoP(H_2O)_2$, 51405-04-0; py, 110-86-1; $CoP(H_2O)(py)$, 53993-53-6; SCN^-, 302-04-5; $S_2O_4^{2-}$, 14844-07-6; $CoP(py)_2$, 53993-54-7.

Supplementary Material Available. Kinetic data for the substitution reactions CoTMpyP with pyridine and for the reduction of CoTMpyP with dithionite will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40150X.

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Electron Transfer through Organic Structural Units. XVIII. Titanium(III) Reductions of Coordinated Cobalt(III)[1]

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Specific rates of reduction, with Ti(III), of 17 pentaamminecobalt(III) complexes (containing a variety of carboxylato groups) have been measured at 25°, in aqueous *p*-toluenesulfonate media. All carboxylato complexes are reduced more rapidly than the derivative of *N,N*-dimethylnicotinamide, I, which reacts *via* an outer-sphere path. In most instances, rate laws feature a prominent inverse-(H^+) term, even when the oxidant has no acidic center, thus implicating $TiOH^{2+}$ as the predominant reducing species. In two cases, an important $(H^+)^{-2}$ term, the first to be reported for reduction of a Co(III) species, is observed as well. Large rate increases associated with the attachment of α-OH to the carboxyl ligand strongly indicate an inner-sphere path, with carboxyl bridging, for reactions in this series; such neighboring hydroxyl accelerations are proportionally more pronounced for Ti(III) than for Cr(II) or Eu(II). Very high rates are observed for several substituted salicylato complexes, but in these reductions the acid-independent term, which is generally negligible for complexes in this series, is preferentially enhanced, and the $(H^+)^{-1}$ term is not observed. In contrast to reductions by Cr(II), no acceleration or alteration of the form of the rate law results from incorporation of a carbonyl group in conjugation with $-COOCo^{III}$. This difference in response with the two reductants is in accord with earlier evidence that such enhanced reductions, irrespective of the position of attack, involve preliminary one-electron transfer to the ligand, a reduction for which the potential of Ti(III) is insufficient.

Relatively few kinetic investigations of the reactions of Ti(III), the most powerfully reducing of the readily accessible d^1 metal centers, have been described.[2] Although this reductant can be prepared and stored with ease, choice of a reaction medium in which to carry out quantitative studies presents problems. Ti(III) is most often generated in aqueous HCl or H_2SO_4, but rate laws for redox reactions in such solutions frequently include chloride- or sulfate-dependent terms.[2a,3] Such reactions may be further complicated by the formation of Ti^{III}–Ti^{IV} complexes.[4] Both nitrate[5] and perchlorate[3b,6] are reduced by Ti(III); the latter reaction is slow enough to allow the study of very rapid reductions in perchlorate solutions[2b,c,3a] but seriously interferes with measurements of the rates of slower reactions, particularly at high acidities.

This article, which deals mainly with reactions in which the supporting electrolyte is *p*-toluenesulfonate (OTs^-), appears to be the first report of redox reactions of Ti(III) in systems containing organic mediating ligands. We here present evidence that Ti(III), like Cr(II),[7] Cu(I),[8] V(II),[9] and Eu(II),[10] undergoes inner-sphere oxidation by a variety of carboxylatocobalt(III) complexes and that these reactions are unusually sensitive both to protonation and to chelation.

Experimental Section

Materials. Lithium perchlorate was prepared as described.[8] The *p*-toluenesulfonates of barium and sodium ($Ba(OTs)_2$ and NaOTs) were prepared by neutralization of *p*-toluenesulfonic acid (HOTs). Solutions of this acid used in rate studies were prepared by mixing the appropriate quantity of concentrated H_2SO_4 with a slight excess of $Ba(OTs)_2$ in deionized water which had been boiled and cooled under N_2, stirring overnight at room temperature, and then filtering off the precipitated $BaSO_4$. The resulting solution, which gave no precipitate when tested with Ba^{2+}, was deoxygenated by passage of N_2 for 4–6 hr and stored under N_2.

The NaOTs solution for rate studies was prepared in oxygen-free water; (Na^+) in this solution was determined by passing an aliquot through a cation-exchange column (Bio-Rad AG 50W-X2, 200–400 mesh) in its H^+ form and then titrating the eluent with standard NaOH.

Carboxylatopentaamminecobalt(III) perchlorates were available from previous studies[8] or were prepared by published procedures.[8,10,11]

Stock Ti(IV) solutions were prepared by stirring 4.0 g of $TiOSO_4 \cdot 2H_2O$ in 100 ml of 1 *M* HOTs and heating to 80° (but no higher). The solution was allowed to stand overnight at room temperature and then was filtered to remove precipitated TiO_2. The filtrate could be stored for 2–3 weeks at room temperature without further precipitation.

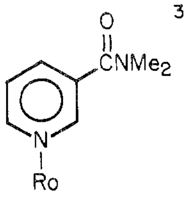
Solutions of Ti(III), free from complexing anions, were prepared by stirring 11 ml of the Ti(IV) solution in HOTs with zinc amalgam, in a vessel stoppered with a rubber serum cap, for 1 hr at 25°. The solution was added (syringe) to a stoppered centrifuge tube containing 1.46 g of powdered $Ba(OTs)_2$. The tube was shaken for 2 min, allowed to stand at 4° overnight, and centrifuged; and the clear purple supernatant was used for rate studies. Such solutions were used within 8 hr after centrifugation although they retained their purple color for several weeks if protected from air. The Ti(III) concentration (approximately 0.1 *M*) was determined by adding a known volume to a solution of excess $Cl(NH_3)_5Co(ClO_4)_2$ under N_2, waiting 30 min, diluting tenfold with concentrated HCl, filtering under pressure, and determining $CoCl_4^{2-}$ at 692 nm in the filtrate (ϵ 560).[11] The acidity of the Ti(III) solution was determined by passage through a cation-exchange resin in its H^+ form, titrating the eluent with NaOH, and correcting for Ti(III), Ba(II), and Zn(II) present in solution before exchange; this method gave acidities of 0.9–1.1 *M*, in agreement with the 1.0 *M* HOTs used initially.

Rate Measurements. Reactions were carried out under pseudo-first-order conditions, using at least a fivefold excess of either Ti(III) or Co(III), and were followed on a Cary spectrophotometer equipped with an 0.0–0.2 absorbance unit scale. The temperature was maintained at 25.0 ± 0.2° for all runs. The ionic strength was kept near 1.0 using HOTs–NaOTs or, in a few cases, $HClO_4$–$LiClO_4$. Reactions were followed at both 502 and 350 nm and were carried out under N_2.[12] Syringes were used for transfer of solutions. In cases where aquation of the cobalt complex was considered to be a problem, this complex was added after thermal equilibration of the supporting medium. Choice of cell size, reagent taken in excess, quantities of materials, and reaction conditions was as described.[13] All reactions were first order each in Co(III) and Ti(III). Except for the very slow reactions, where specific rates were evaluated by the method of Guggenheim,[14] reactions were followed for at least 5 half-lives. Rate constants obtained from successive half-life values within a single run agreed to within 4%. No trends indicative of systematic errors were noted, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 6%. No evidence for autocatalysis, as reported for related systems,[9,10,13,15] nor of autoinhibition[3a] was obtained.

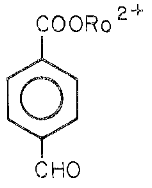
Three of the systems, for which total absorbance changes appeared to be greater than for the others, were studied in the stop-flow spectrophotometer at 500 nm in order to detect reactions occurring within the first second after mixing. Small but reproducible increases in absorbance were observed when 10^{-3} *M* solutions of the salicylato or 3-methylsalicylato derivative of $(NH_3)_5Co^{III}$ were mixed with 10^{-2} *M* Ti(III), after which the absorbance decreased as reduction of Co^{III} became the principal reaction. Much larger increases were observed with the 2,6-pyridinedicarboxylato complex, but the reduction of this complex appeared to be complicated by partial reduction of the ligand. Maximum absorbance values were observed at 0.15 sec after mixing with the salicylato complex, 0.80 sec after mixing with the 3-methylsalicylato complex, and 0.020 sec after mixing with the pyridinedicarboxylato derivative. No rapid absorbance changes attributable to monomer–dimer interconversion, as described by Birk[2b] for Ti(III) and by Wang[16] for U(III), were observed.

Results and Discussion

Typical kinetic data are given in Table I. The initial entry refers to the very slow reduction of the ring-coordinated derivative, I, the organic ligand of which has been shown to be an effective mediator for outer-sphere electron-transfer reactions.[9b,10] Indeed, in reductions with $Ru(NH_3)_6^{2+}$, for which the outer-sphere path is mandatory, complex I has been found to react much more rapidly than carboxylatocobalt(III) complexes as a class.[10] Since the order of reactivity within a series of outer-sphere oxidants is generally independent of the reductant used,[10,17] the general increase in k_{Ti} values here observed as the various carboxylato groups are substituted for *N,N*-dimethylnicotinamide hints strongly that a second, more facile, path has become available for Ti(III) reductions of the carboxylato complexes. Moreover, the further, and more marked, accelerations resulting from attachment of neighboring donor groups in the oxidant leave little doubt that we are dealing with electron transfers through the carboxyl bridge. Specific rates are summarized and compared to those for Cr^{2+}, the prototype inner-sphere reductant, in Table II.



I



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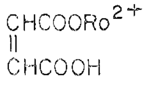
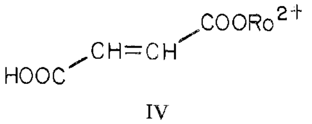


$$\begin{matrix} CHCOORo^{2+} \\ \| \\ CHCOOH \end{matrix}$$

III



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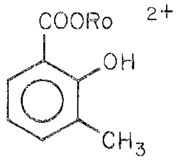

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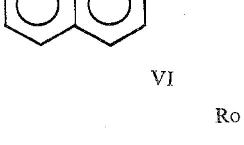

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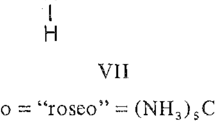
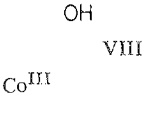


VII



$$\begin{matrix} CH_3CHCOORo^{2+} \\ | \\ OH \end{matrix}$$

VIII

Ro = "roseo" = $(NH_3)_5Co^{III}$

Although we have not looked for acid dependencies with all carboxylato complexes listed, it appears that the inverse-(H^+) relationship found here for the maleato (III),

Table I. Kinetic Data for Titanium(III) Reductions of Pentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$

Organic ligand, R	$(H^+), M$	k^a
N,N-Dimethylnicotinamide (I)	1.0	$<6 \times 10^{-4}$ [b]
o-Methoxybenzoato	1.0	0.0015[b]
p-Formylbenzoato (II)	1.0	0.0022[b]
o-Formylbenzoato	1.0	0.0017[b]
Fluoroacetato	1.0	0.0039[b]
p-Hydroxybenzoato	1.0	0.0042[b]
Acetato	1.0	0.0049[b]
Maleato (III)	0.47	0.0069
	1.0	0.0032
Fumarato	0.47	0.0130
	1.0	0.0053
Formato	0.033	0.21
	0.060	0.125
	0.17	0.043
	0.89	0.0085
3-Phenylsalicylato	0.040	1.46
	0.070	1.46
	0.10	1.38
	0.52	1.33
	0.99	1.36
3-Methylsalicylato (V)	0.020	2.6
	0.084	2.4
	0.12	2.4
	0.22	2.5
	0.48	2.6
	1.00	2.4
2-Hydroxyl-1-naphthoato (VI)	0.094	3.9
	0.22	3.6
	0.52	3.7
	0.99	3.4
Glycolato	0.021	15.1
	0.026	11.9
	0.039	7.5
	0.068	4.6
	0.14	2.1
	0.98	0.29
Lactato (VIII)	0.020	65
	0.025	58
	0.047	29
	0.087	16.1
	0.11	12.7
	0.47	2.8
	0.98	1.28
2-Pyridinecarboxylato (VII)	0.071	0.123
	0.10	0.053
	0.47	0.0064
	1.00	0.0019
Oxalato	0.10	1.2×10^2
	0.12	76
	0.15	56
	0.20	33
	0.25	22
	0.47	5.6
	0.73	2.2
	0.99	1.20

[a] Specific rates in M^{-1} sec^{-1} at 25°. $\mu = 1.0$ unless otherwise indicated. k defined as $-d(Co^{III})/dt(Co^{III})^{-1}(Ti^{III})^{-1}$. Reactions having specific rates less than 10 M^{-1} sec^{-1} run with $(Co^{III})_0 = 7 \times 10^{-5}$–$1 \times 10^{-3}$ M and $(Ti^{III})/(Co^{III}) = 10$–$100$. Faster reactions run with $(Co^{III})_0 = 1 \times 10^{-4}$–$5 \times 10^{-4}$ and $(Ti^{III})/(Co^{III}) = 0.1$–$0.2$.[13] Values are averages of two to five replicate runs; except for the very slow reactions, agreement between runs was better than 6%. [b] $\mu = 1.70$.

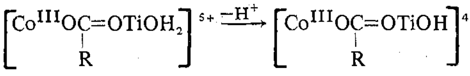
Table II. Specific Rates[a] for Titanium(III) and Chromium(II) Reductions of Pentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$

R	k_{Ti}	k_{Cr}[b]
Formato	$0.0070/(H^+)$	7.2
Maleato	$0.0033/(H^+)$	200
Fumarato	$0.0055/(H^+)$	$1.6 + 4.0(H^+)$[c]
3-Phenylsalicylato	1.40	$0.0140/(H^+)$[d]
3-Methylsalicylato (V)	2.5	$0.046 + 0.0066/(H^+)$[d]
2-Hydroxyl-1-naphthoato (VI)	3.6	$0.10 + 0.084/(H^+)$[d]
2-Pyridinecarboxylato (VII)	$0.0018/(H^+) + 0.0044/(H^+)^2$	$36/(H^+)$
Oxalato	$1.20/(H^+)^2$	$100 + 400/(H^+)$
Glycolato	$0.31/(H^+)$	3.1
Lactato (VIII)	$1.35/(H^+)$	6.7

[a] Specific rates in M^{-1} sec^{-1} at 25°, $\mu = 1.0$. [b] Rates for Cr(II) reactions taken from ref 7–9 unless otherwise indicated. [c] J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1178 (1968). [d] A. Liang, Ph.D. Dissertation, Kent State University, 1972.

fumarato (IV), formato, glycolato, and lactato (VIII) derivatives and reported by Earley[2e] for Ti(III) reductions of the halopentaammine complexes applies also to the six more slowly reacting carboxylato oxidants in Table I. Since proportionality to $(H^+)^{-1}$ is observed with several oxidants not having acidic centers, it must reflect, at least in large part, deprotonation of $Ti(H_2O)_6^{3+}$, a complication which does not enter the picture with the less acidic dipositive aquated reductants. No kinetic leveling effects are observed at acidities as low as 0.02 M, the lower limit in these studies, indicating that the pK_A value of 2.8 reported for Ti_{aq}^{3+} by Krentzien and Brio[18] in aqueous chloride fits our OTs^- systems more closely than does the older set of values near 2.0[19] evaluated for aqueous bromide and iodide.

For those reductions having rates inversely proportional to (H^+), reaction through a transition state of type IX has been overshadowed by the conjugate base path through X. Thus, in these instances, inner-sphere rates are remarkably sensitive to variation in the nonparticipating ligands about the reductant.



$$\left[\begin{matrix}Co^{III}O\underset{\displaystyle R}{\underset{|}{C}}{=}OTiOH_2\end{matrix}\right]^{5+} \xrightarrow{-H^+} \left[\begin{matrix}Co^{III}O\underset{\displaystyle R}{\underset{|}{C}}{=}OTiOH\end{matrix}\right]^{4+}$$

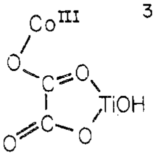
IX X

Formally analogous nonbridging ligand effects associated with the ease of reduction of coordinated Co^{III} have been considered by several workers.[20] Emphasis has been placed on shifts in the energy of the d_{z^2} orbital of cobalt into which the electron moves, but such a rationale, obviously cannot be extended to Ti(III), from which a t_{2g} electron is lost. Although too few examples of nonbridging ligand effects at reducing centers have been reported to establish a pattern,[21] we attribute at least a portion of the rate enhancement associated with the conversion of IX and X simply to the increase of electron density of Ti(III), resulting not only from the loss of H^+ but also from the more effective π donation from the hydroxyl ligand. In energetic terms, coordination of hydroxide to Ti(III) significantly raises its oxidation potential.

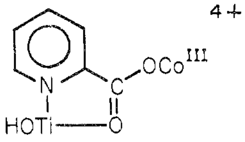
Superimposed on the $(H^+)^{-1}$ dependence for many of the Ti(III) reductions are several striking rate increases associated with attachment of a neighboring hydroxyl to the bridging ligand. Differences in the forms of the rate laws complicate individual comparisons with reductions by other metal centers, but examination of rate ratios within a series may be instructive. For example the ratio k_{lac}/k_{pr}, referring to reduction of the lactato (VIII) and propionato complexes, is <5 for Cu^+, 40 for Cr^{2+}, 77 for Eu^{2+}, and >300 for $TiOH^{2+}$.[8,10,22] Since it is unlikely indeed that substitution of an α-OH group on a saturated side chain can facilitate internal electron transfer within the binuclear precursor complex, the accelerations almost certainly reflect increases, due to chelation, in the formation constants of the lactato precursors.[7] Enhancement is greatest for reduction by the hard Ti(III) center and least with the soft Cu^+ center, in keeping with the "hard-base" character of the hydroxyl group.[23]

Reactions of two members of the present series are extraordinarily sensitive to acidity. Reductions of the oxalato complexes conform closely to a one-term rate law featuring $(H^+)^{-2}$, whereas rates of reduction of the 2-pyridinecarboxylato derivative (VII) fit in a binomial expression having both an

$(H^+)^{-1}$ and an $(H^+)^{-2}$ term (Table II).[24] Since deprotonation of both of these oxidants yields strongly chelating functions, the $(H^+)^{-2}$ paths, the first to be reported for reductions of Co(III), may be taken to represent reaction through transition states XI and XII. Specific rates, corresponding to reduction *via* bimolecular reaction of $TiOH^{2+}$ with the deprotonated form of the oxidant, may be calculated by dividing k_{-2}, the coefficient for the $(H^+)^{-2}$ term, by the product $K^A{}_{Ti}K^A{}_{Co}$.[9a,11,18] The resulting quotients are $8.6 \times 10^4\ M^{-1}\ sec^{-1}$ for the oxalato and $2.7 \times 10^4\ M^{-1}\ sec^{-1}$ for the pyridinecarboxylato complex, both values being comparable to those for Cr(II) reductions.[25]



XI



XII

Although the importance of chelation in inner-sphere electron-transfer reactions has long been recognized,[11,27] the precise manner in which chelation influences the distribution between reaction paths at the various protonation levels is not understood. In the Cr(II) series, attachment of a neighboring carboxyl or phenolic hydroxyl most often accelerates the monodeprotonated path,[27a] but with the maleato derivative (III), it is the acid-independent path which is preferentially enhanced,[28] a contrast which is especially astonishing in view of the relatively high acidity of the uncoordinated carboxyl group.[29b] In the Ti(III) reductions of the 3-methylsalicylato (V), 3-phenylsalicylato, and 2-hydroxyl-1-naphthoato (VI) complexes, substantial rate increases by the neighboring hydroxyl groups are anticipated, but, again unaccountably, the acid-independent, rather than the deprotonated, paths are affected. Indeed, acceleration is so pronounced that the acid-independent term, which is negligible for most complexes in the Ti(III) series, predominates to the virtual exclusion of all other paths.[30]

Note finally that the k_{Ti} values for the *p*-formylbenzoato complex (II), its ortho isomer, and the fumarato (IV) complex lie close to the slow end of the scale for carboxylato complexes, thus contrasting with Cr(II) reductions, in which incorporation of a carbonyl or carboxyl group in conjugation with $-COOCo^{III}$ often results in significant rate increases, and, in some instances, alteration of the form of the rate law.[7,31] Recent evidence indicates that attack in such enhanced reductions sometimes occurs at the remote lead-in group[32a] and sometimes at the bound carboxyl,[32b] but reaction in both cases appears to involve preliminary one-electron reduction of the ligand, followed by internal electron transfer to bound Co(III). A requirement for this pair of mechanistic variations is then that the potential associated with the reducing center be well above the value needed for reduction of the ligand.[33] Hence, such conjugative accelerations are not observed for Ti(III), nor have they been reported for the less effective reducing centers, Cu^+ and Fe^{2+}.

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Registry No. *N,N*-Dimethylnicotinamide$(NH_3)_5Co^{III}$, 31011-70-8; *o*-methoxybenzoato$(NH_3)_5Co^{III}$, 31083-91-7; *p*-formylbenzoato-$(NH_3)_5Co^{III}$, 19743-65-8; *o*-formylbenzoato$(NH_3)_5Co^{III}$, 42532-71-8; fluoroacetato$(NH_3)_5Co^{III}$, 51965-33-4; *p*-hydroxybenzoato-$(NH_3)_5Co^{III}$, 30931-75-0; acetato$(NH_3)_5Co^{III}$, 16632-78-3; maleato$(NH_3)_5Co^{III}$, 17712-86-6; fumarato$(NH_3)_5Co^{III}$, 17712-85-5; formato$(NH_3)_5Co^{III}$, 19173-64-9; 3-phenylsalicylato$(NH_3)_5Co^{III}$, 54063-06-8; 3-methylsalicylato$(NH_3)_5Co^{III}$, 54063-07-9; 2-hydroxyl-1-naphthoato$(NH_3)_5Co^{III}$, 54063-08-0; glycolato-$(NH_3)_5Co^{III}$, 31279-86-4; lactato$(NH_3)_5Co^{III}$, 34464-03-4; 2-pyridinecarboxylato$(NH_3)_5Co^{III}$, 42582-64-9; oxalato$(NH_3)_5Co^{III}$, 19306-87-7; titanium(III), 22541-75-9; *p*-toluenesulfonic acid, 104-15-4.

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(22) When k_{pr} has not been measured, as is the case with Ti(III) and Cu^+, it may be estimated as half the rate for the acetato complex under corresponding conditions.[10] It is further assumed that the reduction, with Ti(III), of the propionato complex, in common with the other slowly reduced complexes for which acidity patterns have been determined, is inverse first order in (H^+).

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(24) For a rate law of the type $k_{obsd} = k_{-1}(H^+)^{-1} + k_{-2}(H^+)^{-2}$, values of k_{-1} and k_{-2} may be conveniently obtained by plotting the product $k_{obsd}(H^+)$ *vs.* $1/(H^+)$. The slope of the resulting least-squares line is k_{-2}; the intercept, k_{-1}.

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(28) Despite earlier claims to the contrary,[29a] the Cr(II) reduction of the maleato complex, III, has been shown[29b] to be independent of acidity in the range 0.01–1.0 *M* H^+. The predominant Cr(III) product from this reaction is a chelate.[29b]

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(30) Equally puzzling are preliminary data for the Ti(III) reduction of the salicylato derivative of $(NH_3)_5Co^{III}$ and for the 4-methyl-, 5-methyl-, and 4-hydroxysalicylato complexes. In both OTs^- and $ClO_4{}^-$ media, each of these reactions is rapid and conforms to a rate law of the type

$$\text{rate} = \frac{(Ti^{III})(Co^{III})k_{lim}}{1 + (H^+)/K} \qquad (1)$$

where k_{lim}, the limiting specific rate at low acidities, falls near 100 M^{-1} sec^{-1} for complexes in this group, and K is approximately 1 *M*. Such

a rate law is appropriate for a system in which either the oxidant or the reductant is partitioned into an inactive acidic form (having an acidity constant K) and an active basic form, with the two forms existing in comparable concentrations in 1 M H^+. However, both $Ti(H_2O)_6^{3+}$ and the phenolic oxidants are very nearly completely protonated at this acidity. Moreover the observed twofold variation in k_{obsd} when (H^+) is increased from 0.02 to 1.0 M appears to be far too great to be attributed to a medium effect. In short, the kinetic behavior of these hydroxy-substituted complexes conforms to no simple mechanistic picture.

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Synthesis of Some Rhodium(I) Complexes Containing Isocyanides and Phosphites, Phosphonites, or Phosphinites and Their Reactions with Cyanoolefins

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The synthesis of $[Rh(RNC)_2L_n]ClO_4$ (R = p-$CH_3OC_6H_4$ or p-$CH_3C_6H_4$; n = 2, L = $P(OPh)_3$; n = 3, L = $PPh(OMe)_2$ or $PPh_2(OMe)$), $[Rh(RNC)_2L_2(\text{cyanoolefin})]ClO_4$ (R = p-$CH_3OC_6H_4$ or p-$CH_3C_6H_4$; L = $P(OPh)_3$, $PPh(OMe)_2$, or $PPh_2(OMe)$; cyanoolefin = tetracyanoethylene (TCNE) or fumaronitrile (FN)), and $Rh(RNC)_2(P(OPh)_3)(\text{cyanoolefin})I$ (R = p-$CH_3OC_6H_4$ or p-$CH_3C_6H_4$; cyanoolefin = TCNE or FN) is described. Their ir and pmr spectra have been obtained to suggest their configurational behavior in solution. In the TCNE complexes TCNE may be coordinated rigidly to the rhodium atom perhaps in a trigonal-bipyramidal environment with axial isocyanides and equatorial phosphorus ligands. The five-coordinated complexes $[Rh(RNC)_2L_3]ClO_4$ (**2** and **3**; R = p-$CH_3OC_6H_4$ and p-$CH_3C_6H_4$; L = $PPh(OMe)_2$ and $PPh_2(OMe)$), undergo the dissociative exchange of L at higher temperatures. Temperature-dependent virtual coupling signals of P-OMe protons of $[Rh(RNC)_2(PPh(OMe)_2)_2(FN)]ClO_4$ (**9**) at lower temperatures are consistent with a gradual change of the interaction between FN and the rhodium atom with lowering temperature. Temperature-dependent pmr signals of FN protons of $Rh(RNC)_2(P(OPh)_3)(FN)I$ (**10**) at lower temperatures are interpreted in terms of a restricted rotation of FN in a time-averaged square pyramid. At higher temperatures **9** and **10** undergo the dissociative exchange of FN.

Introduction

Cyanoolefins have widely been known to form rigid adducts with low-valent transition metal complexes containing tertiary phosphines and/or carbon monoxide.[1] Recently we have reported for the first time a series of nonrigid cyanoolefin adducts with some rhodium(I) isocyanide complexes.[2] This novel result will be related to the fact that isocyanides are known to be moderate σ donors and are probably intermediate in π-acceptor capacity between phosphines and carbon monoxide.[3] Thus, it will be of interest to study the reactions of cyanoolefins with some rhodium(I) complexes containing ligands which may resemble isocyanides in coordinating ability.[4]

Here we report the preparation of some rhodium(I) complexes involving isocyanides and phosphites, phosphonites, or phosphinites and their reactions with tetracyanoethylene (TCNE) and fumaronitrile (FN).

Experimental Section

Isocyanides[5] and phosphorus ligands[6] were prepared by literature methods. $[Rh(1,5\text{-}C_8H_{12})(P(OPh)_3)_2]ClO_4$ was also prepared according to the literature method.[7] $[Rh(1,5\text{-}C_8H_{12})L_3]ClO_4$ (L = $PPh(OMe)_2$ and $PPh_2(OMe)$) were synthesized in manners similar to that of the $P(OPh)_3$ complex. Preparations of the complexes were usually carried out under nitrogen at ambient temperature. Recrystallizations were done in air usually once but repeatedly in some cases (**1a**, **1b**, **3a**, **4a**, and **6b**) until satisfactory analytical data were obtained.

Many of the complexes were prepared by the similar procedures, so only a few representative examples are described in detail. Physical measurements were performed as described elsewhere.[2] The recrystallization solvents and analytical and physical data for the complexes are collected in Table I. Ir and pmr data are summarized in Table II.

Preparation of the Starting Complexes. Bis(p-methoxyphenyl isocyanide)bis(triphenyl phosphite)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2]ClO_4$ (1a). To a solution of $[Rh(1,5\text{-}C_8H_{12})(P(OPh)_3)_2]ClO_4$ (1430 mg, 1.5 mmol) in CH_2Cl_2 (20 ml) was added dropwise a solution of p-$CH_3OC_6H_4NC$ (410 mg, 3.0 mmol) in CH_2Cl_2 (5 ml). The color of the solution turned from orange to yellow. After being stirred for 1.5 hr, the solution was concentrated under reduced pressure. Addition of C_2H_5OH afforded a yellow precipitate, which was filtered and recrystallized from CH_2Cl_2–C_2H_5OH to give yellow plates of **1a** (1520 mg, 91%).

Bis(p-methoxyphenyl isocyanide)tris(dimethyl phenylphosphonite)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_3]ClO_4$ (2a). The product obtained from a reaction of $[Rh(1,5\text{-}C_8H_{12})(PPh(OMe)_2)_3]ClO_4$ (250 mg, 0.31 mmol) with p-$CH_3OC_6H_4NC$ (82 mg, 0.62 mmol) was recrystallized from CH_2Cl_2–ligroin (bp 70–90°) to afford yellow needles of **2a** (230 mg, 76%).

Preparation of the TCNE Complexes. Bis(p-methoxyphenyl isocyanide)bis(triphenyl phosphite)(tetracyanoethylene)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)_2(TCNE)]ClO_4$ (4a). TCNE (26 mg, 0.2 mmol) was added to a solution of **1a** (224 mg, 0.2 mmol) in CH_2Cl_2 (5 ml). The solution was stirred for 1 hr, during which time the color of the solution changed from yellow to almost colorless. The product obtained upon concentration under reduced pressure was recrystallized from CH_2Cl_2–petroleum ether (bp 40–70°) to afford pale yellow crystals of **4a** (180 mg, 72%).

Bis(p-methoxyphenyl isocyanide)bis(dimethyl phenylphosphonite)(tetracyanoethylene)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh(OMe)_2)_2(TCNE)]ClO_4$ (5a). A reaction of **2a** (94 mg, 0.12 mmol) with TCNE (15 mg, 0.12 mmol) gave a product, which was recrystallized from CH_2Cl_2–C_2H_5OH to afford pale brown crystals of **5a** (45 mg, 50%).

Iodobis(p-methoxyphenyl isocyanide)(triphenyl phosphite)(tetracyanoethylene)rhodium, $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)(TCNE)I$ (7a). To a solution of **1a** (76 mg, 0.7 mmol) in CH_2Cl_2 (2 ml) was added TCNE (9 mg, 0.7 mmol) and then NaI (13 mg, 0.9 mmol) in C_2H_5OH (2 ml) and the mixture was stirred for 1 hr. The color of the solution changed from yellow to pale yellow and then to orange. Concentration under reduced pressure precipitated a product, which