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(19) M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc. A*, 2069 (1971).Contribution from the Lash Miller Chemical Laboratories,
University of Toronto, Toronto, Ontario, Canada**Dissymmetric Arsine Complexes. Cobalt Hydrides**

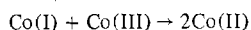
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General methods for the preparation of arsenicobalt hydrides are given and the problems associated with isolating them are discussed. It is shown that, electronically, all the derivatives are formally cobalt(III) complexes despite the dichotomous chemical properties observed with some of the hydrides. No correlation between the variations in the hydride chemical shifts and the ligand field strengths of the axial ligands is found and the possible reasons for this are suggested. An aquo group trans to a hydrido ligand is labilized to the extent that its exchange is observable on an NMR time scale. The presence of two hydrido ligands confers stereochemical nonrigidity to the *cis*-[Co(diars)₂(H)₂]ClO₄ system at room temperature.

Of the non-carbonyl-containing hydrido complexes of the elements Co, Rh, and Ir, those of the first have been the least studied even though the scattered data which exist¹⁻⁵ suggest that these, in a number of ways, may be more interesting than the species derived from Rh and Ir. One of the major problems associated with the study of cobalt-hydrido complexes is that no general methods for their preparation have been developed. It is well-known that three of the distinguishing features of cobalt complexes are, first, the stability of the labile Co(II) state, second, its involvement in the catalytic substitution of the stable and nonlabile Co(III) complexes and, third, the propensity of cobalt complexes in different oxidation states to undergo rapid redox disproportionation reactions. In addition, it is probable that most (formally) cobalt(III)-hydrido complexes are weakly acidic, releasing protons and the highly^{5,6} reactive Co(I) species in basic media. Thus attempts at reducing Co(II) or Co(III) complexes with (basic) hydride ions in protic media, a procedure which is generally successful for Rh(III) complexes,^{3,7} can give Co(I) species in equilibrium with the parent cobalt(III)-hydrido complex. A number of unwanted side reactions may then occur; a redox disproportionation reaction may ensue^{8,9}



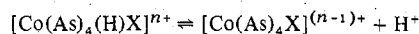
the Co(II) species may catalyze the decomposition of the hydridocobalt(III) product,¹⁰⁻¹² and, in the presence of trace amounts of oxygen, the Co(I) species undergo rapid oxidative addition reactions to produce stable dioxygen adducts.^{5,6}

We have encountered all these problems here, where we describe the preparation and properties of a series of cobalt-hydrido complexes containing tertiary arsine ligands. The three arsines employed are diars, *R,R*:*S,S*-tetars (and *R,R*-*R*-tetars), and *R,S*-tetars (Figure 1) where it will be noted that the chiral inner arsenic atoms of the tetars ligands are stable with respect to thermal inversion under the conditions employed. The one problem which we have not been able to avoid and which is inherent in some, but not all, of the pure species is their tendency to reduce "spontaneously" to the Co(II) state in various solvents, but this property appears to be characteristic of many cobalt(III)-arsine complexes¹² without hydrido ligands.

1. Preparations and Properties

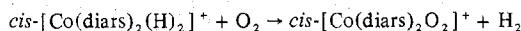
When the Co(III) complexes *trans*-[Co(diars)₂Cl₂]Cl, *trans*-[Co(*R,S*-tetars)Cl₂]Cl, and *cis-α*-[Co(*R,R*:*S,S*-tetars)Cl₂]Cl are treated with BH₄⁻ ions in methanol and/or water solutions, the complexes are reduced and become extremely sensitive to oxygen with which they react to form "sideways" bonded adducts *cis*-[Co(As)₄O₂]⁺⁶. If, however,

the solutions are kept acid, with acetic acid, throughout the reduction, the reduced complexes are no longer sensitive to oxygen and the *trans*-[Co(As)₄(H)Cl]ClO₄ compounds can be isolated. The bromo and iodo adducts are similarly prepared. All the hydrido species of the type *trans*-[Co(As)₄(H)X]^{*n*+} described here are inert to oxygen in acidic or neutral solutions but, in the presence of base, they all react to give the dioxygen adducts. This suggests that the function of the base is to deprotonate the hydrido complexes and release a Co(I) species which is the entity reactive to oxygen. Thus the success of the hydrido complex preparations in mildly acidic conditions depends on constraining the equilibrium



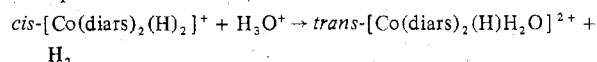
to the left, which not only suppresses the oxygen reaction but also the possible Co(I)-Co(III) redox reaction referred to earlier.

We have observed one apparent exception to this. When excess BH₄⁻ ions are added to solutions of *trans*-[Co(diars)₂Cl₂]Cl, under conditions where the resulting solutions are basic (pH ~8), then, provided BH₄⁻ ions are still present, a pale yellow, almost white complex *cis*-[Co(diars)₂(H)₂]ClO₄ can be isolated at this stage. This is a highly reactive complex and is stable as a solid in air for a few hours developing a pink coating of *cis*-[Co(diars)₂O₂]ClO₄ through reaction with oxygen. In neutral methanol suspensions or acetonitrile solutions the dihydrido complex spontaneously and rapidly reacts with oxygen and gives off 1 molar equiv of H₂. The same reaction occurs in basic media, although in solvents such as DMF and DMSO the complex is indefinitely stable at 0° if oxygen is excluded. Provided it is accepted that the Co(I) species is the reactive entity to oxygen, these reactions indicate that chemically one of the coordinated hydrogen atoms reacts as a proton, while the other behaves as a hydride, i.e.



This chemical dichotomy tends to be confirmed by the following observations.

The *cis*-[Co(diars)₂(H)₂]ClO₄ complex readily reacts with aqueous perchloric acid to liberate 1 molar equiv of hydrogen gas, and the yellow *trans*-[Co(diars)₂(H)H₂O](ClO₄)₂ complex is deposited



The aquo group of this complex is exceedingly labile and can be displaced easily by other unidentate ligands. Thus we have prepared a series of *trans*-[Co(diars)₂(H)X]^{*n*+} complexes, where X = Cl⁻, Br⁻, I⁻, NCS⁻, NO₃⁻, CF₃COO⁻, and CH₃CN.

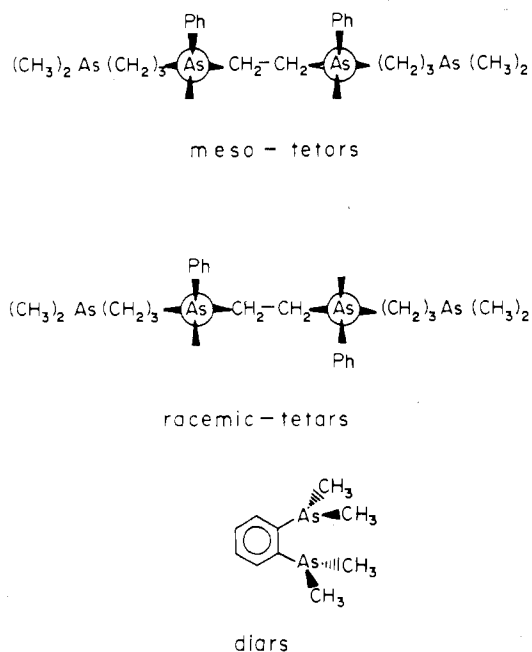


Figure 1.

The complexes where $X = Cl^-$, Br^- , NO_3^- , and CF_3COO^- can also be obtained by treating the appropriate acid with the dihydrido complex. Prolonged heating of the dihydrido complex in moderately concentrated mineral acids does not remove the remaining H group as a hydride; it is only removed, as a proton, in basic solutions. We have found only one exception to this dichotomous behavior; this involves the reaction with (clear) concentrated nitric acid. In this medium the dihydrido complex undergoes a visible two-step reaction. The first involves the release of one H, with the liberation of H_2 and the formation of $trans-[Co(diars)_2(H)NO_3]^+$. This is rapidly followed by the liberation of NO_2 and, if water is added, a quantitative yield of the maroon-red $cis-[Co(diars)_2(NO_3)_2]ClO_4$ ¹¹ complex is precipitated. The second step also occurs by adding the $trans-[Co(diars)_2(H)NO_3]ClO_4$ salt to concentrated HNO_3 . Since the second step does not occur in dilute HNO_3 , we assume that the second H ligand reacts as a hydride with NO_2^+ in the concentrated acid.

The $trans-[Co(diars)_2(H)X]^{n+}$ ions react in methanol with excess BH_4^- ions to regenerate the parent dihydrido complex and in these basic (pH ~ 8) solutions, with excess BH_4^- present, the dihydrido complex is quite stable. This is in sharp contrast to the similar solutions containing the tetars complexes, where the dihydrido species is only formed after the pH has been lowered to about 4 with $HClO_4$. The dihydrido tetars complexes, therefore, appear to be more acidic than the diars analog. The pale yellow tetars-(H)₂ species are exceedingly unstable even as solids, and we have been unable to characterize them satisfactorily.

There is one other method of preparing the tetars-H-I species, which is, in fact, the most satisfactory preparative procedure we have devised for these complexes. This involves the (BH_4^-) reduction of the dichloro complexes in neutral methanol-water solutions in the presence of primary alkyl iodides. Under these circumstances the reaction mixtures are insensitive to oxygen provided excess alkyl iodide is used. From the known reactivity to alkyl halides of the hydrido complexes in basic media, a matter we discuss presently, it is probable that the Co(I) species abstract the iodide directly from the alkyl iodide. Apart from this, however, we are uncertain as to why these reactions proceed so cleanly and are insensitive to oxygen. The addition of iodide ions or starting with iodo complexes gives the dioxygen adducts in the absence of alkyl

iodide. Using CD_3I does not give the deuterated complex.

This series of hydrido complexes spans a perplexing range of stabilities. For example, the $trans-[Co(R,S\text{-tetars})(H)-I]ClO_4$ species is indefinitely stable as the solid whereas the solid $trans-[Co(diars)_2(H)I]I$ complex decomposes within 12 hr. The former can be boiled in concentrated HCl for 5 hr without decomposition or change, and the addition of excess $AgNO_3$ to an aqueous suspension of the complex does not cause the precipitation of AgI after the mixture is boiled for 30 min. The $trans-[Co(diars)_2(H)I]I$, by contrast, when dissolved in freshly distilled DMSO, begins to deposit the insoluble Co(II) complex $[Co(diars)_2I_2]$ within 1 min and is totally converted into it in 5 min. The solution stability of these hydrides depends on the complex and the solvent in which it is dissolved, and we have been unable to perceive any correlative characteristics between the two. We therefore include these data in the Experimental Section as well as the stability of the solids. All the physical measurements we describe are for solvents in which the complexes are stable for the period of measurements.

One recurring problem associated with the preparations of all these complexes is related to devising procedures which give the products in a pure state in the initial preparation. If the initial product is not cleanly isolated then, in all cases, catalytic decomposition rapidly sets in both in solution and in the solid state. This is not unusual for arsinocobalt(III) complexes¹⁰⁻¹² but tends to be more pronounced with these hydrides, where the products are generally cobalt(II)-arsine complexes. The catalyst is undoubtedly¹⁰⁻¹² a Co(II) species which sets off the decomposition via an electron-transfer mechanism. Even when the complexes are pure, this mechanism can operate, after an initial internal electron-transfer reaction from a reducible coordinated ligand to the central cobalt atom. The procedures described here obviate most of these problems.

2. Organometallic Reactivity

If the $trans-[Co(diars)_2(H)H_2O](ClO_4)_2$ complex is suspended in methanol and a large excess of triethylamine added, a deep brown solution is produced at once. It is probable that the color is due to the Co(I) species but, within 1 min, the color fades and $[Co(diars)_2(ClO_4)_2]$ is produced, presumably by a redox Co(I)-Co(III) disproportionation reaction. However, the Co(I) species can be generated in a controlled way by the addition of catalytic amounts of strong base. This generated species rapidly reacts with primary alkyl halides but, in all cases and under a variety of conditions, the major product with any hydride complex was the corresponding cobalt(III)-halogen complex. Thus, for example, the aquo-hydrido complex reacts with methyl iodide in the presence of base to give the $trans-[Co(diars)_2I_2]ClO_4$ complex.

The $cis-[Co(diars)_2(H)_2]ClO_4$ complex also abstracts halogens, even chlorine from chlorobenzene, without the presence of base. If the dihydride is suspended in chloroform, a quantitative yield of $trans-[Co(diars)_2Cl_2]ClO_4$ is deposited with the production of CH_2Cl_2 , CH_3Cl , and CH_4 . Thus in all these cases halogen abstraction, perhaps via a radical mechanism, is preferred over the possible nucleophilic displacement reaction.

The problem appears to reside with the mechanism of the reaction rather than in the stability of the cobalt-carbon bond because we have prepared the $cis-[Co(diars)_2(CH_3)_2]ClO_4$ complex and it is very stable.

3. Electronic Absorption Spectra

This section deals with the d-d absorption spectra of the hydrides, where we attempt to establish, on a spectroscopic basis, the oxidation state of the metal, the ligand field strengths of the hydride and methyl ligands, and the relevant spectroscopic parameters which affect the paramagnetic shifts in the NMR spectra of the hydride ligands. These data have been difficult to obtain previously.

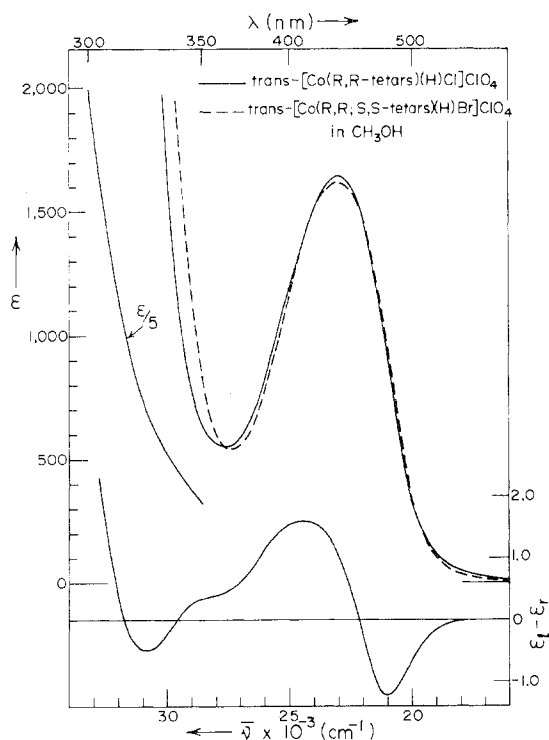


Figure 2.

Cobalt(III)-arsine complexes show^{10,12-14} somewhat modified d-d spectra in the sense that the intensities tend to be high, $\epsilon \sim 1000$, for noncentric complexes and the inter-electronic repulsion between the ${}^1T_{1g}$ and ${}^1T_{2g}$ upper states is drastically reduced,^{10,14} so much so, in fact, that the components of the two manifolds overlap considerably. Furthermore, the transition angular momentum of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ excitation is to a large degree distributed with the components of the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition¹⁰ in complexes with symmetry lower than O_h .

We show the absorption and circular dichroism spectra of *trans*-[Co(*R,R*-tetars)(H)Cl]ClO₄ (Figure 2) and of *trans*-[Co(*R,R*-tetars)(H)I]I (Figure 3); included also are the absorption spectra of *trans*-[Co(*R,R,S,S*-tetars)(H)Br]ClO₄ (Figure 2) and *trans*-[Co(*R,S*-tetars)(H)I]ClO₄ (Figure 3) for comparison. If we assume these are Co(III) complexes, then it should be possible to calculate the energy positions of the 1A_2 and 1E components derived from the ${}^1T_{1g}$ upper state. Using the position¹⁴ of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition observed for [Co(diars)₃](ClO₄)₃ at 23,200 cm⁻¹ (431 m μ) and the observed positions of the 1E_g bands of *trans*-[Co(diars)₂I₂]ClO₄ (14,750 cm⁻¹) and *trans*-[Co(diars)₂Cl₂]ClO₄ (16,447 cm⁻¹) and assuming (vide infra) the hydride has about the same ligand field as CN⁻,¹² where for the *trans*-[Co(As)₄(CN)₂]⁺ chromophore the 1E_g band is at $\sim 26,000$ cm⁻¹, the ${}^1T_{1g}$ components of the *trans*-hydridohalogen complexes can be calculated by a semiempirical molecular orbital method.¹⁵ We find that, in both complexes, the 1A_2 component should occur at the energy of the parent ${}^1T_{1g}$ transition of the [Co(As)₆]³⁺ chromophore ($\sim 23,200$ cm⁻¹) and that the 1E bands should be at 20,900 and 21,700 cm⁻¹ for the *trans*-iodo- and chlorohydrido complexes, respectively. It will be seen that the circular dichroism under the first transition, in both complexes, carries two major components; the higher energy positive component occurs at $\sim 24,000$ cm⁻¹ in both cases whereas the lower energy (negative) components occur at 20,900 cm⁻¹ for the iodo complex and at 21,200 cm⁻¹ for the chloro complex. The two bands are therefore assigned to the 1A_2 (positive) and 1E (negative) components of the ${}^1T_{1g}$ manifold of a d⁶ spin-paired complex. This very close agreement between theory

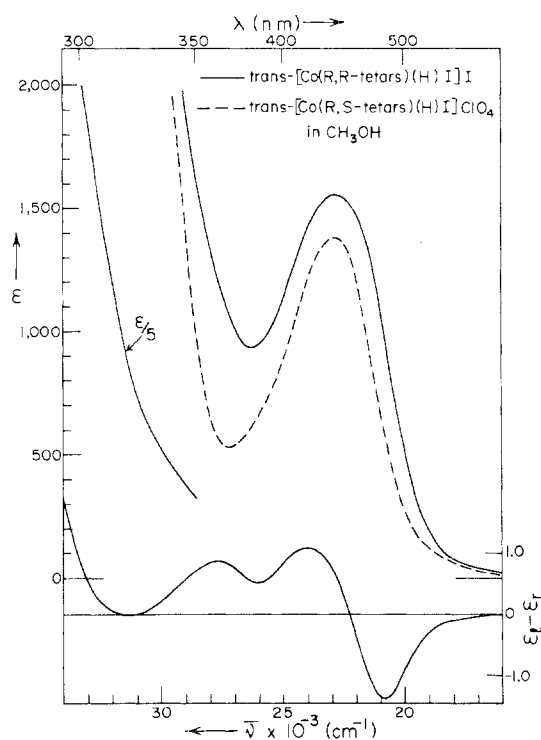


Figure 3.

and experiment is better than is expected for the theoretical method; there are also problems in defining the positions of components of overlapping circular dichroism bands, but it is clear that both the spectra and the robust chemistry support the view that these are Co(III) complexes.

We comment about the circular dichroism observed between about 24,000 and 30,000 cm⁻¹ because this is of significance to the chemical shifts observed for the hydride ligands. It will be noted that the circular dichroism in this region is of the same order of magnitude as that observed at lower energies. This is particularly evident in the case of the iodo complex. These are components of the ${}^1T_{2g}$ transition.¹⁰ The fact that the circular dichroism is equally intense for the ${}^1T_{1g}$ and ${}^1T_{2g}$ manifolds suggests that the 1E components of the two levels are strongly mixed and that the magnetic dipole character of the former is to a large degree distributed into the latter.¹⁶

Figure 4 shows the visible absorption spectra of the series of complexes *trans*-[Co(diars)₂(H)X]ⁿ⁺ where X = Br⁻, Cl⁻, CF₃COOH (vide infra), CF₃COO⁻, NO₃⁻, NCS⁻, and CH₃CN. The low-energy ${}^1T_{1g}$ absorption bands consist of two components 1A_2 and 1E but, since in most of these the axial and equatorial fields are similar, the actual absorption maxima are a good indication of the relative crystal field strengths of the X groups for this series of complexes. Of particular interest is the *trans*-[Co(diars)₂(H)CF₃COO]ClO₄ spectrum which shows a well-resolved band at 29,000 cm⁻¹, which is the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition, and clearly shows the effect of the reduced interelectronic repulsions in these complexes. In the other members of this series, this band is weaker in intensity and is sometimes seen as a poorly resolved shoulder in the absorption troughs at around 29,000 cm⁻¹.

In Figure 5 we show the absorption spectra of *cis*-[Co(diars)₂(CN)₂]ClO₄, *cis*-[Co(diars)₂(H)₂]ClO₄, and *cis*-[Co(diars)₂(CH₃)₂]ClO₄. It is seen that the hydride ligand has a comparable ligand field to that of the cyano group, and, if anything, it is a little stronger in this complex. The ligand field of the methyl carbanion, however, is weaker than either of these two but is stronger than that of the arsine itself. These results, together with previous work^{10,12} and extensive circular dichroism data,¹⁷ allow us to write the spectrochemical order

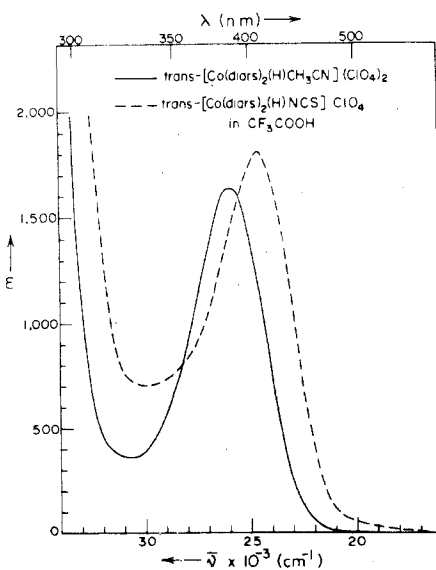
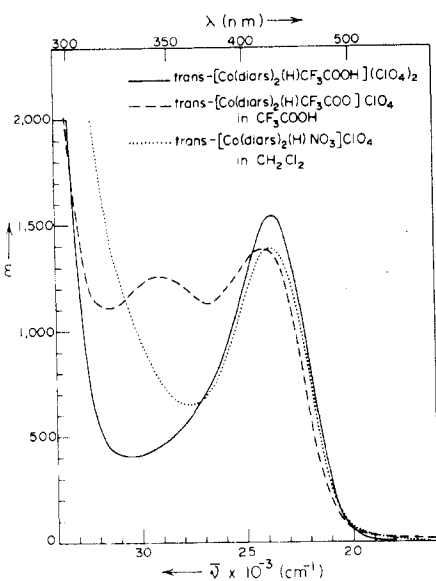
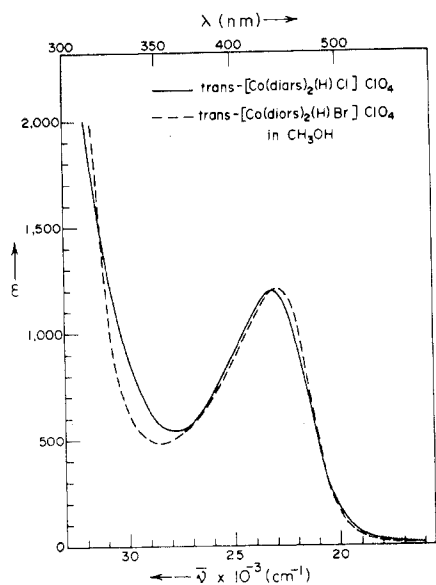


Figure 4.

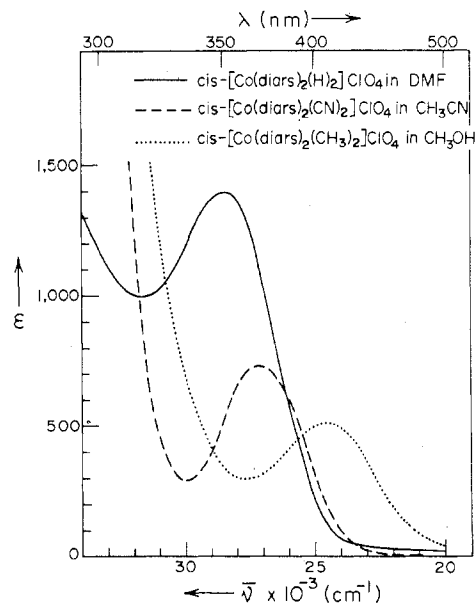


Figure 5.

as $H^- \leq CN^- > CH_3^- > As \leq CH_3CN > \bar{N}CS^- > CF_3COO^- \sim CF_3COOH \sim NO_3^- > Cl^- > Br^- > I^-$. We should point out that the order applies to these cobalt(III)-arsine complexes and may be subject to variations with other systems. For example, CH_3CN has a crystal field about the same as the nitro group in these complexes whereas in cobalt(III)-amine complexes it is of similar strength as the ammine ligand.

4. Chemical Shifts of the Hydrides

It is well-known that octahedral transition metal hydrides show very large upfield chemical shifts which are attributed¹⁸ to the paramagnetic shielding of the unfilled d-electron shells. That this shielding is a major effect seems firmly established but it is, as yet, not clear whether the theory can be applied to include the variations of an extended series of homologous hydrides of the same metal. The present series of complexes together with their fairly precisely determined spectroscopic data should provide a critical test which, hitherto, has not been possible.

Assuming¹⁸ that (a) there is no distortion of the molecular framework throughout the series, (b) that the Co-H bond length remains constant, and (c) that the d orbitals remain of constant "size" throughout, then, since only variations in the axial field occur, the paramagnetic chemical shift of the hydride should depend only on the inverse energy position of the ¹E band derived from the ¹T_{1g} manifold.

Table I lists the Co-H hydride shifts observed for this series of complexes; the crystal fields of the X groups increase in going down the table. The solvent shifts tend to be small and only a little outside the experimental error which is about $\tau \pm 0.1$ because, generally, the signals are broad, perhaps because of coupling with the Co nucleus. We have checked that no paramagnetic displacements occur due to Co(II); the addition of cobalt(II)-arsine complexes leads to loss of resolution. Because the ¹A₂ band remains at constant energy for the *trans*-[Co(As)₄(H)X]ⁿ⁺ chromophore, the theory predicts that the lower the energy of the ¹E component the greater the upfield shift. That is, the weaker the ligand field of X the greater the positive value of τ . Table I reveals no such trend.

Because of the large number of parameters which can affect the chemical shift, it is perhaps not surprising that the theory cannot accommodate these variations in the anisotropy of the complexes. Even if the Co-H bond lengths remain the same and the geometries of the complexes do not vary, it is probable that two major factors contribute to the inconsistencies observed. The first, which has been alluded to before,¹⁸ is related

Table I

| Compd | $\tau(\text{Co-H})^a$ | Solvent (30°) |
|---|-----------------------|--|
| <i>trans</i> -[Co(diars) ₂ (H)I]I | 34.3 | CF ₃ COOH |
| | 34.8 | DMSO- <i>d</i> ₆ |
| <i>trans</i> -[Co(<i>R,R,S,S</i> -tetars)(H)-1]ClO ₄ | 32.5 | DMSO- <i>d</i> ₆ |
| | 32.5 | CD ₃ CN |
| <i>trans</i> -[Co(<i>R,S</i> -tetars)(H)I]ClO ₄ | 31.8 | DMSO- <i>d</i> ₆ |
| | 31.8 | CD ₃ CN |
| | 31.8 | 20% D ₂ O-DMSO- <i>d</i> ₆ |
| <i>trans</i> -[Co(diars) ₂ (H)Br]ClO ₄ | 38.3 | CF ₃ COOH |
| | 38.3 | DMSO- <i>d</i> ₆ |
| <i>trans</i> -[Co(<i>R,R,S,S</i> -tetars)(H)Br]ClO ₄ | 36.0 | DMSO- <i>d</i> ₆ |
| <i>trans</i> -[Co(diars) ₂ (H)Cl]ClO ₄ | 40.8 | CF ₃ COOH |
| | 40.2 | DMSO- <i>d</i> ₆ |
| <i>trans</i> -[Co(<i>R,R,S,S</i> -tetars)(H)-Cl]ClO ₄ | 38.0 | DMSO- <i>d</i> ₆ |
| <i>trans</i> -[Co(diars) ₂ (H)NO ₃]ClO ₄ | 44.5 | DMSO- <i>d</i> ₆ |
| <i>trans</i> -[Co(diars) ₂ (H)CF ₃ COOH]-(ClO ₄) ₂ | 43.0 ^b | CF ₃ COOH |
| <i>trans</i> -[Co(diars) ₂ (H)CF ₃ COO]-ClO ₄ | 43.8 | CF ₃ COOH |
| <i>trans</i> -[Co(diars) ₂ (H)NCS]ClO ₄ | 38.0 | CF ₃ COOH |
| | 38.3 | DMSO- <i>d</i> ₆ |
| <i>trans</i> -[Co(diars) ₂ (H)CH ₃ CN]-(ClO ₄) ₂ | 37.0 | CF ₃ COOH |
| | 36.8 | CD ₃ CN |
| <i>cis</i> -[Co(diars) ₂ (H) ₂]ClO ₄ | 27.0 ^c | DMSO- <i>d</i> ₆ |
| | 27.0 | DMF |

^a Using TMS as an internal and external reference at 60 MHz.

^b Using TMS as an internal and external reference at 100 MHz.

^c Using 0.1 *M* solutions the τ_{H} of the *trans* isomer (~10%) could not be detected (vide infra). It is expected to broad at 30°.

to the possible expansion and contraction of the d orbitals when the formal overall charge of the complex and/or the electronegativity of the X group is varied. From the reduced interelectronic repulsions it is clear that the As donor atoms have made the d orbitals more diffuse and polarizable than when the Co atom is surrounded with "hard" donor atoms. Thus we would expect these highly polarizable d orbitals to

be very sensitive to the formal charge of the complex and the electronegativity of X. Unfortunately, it is with these "soft" donor atom systems, such as As and P, that the metal hydrides are most plentiful and robust. The second factor, which is partly related to the first, is that the magnitude of the circular dichroism under the ¹T_{2g} band suggests that the ¹E component of this band carries a considerable amount of transition angular momentum. Since, in these complexes, this band lies close to the ¹T_{1g} band we expect its contribution to the paramagnetic shielding to be significant. Furthermore, because the ¹T_{2g} excited state contains an electron in the d_{z²} orbital which bonds to the hydride ligand we expect this to make the effect of the ¹T_{2g} contribution more pronounced as well as being sensitive to the electronegativity of the X group.

The *cis*-[Co(diars)₂(H)₂]ClO₄ complex with its lower hydride shift, however, is in conformity with the theory.

5. Stereochemistry

The structures of these complexes are easily determined by NMR. Thus, simple symmetry arguments predict that the systems *trans*-[Co(diars)₂X₂]ⁿ⁺, *trans*-[Co(diars)₂XY]ⁿ⁺, *cis*-[Co(diars)₂X₂]ⁿ⁺, and *cis*-[Co(diars)₂XY]ⁿ⁺ should show, one, two, four, and eight methyl proton resonances, respectively.¹¹ Provided only one isomer is formed,¹⁰ the *trans*-[Co(*R,S*-tetars)(H)I]⁺ should show two methyl proton resonances for either isomer, while the *trans*-[Co(*R,R,S,S*-tetars)(H)X]⁺ complexes should show four methyl proton resonances.⁹ Table II lists these resonances as well as the Co-H stretching frequencies. It will be seen that the structural assignments are unambiguous in the absence of accidental degeneracy. A single-crystal X-ray structure of *trans*-[Co(*R,S*-tetars)(H)I]ClO₄ shows that the hydride ligand is on the same side of the equatorial plane as the phenyl groups.¹⁰ The Co-H bond length is 1.6 ± 0.1 Å.¹⁹ We perceive little chemical significance in the variations of the Co-H stretching frequencies. The NMR of the *trans*-[Co(diars)₂(H)H₂O](ClO₄)₂ complex in CF₃COOH and the *cis*-[Co(diars)₂(H)₂]ClO₄ complex in DMSO and DMF require comment.

Figure 6 shows the 100-MHz temperature dependence of the methyl proton resonances observed for *trans*-[Co-

Table II

| Compd | NMR data (As-CH ₃) | | Ir data (Co-H str), cm ⁻¹ | |
|---|-------------------------------------|--|--------------------------------------|---|
| | τ^a | Solvent | Solid ^b | Soln ^c |
| <i>trans</i> -[Co(diars) ₂ (H)I]I | 8.11, 7.83 | CD ₂ Cl ₂ | 1883 | |
| <i>trans</i> -[Co(<i>R,R,S,S</i> -tetars)(H)I]ClO ₄ | 8.70, 8.33, 8.30, 8.23 | DMSO- <i>d</i> ₆ | 1910 | 1928 (CH ₂ Cl ₂) |
| | 8.72, 8.32, 8.29, 8.27 | CD ₃ CN | | |
| <i>trans</i> -[Co(<i>R,S</i> -tetars)(H)I]ClO ₄ | 8.39, 8.29 | DMSO- <i>d</i> ₆ | 1945 | 1950 (CH ₂ Cl ₂) |
| | 8.45, 8.40 | CD ₃ CN | | |
| | 8.43, 8.33 | 25% D ₂ O-DMSO- <i>d</i> ₆ | | |
| <i>trans</i> -[Co(diars) ₂ (H)Br]ClO ₄ | 8.12, 7.87 | CF ₃ COOH | 1927 | |
| | 8.17, 7.98 | DMSO- <i>d</i> ₆ | | |
| <i>trans</i> -[Co(<i>R,R,S,S</i> -tetars)(H)Br]ClO ₄ | 8.73, 8.40, 8.37, 8.23 | DMSO- <i>d</i> ₆ | 1923 | 1930 (CH ₂ Cl ₂) |
| <i>trans</i> -[Co(diars) ₂ (H)Cl]ClO ₄ | 8.09, 7.93 | CF ₃ COOH | 1930 | |
| | 8.15, 7.90 | DMSO- <i>d</i> ₆ | | |
| <i>trans</i> -[Co(<i>R,R,S,S</i> -tetars)(H)Cl]ClO ₄ | 8.73, 8.63, 8.60, 8.27 | DMSO- <i>d</i> ₆ | 1925 | 1930 (CH ₂ Cl ₂) |
| <i>trans</i> -[Co(diars) ₂ (H)NO ₃]ClO ₄ | 8.33, 8.13 | CD ₃ CN | 1918 | |
| <i>trans</i> -[Co(diars) ₂ (H)CF ₃ COOH]-(ClO ₄) ₂ | 8.15, 7.87 | CF ₃ COOH | 1940 ^d | |
| <i>trans</i> -[Co(diars) ₂ (H)CF ₃ COO]ClO ₄ | 8.05, 8.00 | CF ₃ COOH | 1917 | |
| <i>trans</i> -[Co(diars) ₂ (H)NCS]ClO ₄ | 8.03, 7.97 | CF ₃ COOH | | 1915 (CH ₃ NO ₂) |
| | 8.07 ^e | DMSO- <i>d</i> ₆ | | |
| <i>trans</i> -[Co(diars) ₂ (H)CH ₃ CN]-(ClO ₄) ₂ | 7.97, 7.85 ^f | CF ₃ COOH | 1936 | |
| | 8.08, 7.95 ^g | CD ₃ CN | | |
| <i>cis</i> -[Co(diars) ₂ (H) ₂]ClO ₄ | 8.30 | DMSO- <i>d</i> ₆ | 1860, 1850 sh | 1875, 1865 sh (DMF) |
| | 8.25 | DMF | | |
| <i>cis</i> -[Co(diars) ₂ (CH ₃) ₂]ClO ₄ | 8.82, 8.62, 8.40, 8.27 ^h | CD ₂ Cl ₂ | | |
| <i>cis</i> -[Co(diars) ₂ (CN) ₂]ClO ₄ | 8.72, 8.25, 7.92, 7.78 | DMSO- <i>d</i> ₆ | | |

^a TMS as an internal and external reference at 60 MHz. ^b Nujol-NaCl plates. ^c Arsenic trisulfide glass cell. ^d Hydride stretch of *trans*-[Co(diars)₂(H)H₂O](ClO₄)₂. ^e Consisting of two accidentally degenerate methyl peaks. ^f Coordinated CH₃CN at τ 7.75. ^g Coordinated CH₃CN at τ 7.85. ^h Co-CH₃ peak at τ 8.87.

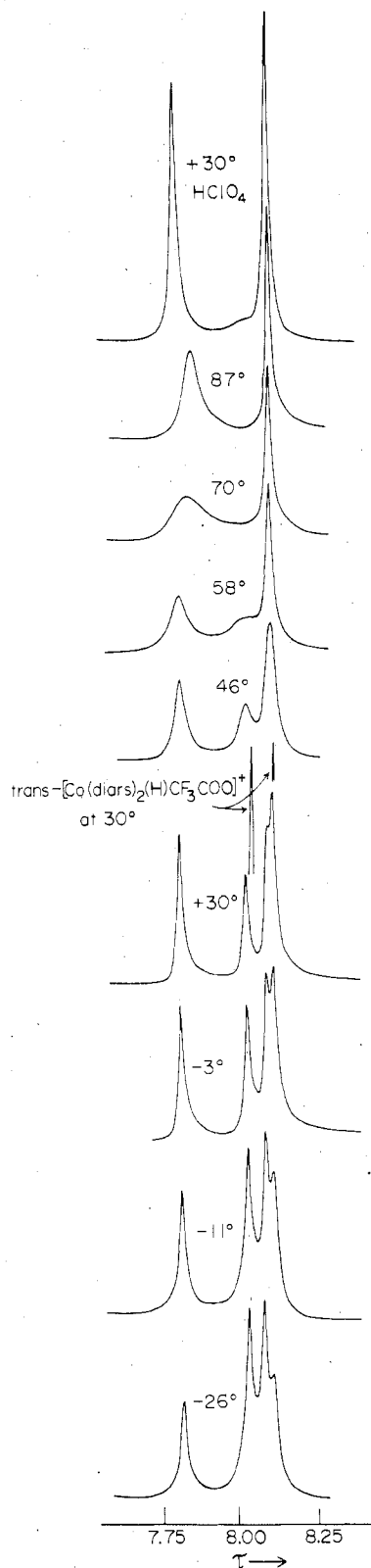


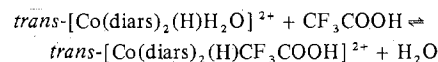
Figure 6. The temperature-dependent 100-MHz NMR spectrum of the methyl proton region of $\text{trans-}[\text{Co}(\text{diars})_2(\text{H})\text{H}_2\text{O}]\text{ClO}_4$ (0.1 M) dissolved in CF_3COOH containing added water (0.8 M). The spectrum at the very top is at 30° and refers to the same mixture containing 1 drop of concentrated HClO_4 . The two methyl proton peaks of the $\text{trans-}[\text{Co}(\text{diars})_2(\text{H})\text{CF}_3\text{COO}]\text{ClO}_4$ in the same solution are also shown. The relative amplitudes are not exact because of the difficulty of locking onto the TMS signal at temperatures above 50° .

$(\text{diars})_2(\text{H})\text{H}_2\text{O}](\text{ClO}_4)_2$ (0.1 M) in CF_3COOH containing water (0.8 M). It will be seen that below 30° four sharp methyl

proton peaks are observed which vary in relative intensity as the temperature is lowered. As the temperature is raised, the two closely spaced higher field peaks first coalesce and then sharpen. The two lower field peaks, having a larger frequency separation, broaden and coalesce more slowly, until at 90° essentially two peaks are observed. It is clear that if it were possible to raise the temperature, only two sharp peaks would be observed; in fact, at 60 MHz both peaks are almost at their minimum bandwidths at 90° . In anhydrous CF_3COOH the inner two peaks are about one-tenth of the intensity of the outer two resonances at 30° . As the amount of water is increased, so the relative intensity of the inner two peaks increases until at 12:1 water to complex (0.1 M), the inner two resonances constitute about twice the intensity of the outer two at 30° . When, however, the ratio of water to complex (0.1 M) reaches about 20:1, all four peaks disappear and the sharp two-line spectrum of $\text{trans-}[\text{Co}(\text{diars})_2(\text{H})\text{CF}_3\text{COO}]^+$ is observed (Figure 6). The addition of anhydrous lithium perchlorate does not change any of these spectra but 1 drop of concentrated perchloric acid causes the collapse of the four-line spectrum which, at 30° , resembles the one at 90° without the acid (Figure 6). As the solution containing the perchloric acid is cooled, the spectrum broadens until at about -30° it resembles the one observed at 30° without acid.

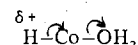
A broad hydride resonance, the area of which corresponds to less than one proton,²⁰ is observed at 30° ; it sharpens as the temperature is lowered. If acid is added, the hydride peak disappears at 30° but reappears at -30° , at which temperature the methyl proton resonance resembles the unacidified 30° spectrum. In CF_3COOD there is no deuterium exchange with the hydrido ligand during the time of measurement of these events, about 6 hr. From these results we conclude the following.

We assume that in dry or nearly dry CF_3COOH the equilibrium



exists. The species on the right is assumed to be a trifluoroacetic acid adduct. In view of the water dependence of the spectrum, the inner two peaks are assigned to the aquo complex and the outer two, to the trifluoroacetic acid adduct. As the temperature is lowered from 30° the resonances sharpen a little but the main variation arises from changes in the equilibrium constant, which moves to the left as the temperature is lowered. On raising the temperature the equilibrium shifts to the right but, at the same time, the rate of exchange of the aquo and trifluoroacetic acid ligands increases to a point where the two complexes become indistinguishable on an NMR time scale. The addition of perchloric acid, we believe, catalyzes the exchange rate by protonation of the coordinated aquo and trifluoroacetic acid ligands; a catalysis which has been noted before.²¹ If this explanation is correct, the rate of exchange of the aquo group in this cobalt(III) complex is quite remarkable when compared to that of other cobalt(III) complexes.²¹ Even the rate of water exchange of $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ with its strong-field CN^- ligands is relatively slow.²² This suggests that it is the hydrido ligand which is responsible for the lability. The trans-labilizing influence of the hydrido ligand is well-known, although the precise reasons for the effect are not understood. We offer the following for "hard" donor atom leaving groups.

In the process of removing the aquo group trans to the hydrido ligand the separation of charge



must occur. That is, the transition state may resemble a protonated cobalt(I) complex which is expected to be very

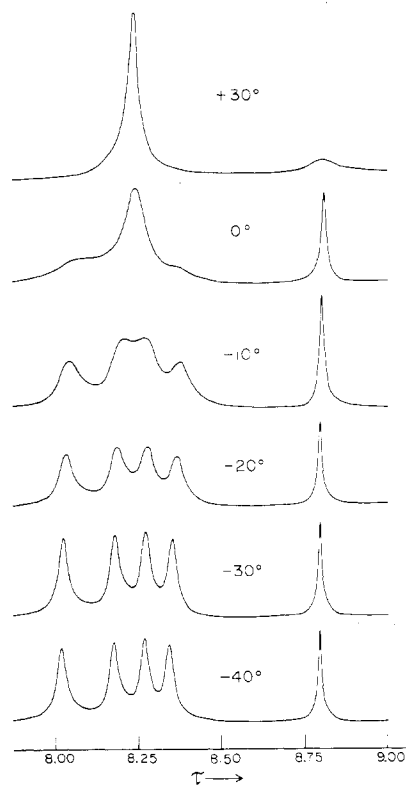


Figure 7. The temperature-dependent 100-MHz NMR spectrum of the methyl proton region of *cis*-[Co(diars)₂(H)₂]ClO₄ in DMF.

labile. As the energy between the hydridocobalt(III) and protonated cobalt(I) species decreases, we would expect dissociative exchange reactions trans to the hydrido to be more facile. It is known that in the ground state metal hydrides chemically span the spectrum of implied bond polarity ranging from hydrides to protonated complexes. This suggests that for any given complex the two states may not be far from each other in energy. If this is so, the electronic demands of a leaving group trans to a hydride may be easily met. A similar explanation may be evoked for the trans effects of the methyl and sulfite ligands provided the states corresponding to complexes containing carbonium ion and sulfur trioxide adducts are close in energy to the ground state.

The properties of the *cis*-[Co(diars)₂(H)₂]ClO₄ complex are interesting in a different way. The solution and solid-state (KBr disk) electronic spectra are similar suggesting that the structures are the same in both media. In the solid two Co-H infrared stretching frequencies are observed at 1850 and 1860 cm⁻¹ of about the same intensity. In DMSO solution, the Raman spectrum also shows two Co-H stretching frequencies at 1876 and 1896 cm⁻¹; the (stronger) lower energy band is polarized while the other is depolarized. We assign these bands to the symmetric and antisymmetric Co-H stretching frequencies, respectively. In both DMSO and DMF the NMR spectrum at 30°, however, shows a single strong, sharp methyl resonance and to higher fields a broad weaker feature which represents about 10% of the total integrated methyl proton signal. As the temperature is lowered in DMF, the small peak sharpens and the major peak broadens and finally collapses into a four-line spectrum (Figure 7). The process is completely reversible between +30 and -40° and is unaffected by (a) the concentration of the complex, (b) the addition of free diars, and (c) the addition of [Co(diars)₂(ClO₄)₂], except that in the last the resolution of the spectrum is diminished. The addition of 10% D₂O does not lead to observable exchange with the hydrido ligands during the time of measurement of these events, about 3 hr. Indeed, none of these hydrido complexes

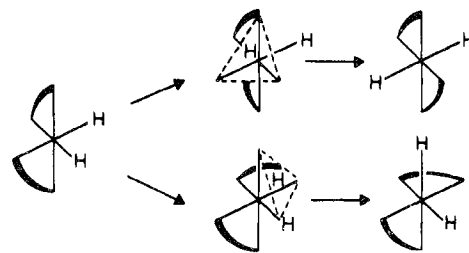


Figure 8. A schematic representation of the proposed mechanisms leading to site exchange. The top one is the *cis*-*trans* exchange and the bottom one is the *cis*-*cis* exchange.

exchange their hydride ligands in acidic or neutral solutions for at least 8 hr. Thus we conclude the *cis*-[Co(diars)₂(H)₂]ClO₄ in DMF (and DMSO) at 30° is fluxional and undergoes an intramolecular rearrangement. Above 30° in both DMF and DMSO, the complex decomposes, to what appears to be cobalt metal in DMF, and, in DMSO, dimethyl sulfide is liberated; the possibility that the major and minor peaks might coalesce at higher temperatures could not be observed. It is highly probable, however, that the major peak represents the *cis* isomer and the minor peak the *trans* and that these are in rapid equilibrium at 30°.

We suggest²³ that the intramolecular rearrangement occurs by the transfer of a hydride across an octahedral face with the nearly simultaneous movement of one of the arsenic donor atoms across an octahedral edge. There are six faces in a *cis* complex over which the hydride may flow, four which include the As-As-H triangles and two which include the As-H-H triangles. Movement across the former, accompanied by a single (As) edge displacement, leads to the *trans* isomer; the same process across the latter produces *cis* isomers (Figure 8). Either process, alone, can lead to the required permutation of the four methyl group environments. The results indicate that both processes occur. At 30° the minor *trans* peak is broad. As the temperature is lowered, the minor peak resolves and reaches its maximum sharpness at about -20°, but the incipiently emerged four-peak spectrum continues to sharpen down to -40°. This suggests that below about -20° a *cis*-*cis* site exchange is occurring and that between +30 and -10° both *cis*-*cis* and *cis*-*trans* site-exchange mechanisms operate to produce the magnetic equivalence in the *cis* isomer.

We know of only one other reported example²⁴ of an accessible fluxional Co(III) molecule which is believed to undergo an intramolecular "twist" because of the small "bite" of the three bidentate ligands. The fluxionality of the present molecule is undoubtedly associated with the presence of the two hydride ligands and we find it attractive to view the transition state as resembling a protonated Co(I) complex where a quasiproton moves over the metal atom of a structurally labile d⁸ complex.

6. Experimental Section

For those inherently unstable (*vide infra*) compounds, all physical measurements and analyses were carried out immediately after they were prepared. Where necessary air was excluded. The stabilities listed after the preparations refer to pure compounds; in all cases very small amounts of impurity will drastically reduce the stability. All measurements were carried out as quickly as possible.

Routine 30° NMR spectra were recorded on Varian T60 and HA100 spectrometers using TMS as an internal as well as an external standard. No shifts in the two standards occurred even when some decomposition had taken place, notably with *trans*-[Co(diars)₂(H)I]I and *trans*-[Co(diars)₂(H)NO₃]ClO₄ complexes in DMSO. Sample concentrations were 0.02-0.1 *M*.

Solid infrared spectra in Nujol were measured on a Perkin-Elmer 180 spectrometer, as were the solution spectra, using cells with arsenic trisulfide windows. Absorption and circular dichroism spectra were obtained using a Unicam SP 820 spectrometer and a Roussel-Jouan Dichrographe II, respectively. Optical rotations were obtained using

a Perkin-Elmer 141 digital polarimeter.

tetars Complexes. *trans*-[Co(*R,R,S,S*-tetars)(H)Cl]ClO₄. *cis*- α -[Co(*R,R,S,S*-tetars)Cl₂]Cl¹⁰ (1.0 g) was dissolved in methanol (30 ml) and glacial acetic acid (2 ml). The whole system was flushed with nitrogen as NaBH₄ (0.2 g) in methanol (30 ml) was added at a rate of about 5 drops/sec to the vigorously stirred solution. After the addition was complete, NaClO₄ (4.0 g) in water (200 ml) was added without delay to the resulting brown solution. The mixture was stirred for 5 min, and the brown powder was filtered and washed with water, then with methanol-ether (1:10), and finally with ether. The product was recrystallized from acetone (150 ml) by the slow addition of ether (450 ml) and deposited as fine brown needles. These were collected and washed with ether (0.6 g).

Stability: stable in methanol, acetonitrile, and DMSO for at least 2 hr; stable as the solid indefinitely. $\Delta_M = 85 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($3.5 \times 10^{-4} M$ in methanol at 25°). Anal. Calcd for [Co(C₂₄H₃₈As₄)(H)Cl]ClO₄: C, 34.4; H, 4.7; Cl, 8.5. Found: C, 35.0; H, 4.9; Cl, 8.8.

trans-[Co(*R,R*-tetars)(H)Cl]ClO₄. *cis*- α -[Co(*R,R*-tetars)Cl₂]Cl¹⁰ (0.5 g) was reduced by a method similar to that given for the racemic analog but the initial precipitate required a different method of purification. The initial product was quickly reprecipitated from a minimum volume of acetone by the addition of NaClO₄ (5.0 g) in water (200 ml) leaving a pink supernatant liquid. It was collected, washed with water, then methanol-ether (1:10), and finally ether. It was recrystallized from acetone by the slow addition of ether. Brown needles were formed (0.08 g).

$\alpha_D 30 \pm 10$, $\alpha_{578} 30 \pm 10^\circ$, $\alpha_{365} -200 \pm 10^\circ$ in methanol, $2.50 \times 10^{-4} \text{ g/ml}$ at 25°. Anal. Calcd for [Co(C₂₄H₃₈As₄)(H)Cl]ClO₄: C, 34.4; H, 4.7; Cl, 8.5. Found: C, 35.1; H, 4.6; Cl, 8.6.

trans-[Co(*R,R,S,S*-tetars)(H)Br]ClO₄. This compound was prepared from *cis*- α -[Co(*R,R,S,S*-tetars)Br₂]Br¹² (0.5 g) in methanol (20 ml) and glacial acetic acid (1 ml) by the dropwise addition of NaBH₄ (0.1 g) in methanol (20 ml) and isolated at once by the addition of NaClO₄ (2.0 g) in water (100 ml). The method closely followed that described for the chloro analog. It was twice recrystallized from acetone by the slow addition of ether and deposited as brown needles (0.25 g).

Stability: same as for the chloro analog. Anal. Calcd for [Co(C₂₄H₃₈As₄)(H)Br]ClO₄: C, 32.7; H, 4.5; Br, 9.1; Cl, 4.0. Found: C, 32.5; H, 4.6; Br, 9.7; Cl, 4.3.

trans-[Co(*R,R,S,S*-tetars)(H)I]ClO₄. To a well-stirred solution of *cis*- α -[Co(*R,R,S,S*-tetars)Cl₂]Cl (1.5 g) in methanol (75 ml) and iodopropane (7.5 ml) was added at a rapid drop rate a solution of NaBH₄ (0.6 g) in methanol (60 ml). After the addition was complete, NaClO₄ (12 g) in water (150 ml) was added immediately to the resulting deep brown solution. The mixture was vigorously stirred for a few minutes to allow the crystals to form and then a further 450 ml of water was added. Stirring was continued for 0.5 hr and the yellow solid was filtered. It was washed first with water and then with ether to remove traces of the iodopropane, followed by methanol-ether (1:10) and finally ether. The crude product was taken up in methanol (300 ml) and precipitated by the addition of NaClO₄ (6.0 g) in water (350 ml). The mixture was allowed to stand for 0.5 hr and filtered and the product was washed as before. It was recrystallized from hot methanol (250 ml) by the slow addition of ether and deposited as deep brown needles (1.0 g).

Stability: same as for the chloro analog. $\Delta_M = 89 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.2 \times 10^{-4} M$ in methanol at 25°). Anal. Calcd for [Co(C₂₄H₃₈As₄)(H)I]ClO₄: C, 31.0; H, 4.2; I, 13.7; Cl, 3.8. Found: C, 31.7; H, 4.3; I, 13.9; Cl, 4.0.

trans-[Co(*R,R*-tetars)(H)I]Cl. *cis*- α -[Co(*R,R*-tetars)Cl₂]Cl (0.3 g) was dissolved in methanol (15 ml) containing iodopropane (2 ml). To this well-stirred solution NaBH₄ (0.2 g) in methanol (20 ml) was added at a fast drop rate. When the addition was complete, NaClO₄ (4.0 g) in water (150 ml) was immediately added and the mixture extracted with dichloromethane (three 80-ml portions). The combined CH₂Cl₂ extracts were dried by filtering them twice through double filter papers under gravity. The extracts were then pumped to dryness at 30°. (Attempts to isolate the perchlorate salt were unsuccessful because of the rapid catalytic decomposition which occurred at the crystallization point). The brown residue was dissolved in acetone (20 ml) and stirred as NaI (0.2 g) in a minimum of acetone was added. The addition of ether (50 ml) completed the precipitation of the brown product, which was collected and washed with acetone-ether (2:5) and then ether. It was taken up in hot acetone (50 ml) and diluted

with ether (100 ml). The solution was allowed to stand at 4° for 1 hr and the dark brown needles were then collected (0.1 g).

$\alpha_D -70 \pm 10^\circ$, $\alpha_{578} -80 \pm 10^\circ$, $\alpha_{546} -90 \pm 10^\circ$ ($2.51 \times 10^{-4} \text{ g/ml}$ in methanol at 25°). Anal. Calcd for [Co(C₂₄H₃₈As₄)HI]Cl: C, 30.2; H, 4.1; I, 26.5. Found: C, 30.6; H, 4.1; I, 27.0.

trans-[Co(*R,S*-tetars)(H)I]ClO₄. A solution containing *trans*-[Co(*R,S*-tetars)Cl₂]Cl¹⁰ (0.5 g) in methanol (25 ml) and iodopropane (2.5 ml) was treated with NaBH₄ (0.2 g) in methanol (20 ml) as described for the racemic analog. The dark brown oil which separated upon the addition of NaClO₄ (4.0 g) in water (200 ml) was extracted into methylene chloride (three 80-ml portions). The filter paper dried extracts were pumped to dryness at 30°. The residue was taken up in methanol (80 ml) and filtered under gravity, and the product was precipitated by the addition of NaClO₄ (4.0 g) in water (200 ml). It was collected and precipitated once more from methanol by the addition of aqueous NaClO₄. Finally, it was taken up in hot methanol (80 ml) and crystallized by the slow addition of ether (300 ml). The deep brown needles were collected and washed with methanol-ether (1:10) and finally ether (0.32 g).

Stability: very stable in all media. $\Delta_M = 81 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($3.41 \times 10^{-4} M$ in methanol at 25°). Anal. Calcd for [Co(C₂₄H₃₈As₄)HI]ClO₄: C, 31.0; H, 4.2; I, 13.7; Cl, 3.8. Found: C, 31.6; H, 4.4; I, 14.0; Cl, 3.9.

diars Complexes. *cis*-[Co(diars)₂(H)₂]ClO₄. *trans*-[Co(diars)₂Cl₂]Cl¹¹ (2.0 g) in methanol (100 ml) and HCl (2 ml; 11 *N*) was brought to the boil on a steam bath.²⁵ The hot solution was then vigorously stirred and flushed with nitrogen as a freshly prepared solution of NaBH₄ (2.0 g) in methanol (150 ml) was added at a rapid drop rate. Halfway through the addition, the color of the solution changed from green to golden brown and [Co(diars)₂Cl₂] began to precipitate. On further addition of NaBH₄, however, the precipitate dissolved and a dark brown clear solution resulted at the end of the addition. Sodium perchlorate (10.0 g) in methanol (60 ml) was then immediately added to deposit very pale yellow sandlike crystals. After stirring for 1 min, water (100 ml) was added and the mixture was stirred for 5 min. The pale yellow solid was collected and washed with water, then with 25% methanol-ether, and immediately with ether (1.7 g). The compound was dried at 80° for 0.25 hr and analyzed at once.

Stability: stable in DMSO and DMF in the absence of O₂ for 7 days at 0°; unstable in acetonitrile and chlorinated solvents; stable in the solid for 6 hr. $\Delta_M = 62 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($1.25 \times 10^{-3} M$ in DMF at 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(H)₂]ClO₄: C, 32.8; H, 4.7; Cl, 4.8. Found: C, 32.8; H, 4.7; Cl, 5.0.

cis-[Co(diars)₂(CH₃)₂]ClO₄. *trans*-[Co(diars)₂Cl₂]Cl (1 g) was dissolved in methanol (50 ml) and methyl iodide (3 ml), and, then, water (50 ml) was added. The solution was stirred vigorously under nitrogen as NaBH₄ (0.5 g) in methanol (20 ml) was added dropwise. The solution began to deposit [Co(diars)₂Cl₂] and turned a light brown. After the addition was complete, the mixture was stirred for 5 min and was filtered twice under gravity to remove the insoluble [Co(diars)₂Cl₂] complex. To the clear filtrate was added NaClO₄ (5.0 g) in water (400 ml) whereupon the yellow-brown product precipitated. It was collected and washed with water, 10% acetone-ether, and then ether. The compound was reprecipitated from a minimum of acetone by the addition of NaClO₄ (5.0 g) in water (400 ml). It was finally recrystallized from acetone by the slow addition of ether and gave yellow-brown plates (0.15 g).

Stability: very stable in all media. $\Delta_M = 90 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($3.1 \times 10^{-4} M$ in methanol at 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(CH₃)₂]ClO₄: C, 34.7; H, 5.0; Cl, 4.7. Found: C, 34.8; H, 5.0; Cl, 4.8.

trans-[Co(diars)₂(H)Cl]ClO₄. This compound can be prepared by three methods: (a) by the addition of 5 *N* HCl to *cis*-[Co(diars)₂(H)₂]ClO₄; (b) from the *trans*-[Co(diars)₂(H)H₂O](ClO₄)₂ by the addition of 5 *N* HCl; (c) by direct reduction. We describe the third method. *trans*-[Co(diars)₂Cl₂]Cl (2 g) was dissolved in methanol (150 ml) and acidified with glacial acetic acid (5 ml). The system was flushed with nitrogen and the solution was vigorously stirred as NaBH₄ (0.5 g) in methanol (25 ml) was added at a rapid drop rate. The solution changed to a deep golden brown and [Co(diars)₂Cl₂] precipitated. After complete addition, the mixture was stirred for 1 min and then filtered under suction into NaClO₄ (10.0 g) in water (400 ml). The bright yellow product was collected and washed with water, 10% acetone-ether, and finally ether. The compound was recrystallized from acetone (300 ml) by adding ether

(200 ml) with vigorous scratching to induce crystal formation. More ether (400 ml) was added during the course of 0.5 hr, and the golden brown crystals were collected and washed with 50% acetone-ether and finally with ether (1.7 g).

Stability: stable in methanol for 2 hr at 30°; less stable in acetonitrile, DMSO, and CF₃COOH; stable as the solid. $\Lambda_M = 87 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.9 \times 10^{-4} M$ in methanol at 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(H)Cl]ClO₄: C, 31.4; H, 4.3; Cl, 9.2. Found: C, 31.5; H, 4.3; Cl, 9.4.

trans-[Co(diars)₂(H)CF₃COO]ClO₄. Trifluoroacetic acid (5 ml) was poured onto solid *cis*-[Co(diars)₂(H)₂O]ClO₄ (0.5 g) under an atmosphere of nitrogen. Hydrogen gas was evolved as the dihydride dissolved to give a brown solution. The solution was allowed to stand for 5 min after the effervescence ceased and ether (5 ml) was added slowly to precipitate the bright yellow product. It was collected and washed with 50% trifluoroacetic acid-ether and then ether (0.3 g).

Stability: stable in CF₃COOH for 2 hr at 30°; stable in methanol for 15 min at 30°; solid decomposes in 6 hr. $\Lambda_M = 96 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($7.1 \times 10^{-4} M$ in methanol at 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(H)CF₃COO]ClO₄: C, 31.3; H, 3.9; Cl, 4.2. Found: C, 31.3; H, 3.9; Cl, 4.4.

trans-[Co(diars)₂(H)H₂O](ClO₄)₂. *cis*-[Co(diars)₂(H)₂O]ClO₄ (1.0 g) was suspended in HClO₄ (20 ml; 12 M) under nitrogen and vigorously stirred. Hydrogen gas was evolved as the dihydride transformed to the bright yellow product. Stirring was continued until all lumps of solid were broken up and until the evolution of gas ceased (~5 min). Water (40 ml) was then added and the mixture was heated on a steam bath for 0.5 hr while being occasionally stirred. The bright yellow precipitate was collected and washed with a small volume of water, 10% acetone-ether, and finally ether (0.7 g).

Stability: stable in CF₃COOH for 6 hr at 30°; decomposes at once in DMSO and DMF; stable in acetone for 15 min at 25°; solid decomposes in 3 days. $\Lambda_M = 160 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($8.60 \times 10^{-4} M$ in acetone at 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(H)-(OH₂)](ClO₄)₂: C, 28.3; H, 4.2; Cl, 8.4. Found: C, 28.1; H, 4.1; Cl, 8.5.

trans-[Co(diars)₂(H)Br]ClO₄. *trans*-[Co(diars)₂(H)H₂O](ClO₄)₂ (0.25 g) in 25% acetone-water (100 ml) was acidified with 1 drop of concentrated HClO₄. It was filtered at once into a stirred solution of LiBr (0.25 g) in 50% acetone-water (25 ml). After the addition was complete, NaClO₄ (4.0 g) in water (200 ml) was immediately added to precipitate the yellow product. It was collected and washed with water, then 10% acetone-ether, and finally ether. This crude product was reprecipitated from a minimum amount of acetone by the addition of NaClO₄ (4.0 g) in water (200 ml); it was collected and washed as before. The compound was finally recrystallized from acetonitrile (50 ml) by the slow addition of ether (100 ml). It deposited as fine yellow-brown crystals (0.15 g).

Stability: same as the chloro analog. $\Lambda_M = 69 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($6.5 \times 10^{-4} M$ in methanol at 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(H)Br]ClO₄: C, 29.6; H, 4.1; Br, 9.9; Cl, 4.4. Found: C, 29.6; H, 4.1; Br, 9.9; Cl, 4.4.

trans-[Co(diars)₂(H)NCS]ClO₄. *trans*-[Co(diars)₂(H)H₂O](ClO₄)₂ (0.25 g) was dissolved in 25% acetone-water (100 ml) and acidified with 1 drop of concentrated HClO₄. The resultant solution was filtered into a stirred solution of NaNCS (0.1 g) in water (10 ml) and acetone (10 ml). The *trans*-[Co(diars)₂(H)NCS]⁺ ion, which precipitated immediately as the NCS⁻ salt, was collected and washed with water, then 10% acetone-ether, and finally ether. The complex was precipitated from acetone (100 ml) as the perchlorate salt by the addition of NaClO₄ (5.0 g) in water (200 ml). It was collected, taken up in acetone again, and slowly precipitated with aqueous NaClO₄. The product deposited as bright yellow plates which were collected and washed as for the NCS⁻ salt (0.12 g).

Stability: stable in DMSO and CF₃COOH for 1 hr at 30°; stable in methanol for 15 min at 25°; stable in the solid. $\Lambda_M = 85 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($3.34 \times 10^{-4} M$ in methanol 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(H)NCS]ClO₄: C, 31.9; H, 4.2; N, 1.8; S, 4.1; Cl, 4.5. Found: C, 32.1; H, 4.2; N, 2.0; S, 4.3; Cl, 4.6.

trans-[Co(diars)₂(H)NO₃]ClO₄. *trans*-[Co(diars)₂(H)H₂O](ClO₄)₂ (0.3 g) was dissolved in acetone (50 ml) and filtered under gravity. To the stirred filtrate was added a solution of LiNO₃ (0.028 g; 1:3 equiv) and LiClO₄·3H₂O (0.3 g) in a minimum of acetone. Ether (100 ml) was then slowly added to precipitate the yellow-brown product, which was collected and washed with 30% acetone-ether and then with ether (0.25 g).

Stability: stable in CH₂Cl₂ and CH₃CN for 15 min at 25°; stable in DMSO for 3 min at 30°; solid decomposes in 6 hr. $\Lambda_M = 140 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($5.6 \times 10^{-4} M$ in CH₃CN at 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(H)NO₃]ClO₄: C, 30.3; H, 4.1; N, 1.8; Cl, 4.5. Found: C, 30.3; H, 4.2; N, 1.5; Cl, 4.1.

trans-[Co(diars)₂(H)I]-0.5(CH₃)₂CO. *trans*-[Co(diars)₂(H)-H₂O](ClO₄)₂ (0.3 g) was dissolved in acetone (50 ml) and filtered. To the well-stirred filtrate was added NaI (0.2 g) in a minimum amount of acetone. The solution turned dark brown at once and the product began to precipitate at once. The mixture was stirred for 3 min, and the brick brown solid was collected and washed with acetone and then with ether (0.2 g). The presence of 0.5 mol of acetone was confirmed by NMR.

Stability: stable in DMSO and CF₃COOH for 1 min at 30°; stable in methanol for 5 min at 25°; stable in the solid for 12 hr. $\Lambda_M = 46 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($2.86 \times 10^{-4} M$ in methanol at 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(H)I]-0.5(CH₃)₂CO: C, 28.3; H, 3.9; I, 27.8. Found: C, 28.4; H, 3.8; I, 27.0.

trans-[Co(diars)₂(H)CH₃CN](ClO₄)₂. *trans*-[Co(diars)₂(H)-H₂O](ClO₄)₂ (0.25 g) was dissolved in acetonitrile (25 ml) under nitrogen. Ether (100 ml) was then added over a period of 5 min to precipitate the product as fine yellow needles. These were recrystallized from acetonitrile (25 ml) by adding ether (100 ml) over a 5-min period. The needles were collected and washed with 30% acetonitrile-ether and then ether (0.2 g).

Stability: stable in acetonitrile and DMSO for 10 min at 30°; stable in CF₃COOH for 2 hr at 30°; solid decomposes in 6 hr. $\Lambda_M = 290 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($6.1 \times 10^{-4} M$ in acetonitrile at 25°). Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(H)CH₃CN](ClO₄)₂: C, 30.3; H, 4.2; Cl, 8.1; N, 1.6. Found: C, 30.5; H, 4.2; Cl, 8.2; N, 1.6.

cis-[Co(diars)₂(CN)₂]ClO₄. To a well-stirred solution of *trans*-[Co(diars)₂Br₂]Br (1.0 g) in methanol (75 ml) and water (5 ml) was added NaCN (0.25 g) in water (20 ml). The solution rapidly turned bright yellow and was stirred for 0.5 min. Sodium perchlorate (4 g) in water (400 ml) was then added and the stirring was continued for 5 min. The pale yellow solid was collected, washed with water, and sucked dry with ether. The product consisted of a mixture of *cis*- and *trans*-dicyano complexes, mainly *trans*. The *cis* isomer was isolated by repeatedly washing the solid with 30° CH₃CN (six 10-ml portions) until a pale yellow solid remained. This solid compound was recrystallized from warm DMF (40 ml) by the addition of ether. It deposited as very pale yellow crystals (0.1 g).

Anal. Calcd for [Co(C₁₀H₁₆As₂)₂(CN)₂]ClO₄: C, 33.8; H, 4.1; N, 3.6; Cl, 4.5. Found: C, 33.7; H, 4.2; N, 3.7; Cl, 4.8.

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Registry No. *trans*-[Co(*R,R,S,S*-tetars)(H)Cl]ClO₄, 54517-25-8; *trans*-[Co(*R,R*-tetars)(H)Cl]ClO₄, 54676-74-3; *trans*-[Co(*R,R,S,S*-*S*-tetars)(H)Br]ClO₄, 54517-27-0; *trans*-[Co(*R,R,S,S*-tetars)(H)-I]ClO₄, 54517-29-2; *trans*-[Co(*R,R*-tetars)(H)I]ClO₄, 54548-80-0; *trans*-[Co(*R,S*-tetars)(H)I]ClO₄, 54548-82-2; *cis*-[Co(diars)₂(H)₂]ClO₄, 54517-36-1; *trans*-[Co(diars)₂(H)₂]ClO₄, 54548-84-4; *cis*-[Co(diars)₂(CH₃)₂]ClO₄, 54517-38-3; *trans*-[Co(diars)₂(H)-Cl]ClO₄, 54517-40-7; *trans*-[Co(diars)₂(H)(CF₃COO)]ClO₄, 54517-42-9; *trans*-[Co(diars)₂(H)H₂O](ClO₄)₂, 54517-44-1; *trans*-[Co(diars)₂(H)Br]ClO₄, 54517-32-7; *trans*-[Co(diars)₂(H)-NCS]ClO₄, 54667-55-9; *trans*-[Co(diars)₂(H)NO₃]ClO₄, 54517-46-3; *trans*-[Co(diars)₂(H)I]I, 54517-47-4; *trans*-[Co(diars)₂(H)-CH₃CN](ClO₄)₂, 54517-49-6; *cis*-[Co(diars)₂(CN)₂]ClO₄, 54517-34-9; *trans*-[Co(diars)₂(H)CF₃COOH](ClO₄)₂, 54517-51-0; NaBH₄, 16940-66-2; *cis*- α -[Co(*R,R,S,S*-tetars)Cl₂]Cl, 50805-06-6; *cis*- α -[Co(*R,R*-tetars)Cl₂]Cl, 50805-13-5; *cis*- α -[Co(*R,R,S,S*-tetars)Br₂]Br, 50804-74-5; C₃H₇I, 107-08-4; *trans*-[Co(*R,R*-tetars)Cl₂]Cl, 54517-30-5; *trans*-[Co(diars)₂Cl₂]Cl, 14170-33-3; CH₃I, 74-88-4; CH₃CN, 75-05-8; *trans*-[Co(diars)₂Br₂]Br, 54517-52-1.

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Kinetics of the Chromium(II) Reduction of *m*- and *p*-Acetylbenzotrile Complexes of Pentaamminecobalt(III). Observation of a Chromium(III) Intermediate

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The kinetics of the Cr(II) reduction of the pentaamminecobalt(III) complexes of *m*- and *p*-acetylbenzotrile have been studied. In both cases, the rate law for reduction is $-d \ln [\text{complex}]/dt = k_{\text{obsd}}[\text{Cr(II)}]$. The kinetic parameters for the reaction are $k(25^\circ) = 0.28 \pm 0.035$ and $(6 \pm 2) \times 10^3 M^{-1} \text{sec}^{-1}$, $\Delta H^\ddagger = 3.2 \pm 0.7$ and $-2.0 \pm 1.5 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -50 \pm 2$ and $-48 \pm 5 \text{ eu}$ for the meta and para complexes, respectively. An inner-sphere mechanism for the reduction of the para complex is indicated by the observation of a Cr(III) intermediate which rapidly aquates to give Cr(OH₂)₆³⁺. The rate law for the aquation of the intermediate is $-d \ln [\text{intermediate}]/dt = (k' + k''[\text{H}^+]^{-1})[\text{Cr(II)}] + k'''[\text{H}^+]^{-1}$. At 25° the values for the rate constants are $420 \pm 150 M^{-1} \text{sec}^{-1}$, $6.8 \pm 6.6 \text{ sec}^{-1}$, and $0.91 \pm 0.13 M \text{sec}^{-1}$ for k' , k'' , and k''' , respectively. The rate differences for the reduction process are explained by considering the conjugation of the carbonyl group with the aromatic ring and the various mechanisms available for transfer of the electron from reductant to oxidant.

Introduction

It has been pointed out that when attempting to assess the mechanistic details of the reduction kinetics of pentaamminecobalt(III) complexes (NH₃)₅CoXR, several potential advantages exist if X is a nitrile linkage, $-\text{N}\equiv\text{C}-$, vs. the corresponding carboxylato linkage, $-\text{O}-\text{C}(=\text{O})-$.¹ In a recent study Taube and Zanella^{2a} reported the observation of a carbonyl-bonded Cr(III) intermediate in the Cr(II) reduction of the *p*-formylbenzoato complex of pentaamminecobalt(III). In this study the interpretation of the results is complicated by the observation of a first-order hydrogen ion term in the rate law for reduction, as well as possible hydration of the remote formyl group. A similar Cr(III) intermediate has been reported in the Cr(II) reduction of the *p*-formylcinnamato complex of pentaamminecobalt(III).^{2b} Here again a strong first-order hydrogen ion term is present in the reduction rate expression. We wish to report a study of the Cr(II) reduction of the *m*- and *p*-acetylbenzotrile complexes of pentaamminecobalt(III), the MAB and PAB complexes, respectively. We were interested primarily in seeing if similar intermediates were produced with either or both of the nitrile complexes and what effects the position of ring substitution has on the rate of electron transfer. This system is potentially simpler than the carboxylato systems mentioned above since it has been shown that hydration does not occur for the remote acetyl group. We also expected that the rate law would be independent of hydrogen ion concentration.¹

Experimental Section

Reagents. All reagent solutions were prepared in water doubly distilled from alkaline permanganate in an all-glass apparatus. Lithium perchlorate stock solutions were prepared using G. F. Smith anhydrous reagent grade LiClO₄ and filtered through a 0.5-μ Millipore filter. The solutions were standardized by charging an aliquot onto an ion-exchange column of Amberlite IR-120(H) cation-exchange

resin and titrating the HClO₄ liberated from the column with standard NaOH to a Bromothymol Blue end point.

Perchloric acid stock solutions were prepared from G. F. Smith double-vacuum-distilled 70% HClO₄. The solutions were standardized with standard base.

Chromium(II) perchlorate solutions were prepared by reduction of solutions of G. F. Smith chromium(III) perchlorate with zinc amalgam. Chromium(II) concentrations were determined every few days by a titration procedure described previously.³ Solutions were stored under an atmosphere of high-purity argon.

Cobalt(III) Complexes. The preparation, purification, and characterization of the PAB complex has been described elsewhere.⁴ The MAB complex was prepared and purified in an analogous fashion. The complex was identified as the nitrile-bonded [(NH₃)₅CoNC-C₆H₄COCH₃](ClO₄)₃.

Anal. Calcd for C₉H₂₂N₆Cl₃O₁₃Co: C, 18.40; H, 3.77; N, 14.30. Found: C, 18.40; H, 4.06; N, 14.40.

Infrared spectrum: CN stretch, 2235 cm⁻¹ (free ligand), 2300 cm⁻¹ (complex); CO stretch, 1690 cm⁻¹ (free ligand), 1685 cm⁻¹ (complex).

Visible spectrum: λ_{max} 468 nm; molar extinction coefficient 75.9 M⁻¹ cm⁻¹.

NMR spectrum: methyl protons, τ 7.40; *trans* amines, τ 6.75; *cis* amines, τ 6.15; aromatic protons, τ 1.82 (center of multiplet).

Kinetic Measurements. Solutions for kinetic studies were deoxygenated using high-purity argon. Due to the facile base hydrolysis of cobalt(III) nitrile complexes,^{4,5} these solutions were prepared just prior to use in acidic solution.

The rates of reduction of the cobalt(III) complexes were measured by observing the change in absorbance due to the disappearance of the complex at both 280 and 470 nm. Kinetic runs for the MAB complex system were performed on a Beckman Acta CIII spectrophotometer equipped with a Thermistemp Model 73 temperature controller from Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio. Kinetic runs for the PAB complex were carried out on a Durrum Model D-110 stopped-flow spectrophotometer.

Treatment of Kinetic Data. All kinetic runs were carried out under pseudo-first-order conditions using an excess of Cr(II) reductant. Under these conditions the rate of reduction of the MAB complex