for the two conformers. For 2,3-butanedione, where only the trans conformer was detected, it is possible to obtain only a value for V^* (in the harmonic approximation $V^* = V_1 + 4V_2 + 9V_3 = 2RT/\delta^2$, where δ is the rms torsional amplitude) and thereby to calculate a value for the torsional frequency $\nu = (2\pi)^{-1}(k/\mu_I)^{1/2} = (2\pi)^{-1}(V^*/2\mu_I)^{1/2}$ (here μ is the reduced moment of inertia). The results are $V^* = 11.4$ kcal/mol ($\sigma = 2.5$) and $\nu = 53$ cm^{-1} ($\sigma = 6$). The latter is in excellent agreement with the reported values[3,4] of 52 and 48 cm^{-1}.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Supplementary Materials Available. The data for the intensity curves 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, 20 × 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 JACS-73-8266.

Metal Complexes of Dissymmetric Arsines. Stereochemistry, Topological Stability, and Spectra of Cobalt(III) Complexes Containing a Linear Quadridentate Tetra(tertiary arsine) Ligand

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Abstract: The stable racemic and meso isomers of the arsine $[(CH_3)_2As(CH_2)_3As(C_6H_5)CH_2]_2$, tetars, have been separated *via* their Co(III) complexes and then obtained in their pure forms free of their complexes. Complexes of the racemic ligand are stereospecifically formed because of the steric constraints of the chiral inner arsenic atoms. All five possible dichloro isomers, cis-α, cis-β, and trans of the racemic ligand and cis-β and trans of the meso ligand, have been isolated and their topological equilibria have been investigated. It is found that the racemic ligand does not impose strong topological preferences but the meso ligand prefers the trans topology. Two *trans*-chloronitro isomers of the meso ligand have been isolated, thus establishing the identity of the meso ligand. All the complexes of the racemic ligand have been obtained in pure optical forms from which the free pure optically active arsine has been obtained, thus establishing the identity of the racemic ligand. From an analysis of their nmr the topologies of the complexes have been established and their conformations have been inferred from both the nmr and exciton circular dichroism spectra. The absorption and circular dichroism spectra reveal a collapse of interelectronic repulsion and extensive mixing within the d-electron manifold which may correlate with the organometallic reactivity of these arsine complexes. A hitherto unknown method of inverting coordinated arsenic atoms has been discovered.

Tertiary arsine and phosphine ligands form crystalline derivatives with most transition metals, often in unusual sterochemistries, coordination numbers, and oxidation states. Because of this, and because the complexes of these ligands tend to display catalytic activity with small organic molecules, there has been widespread interest in these systems, particularly with metals of the latter half of the transition series. A more recent interest in tertiary arsines and phosphines stems from the established but not widely recognized optical stability of the complexed ligands.

Horner[1,2] and Mislow[3] reported that the uncatalyzed thermal barriers to inversion were about 28–30 kcal mol^{-1} for tertiary phosphines and about 42–43 kcal mol^{-1} for tertiary arsines. This chiral stability persists in the metal complexes;[4,5] indeed there is no reported case where an arsine or phosphine has been induced to racemize on a metal. The implications of this stability to the preparation of asymmetric catalysts are obvious[6,7] and our interest in these systems stems in part from this. However, in the systems studied so far, the precise orientation of the substituents about the chiral centers is unknown, either because of free rotation or conformational lability, and hence the origin of the chiral steric discrimination is largely speculative. We therefore sought systems which would provide, among other things, a more certain knowledge of the stereochemistry.

Two recent reports[8,9] of the preparation of linear quadridentate ligand systems containing either four arsenic or four phosphorus donor atoms, and a recent crystal structure[10] of a palladium complex of one of these, suggested that these types of ligands might provide

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(1) L. Horner and H. Winkler, *Tetrahedron Lett.*, 461 (1964).

(2) H. D. Munro and L. Horner, *Tetrahedron*, **26**, 4621 (1970).

(3) G. H. Senkler and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 291 (1972).

(4) L. Horner, J. P. Berez, and C. V. Bertz, *Justus Liebigs Ann. Chem.*, **703**, 17 (1967).

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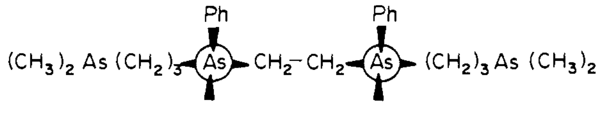
(6) W. S. Knowles, M. J. Sabacky, and B. D. Vinegard, *Chem. Commun.*, 10 (1972).

(7) H. B. Kagan and T.-P. Dang, *J. Amer. Chem. Soc.*, **94**, 6429 (1972).

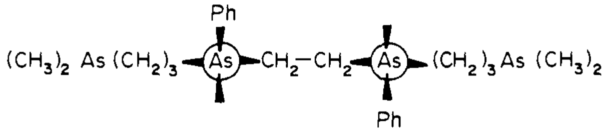
(8) R. S. Nyholm, M. L. Tobe, and A. T. Phillip, "Proceedings of the XIIIth I.C.C.C.," Sydney, Australia, 1969, p 164.

(9) R. B. King, *Accounts Chem. Res.*, **5**, 177 (1972).

(10) T. L. Blundell and H. M. Powell, *J. Chem. Soc. A*, 1650 (1967); for bond angles see also R. B. Mais and H. M. Powell, *J. Chem. Soc.*, 7471 (1965).



meso – tetars



racemic – tetars

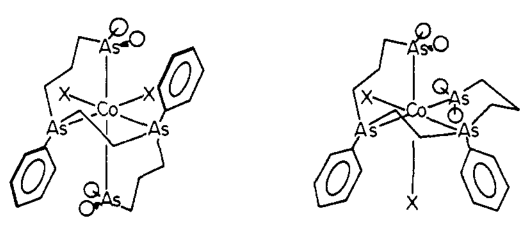
Figure 1.

the necessary stereochemical rigidity for a rational discussion of the steric requirements for asymmetric synthesis. In neither of these two reports was a recognition of the chiral stability of the donor atoms alluded to nor the possibility of more than one chemical isomer recognized. Thus, as a prelude to any attempt at using these systems as asymmetric catalysts, the problems associated with the separation of meso and racemic forms, the resolution of the latter, and the consequences of the chiral stability on the stereochemistry of the derived complexes remain to be solved. It is the purpose of this note to show how these problems can be solved by methods which we believe to be of considerable generality.

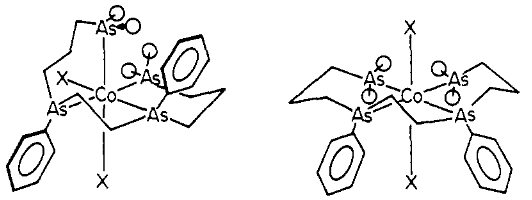
The linear quadridentate arsine we have chosen is shown in Figure 1 where both the meso and racemic isomers are depicted. We will show how these isomers may be separated on a metal, how the racemic form can be resolved, how the two stereoisomers and the pure optical isomers may be obtained free of the metal, and how the chiral stability of the inner arsenic atoms affects the stereochemistry of the complexes. Apart from considerations of economy the kinetically robust cobalt(III) complexes seemed to present the most promising systems for achieving the separations and displaying the greatest variety of stereochemical possibilities. This has been proved to be the case and we now describe these complexes and their properties.

1. Preparation of the Arsine Ligand

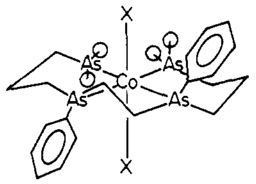
Reaction between ethylene-1,2-bis(phenylchloroarsine) ($Cl(Ph)As(CH_2)_2As(Ph)Cl$) and the ethereal Grignard reagent of chloropropyldimethylarsine ($ClMg(CH_2)_3As(CH_3)_2$) gave, after hydrolysis and ether extraction, a viscous malodorous syrup which could not be distilled (bp >200° (0.01 mm)). Analysis and nmr confirmed the expected constitution of the product as consisting mainly (>90%) of the linear quadridentate arsine, $(CH_3)_2As(CH_2)_3As(Ph)(CH_2)_2As(Ph)(CH_2)_3As(CH_3)_2$ (tetars). The nmr spectrum showed the expected but small diastereotopic splitting of the methyl resonances (~1 Hz at 60 Mcps; $CDCl_3$) and the correct proton integration. At 60 Mcps the nmr resolution was insufficient to reveal the presence of the meso and racemic forms. This is not unusual, however, and has been noted before with another similar arsine[5] and phosphine.[4]



Λ-cis-α-[Co(R,R-tetars)X$_2$]$^+$ Δ-cis-β-[Co(R,S-tetars)X$_2$]$^+$



Δ-cis-β-[Co(R,R-tetars)X$_2$]$^+$ trans-[Co(R,S-tetars)X$_2$]$^+$



trans-[Co(R,R-tetars)X$_2$]$^+$

Figure 2. The five topological isomers of the racemic (left) and meso (right) tetars ligand. The balls at the terminal arsenic atoms represent methyl groups.

2. Mode of Chelation

In Figure 2 we show the five possible isomers that may be formed when the racemic and meso ligands are coordinated to an octahedral metal. The considerations involved in arriving at this set of isomers are fully explored elsewhere[11] and they will not be pursued here except to make the following observations. It will be noted that the (stable) geometry of the inner phenyl-substituted arsenic atoms plays a determining role in the final topology of the metal complex. Thus, the racemic ligand can form the symmetrical cis-α isomer, the unsymmetrical cis-β isomer, and the trans isomer, whereas the meso ligand can only exist in the cis-β and trans topologies. A cis-α isomer of the meso ligand cannot form because both the terminal chelate arms are constrained to move to the same apical octahedral position; in contrast the racemic ligand constrains these same chelate arms to move in opposite directions (Figure 2). This steric restriction is important in another respect, because, for the racemic ligand, the chirality of the inner arsenic atoms exclusively determines the chirality of the overall topology of the cis complexes. That is, the ligand is completely stereospecific in that, for example, the coordinated *R*,*R*-tetars[12] can only give Λ-cis-α and Δ-cis-β optical isomers and of course the trans complex is optically active. It therefore follows that only one internal diastereoisomer is possible and the complete resolution of any of the complexes of the racemic ligand also involves the complete resolution of the ligand. The final

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(11) B. Bosnich, W. R. Kneen and A. T. Phillip, *Inorg. Chem.*, 8, 2567 (1969).

(12) It should be noted that the designations *R* or *S* change according to whether the arsenic is coordinated or free. Thus, *S*,*S*-tetars (free) becomes $[Co(R,R\text{-tetars})X_2]^{n+}$ (coordinated) even though no inversion of the organic substituents occurs.

topological observation is that the two trans isomers are structurally differentiated by the fact that the two axial octahedral positions are identical in the trans complex of the racemic ligand whereas they are structurally different in the trans complex of the meso ligand.

In addition to the geometry of the inner arsenic atoms and the general topologies of the complexes shown in Figure 2, we have represented a particular set of conformational isomers which have chair six-membered chelate rings and gauche conformations of the inner five-membered chelate rings.[11] The precise conformations of these rings is difficult to predict and the ones we have drawn are to be taken as little more than an illustrative convenience so that we may focus on a number of important conformational implications which bear on the physical properties of these complexes.

In Figure 2 we show, for all three isomers of the racemic tetars ligand, the inner arsenic atoms in the coordinated R,R absolute configurations, the δ conformations for the inner five-membered chelate rings and hence axially disposed phenyl groups. While retaining the coordinated R,R configurations of the arsenic atoms, it is equally plausible to invert the five-membered rings to λ conformations and hence dispose the phenyl groups equatorially. There appear to be no obvious reasons for preferring either of the two conformations. Similarly the six-membered terminal rings are drawn as the essentially achiral chair conformations although it is equally reasonable to arrange them in the chiral skew conformations or distorted variations of the latter. Of course, the chirality of the arsenic centers, the inner ring, and the chirality of the skew terminal rings are interrelated, but within this restriction there are a large number of possible conformations.

A rather striking feature which results in part from the conformations is the fact that, in the cis-α topology one methyl group, on *each* of the terminal arsenic atoms, lies close to and is almost directly pointing at the center of the corresponding phenyl groups, while only one (apical) methyl group points at a neighboring phenyl substituent in the cis-β topology of the racemic ligand; in the other three isomers the phenyl and methyl groups are well away from each other (Figure 2). This shielding of the methyl groups is greatest for the conformers we show in Figure 2 and becomes progressively less pronounced as the phenyl groups are made equatorial and/or as the six-membered rings are twisted into skew conformations. Finally, it will be noted that, in the *trans*-[Co(R,S-tetars)X_2]$^+$ ion the inner ring is drawn in the δ conformation, but this is energetically indistinguishable from the λ conformation, and the barrier to flipping is probably small.

3. Chemistry

When an ether solution of the crude arsine is added to a methanol solution of cobaltous chloride containing 1 mol of hydrochloric acid, an immediate dark green solution develops which intensifies in color as air is drawn through it for several hours. On removal of the solvent a very dark blue-green residue remains, which is sparingly soluble in water in which it gives a blue-green color. If this residue is taken up in a large volume of boiling water in the presence of a little HCl, blue-black crystals form on cooling and standing leaving a bright green supernatant liquid from which fine grass-green crystals are deposited upon the addition of more HCl. After these two compounds are purified, the total yield based on cobalt is over 80% of which 60% is the blue complex and 40% the green.

When the blue complex is heated in water, an equilibrium is set up between itself and a brown species which is isolated as deep brick-brown crystals. In methanol solution, a different equilibrium exists and in addition to the starting blue species and a little of the brown complex a green complex is formed which is isolated as apple-green crystals.

The initial grass-green complex, isolated from the original reaction mixture, reacts with carbonate ions to give an orange-red carbonato complex which is decomposed with HCl to give another brown complex.

All five compounds, the blue-brown-green set and the green-brown set, analyze for the compositions [Co(tetars)Cl_2]Cl. The blue-brown-green set can be interconverted into one another and so can the green-brown set, but no interconversion between sets occurs in water or methanol.

The original grass-green complex from the reaction mixture may be reacted with NO_2^- ions under controlled conditions to give two trans isomers of the [Co(tetars)NO_2Cl]$^+$ ion.

The blue complex is readily resolved with active dibenzoyl hydrogentartrate into pure optical forms. This resolved blue complex is converted into the brown and green forms, both of which are optically active, and, furthermore, the active green species regenerates the brown and blue forms with full retention of activity.

Reaction with cyanide ions decomposes the blue complex liberating an arsine, which is a liquid at room temperature, which is optically active if active complex is used, and which analyzes for tetars. The arsine may be reacted with cobalt chloride, in the absence of HCl, to give the blue complex with exactly the same activity as the originally resolved species; no other diastereomer of the blue complex is formed. Furthermore, when the active or racemic ligand is reacted with cobalt only the blue-brown-green set of isomers is formed; there is none of the brown-green set formed.

A similar reaction with cyanide ions occurs with the grass-green complex of the brown-green set and an arsine analyzing for tetars is obtained which is a white crystalline sold. This arsine reacts with cobalt to give only the green isomer of the brown-green set; there is none of the blue isomer.

From these results we conclude that the blue-brown-green set of cobalt isomers contains the racemic ligand and the brown-green set contains the meso ligand. Both conclusions are positively confirmed by the resolution of the free arsine and the existence of two *trans*-nitrochloro isomers of the meso ligand. In addition the racemic ligand is completely stereospecific because the active ligand gives only one active diastereomer. Since the blue isomer only occurs with the racemic ligand its topology is cis-α; the two green isomers have the characteristic d–d spectra of the *trans*-[Co(As)$_4$Cl$_2$]$^+$ chromophore and are assigned the trans topology; therefore the two brown isomers have the cis-β topology. We have thus isolated all the possible (five) topological isomers (Figure 2), and the chemical rela-

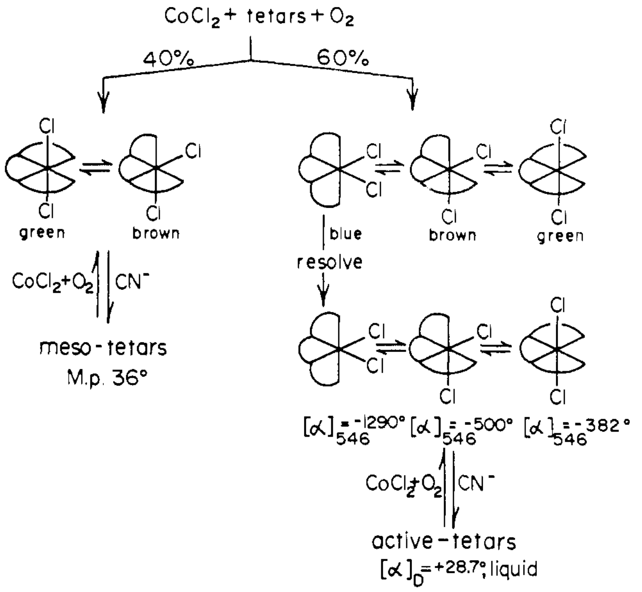

Figure 3.

tionships between the isomers are summarized in Figure 3. The assignments are confirmed by their nmr spectra which we now discuss.

4. Stereochemistry

The two free isomeric arsines show nmr spectra in $CDCl_3$ which are indistinguishable at low resolution but are detectably different at high resolution. Thus, at 100 Mcps, small differences in the phenyl and methylene regions are observed and the diastereotopically split methyl protons are observed at τ 9.164 and 9.142 for the racemic ligand and at τ 9.148 and 9.134 for the meso arsine. It is therefore not surprising that the nmr of the original mixture of arsines did not clearly reveal the presence of the two isomers.

The five isomeric complexes of the arsines all have the constitution $[Co(tetars)Cl_2]Cl$, all are diamagnetic, and all have molar conductivities typical of 1:1 electrolytes, about 65 $ohm^{-1}\ cm^2\ mol^{-1}$ in methanol at 10^{-3} M. These are therefore octahedral cobalt(III) complexes. The chemically inferred structures of these isomers are unambiguously confirmed by their nmr spectra which are shown in Figure 4 and where it will be seen that the expected number of methyl proton resonances are observed.

If we assume that the cis-α and cis-β isomers of both ligands and the trans isomer of the racemic ligand have either rigid conformations or that they are rapidly flipping on an nmr time scale, simple symmetry arguments predict that the cis-α and trans-di-X isomers of the racemic ligand should show two methyl proton resonances each representing two environmentally equivalent methyl groups; all four methyl groups are environmentally inequivalent in the cis-β isomers of either ligand and four methyl proton resonances should be observed. The methyl proton nmr spectra of either the trans-di-X or trans-X,Y isomers of the meso ligand should show four methyl proton resonances if the central five-membered ring is rigid on an nmr time scale, but if this ring is flipping rapidly, only two methyl proton resonances will be observed for both of the two trans complexes. This argument holds because the movements of the inner and outer chelate rings are partly dependent and provided the two terminal rings are either rigid or rapidly flipping on an nmr time scale. In addition to these symmetry arguments, the molecular relationships suggest that the cis-α complex should have two highly shielded methyl protons and the cis-β complex of the racemic ligand should have only one shielded proton; none of the other isomers should show this shielding.

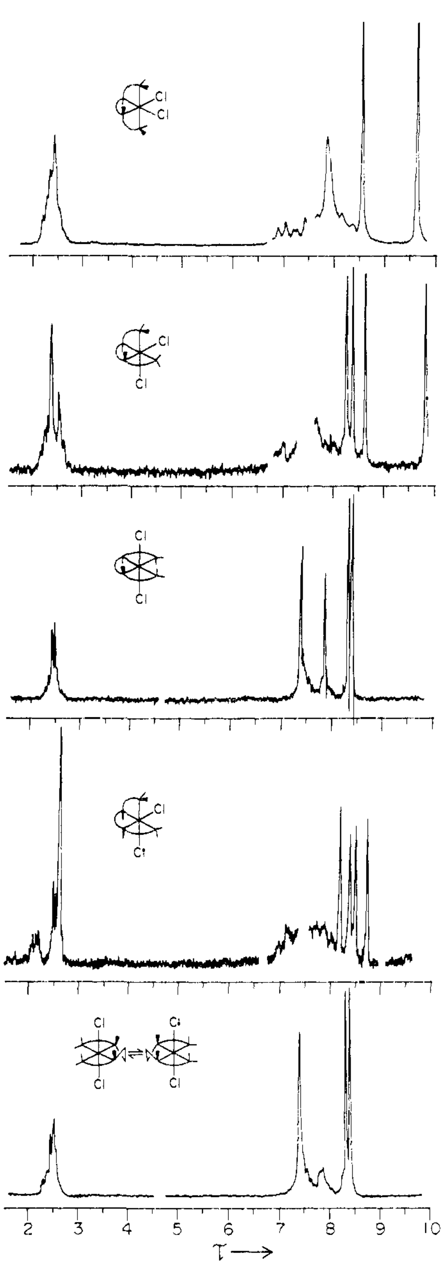

Figure 4. The nmr at 60 Mcps of the five $[Co(tetars)Cl_2]ClO_4$ isomers. Both trans isomers are in CD_2Cl_2; the others are in $(CD_3)_2SO$.

It will be seen in Figure 4 that the cis-α and cis-β complexes of the racemic ligand show methyl proton resonances shifted upfield to nearly coincide with TMS, and we assign these signals to those methyl groups which point at the phenyl groups (Figure 2). We have observed this diamagnetic shielding in over 20 derivatives of these two isomers where the X groups have been varied; it is therefore a general phenomenon. This effect has proved useful in assigning structure when symmetry arguments are no longer useful; thus, for example, the unsymmetrically substituted *cis*-α-[Co-($R,R;S,S$-tetars)NCSCl]ClO$_4$ complex shows four methyl proton resonances but is distinguished from the cis-β and trans analogs by the fact that *two* of the resonances are very close to TMS. Provided there are no large distortions of the octahedral bond angles, molecular models suggest that in order to get these large upfield shifts the terminal six-membered chelate rings must be in approximately chair conformations. This suggestion does not seem unreasonable since crystal structures on three different cobalt complexes of these ligands reveal that both terminal rings are in all cases in slightly distorted chair conformations.[13] As expected none of the other isomers show any high field protons.

In the case of the *trans*-dichloro complex of the meso ligand only two methyl proton resonances are observed indicating that, at least, the inner ring is rapidly flipping, and for the same reason only two resonances are observed for each of the two *trans*-nitrochloro isomers of the meso ligand (Figure 5). We note also that the methylene protons of the *trans*-dichloro complexes of both the meso and racemic ligands are very sharp; they remain so at 100 Mcps. Although they give the appearance of methyl protons, they are easily distinguished by integration. We are unsure why these resonances are so sharp in these two complexes and why they should have the "normal" spread multiplets in all the other trans-di-X complexes we have measured, some 15 others.

Finally, it should be pointed out that these basic nmr patterns are essentially independent of the complex concentration and the nature of the counter anion and are much the same in acetonitrile, dimethyl sulfoxide, methylene chloride, or chloroform.

5. Stereochemical Equilibria and Optical Stability

The optically active free arsine is racemized and free meso arsine is isomerized rapidly in methanol–ether (2:1) in the presence of HCl and an equilibrium mixture is derived from either arsine consisting of the meso ligand (55%) and the (racemized) racemic ligand (45%). This constitution of the mixture was determined by nmr of the re-formed cobalt(III) complexes. When the cobalt(III) chloro complexes of either of the two ligands are refluxed in water or methanol in the presence of HCl, topological changes occur, but there is no detectable inversion at the arsenic atoms. Within a given configuration of the arsenic atoms, the equilibrium topologies depend on a number of subtle factors.

In addition to the chloro complexes we describe here, we have prepared a large number of derivatives of these complexes in which the two chloro groups have been replaced by other unidentate or bidentate ligands, and we have studied their topological equilibria. We will report on these results elsewhere, but we briefly allude to these here in order to put the stereochemical equilibria of the chloro complexes in perspective. With anionic unidentate ligands the meso arsine gives trans complexes exclusively at equilibrium in water or methanol. It is only with neutral unidentate ligands such as water or acetonitrile that cis-β complexes of the meso arsine are found at equilibrium. It is a common general observation among cobalt(III) complexes, that as the overall charge of the complex is increased the tendency to form cis complexes increases in dipolar solvents and thus the appearance of cis-β complexes for the two tripositively charged species is probably largely a solvation phenomenon. We therefore suppose that the meso ligand intrinsically prefers a planar arrangement of its arsenic atoms about cobalt(III). There appears to be no particular preference for any of the three topologies when the racemic ligand is coordinated to cobalt(III). Thus, we have found for a variety of anionic ligands a miscellaneous assortment of isomers, the proportions of which varied with and seemed to depend upon the nature of the coordinated anionic ligands. For example, the dinitro complex gave almost 100% trans while the dibromo complex gave exclusively the cis-α topology at equilibrium in water or methanol, while many of the other anionic ligands gave varying proportions of all three isomers.

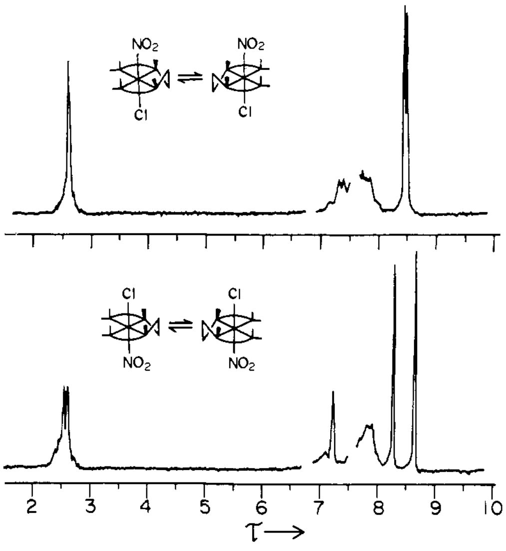

Figure 5. The nmr at 60 Mcps of the two *trans*-[Co(R,S-tetars)-ClNO$_2$]ClO$_4$ isomers. The top spectrum refers to isomer I. The specific isomers shown in the inserts are arbitrary since the structures are not established.

This lack of topological preference of the racemic ligand is also revealed with the dichloro complexes. When *cis*-α-[Co($R,R;S,S$-tetars)Cl$_2$]Cl ($10^{-3}M$) is heated in boiling aqueous HCl (10^{-2} N), an equilibrium is established in about 1 hr which consists of 80% of the cis-α isomer, 20% of the cis-β isomer and no detectable amount of *trans*-dichloro isomer. In dilute (10^{-3} M) neutral boiling methanol, equilibrium is established after 24 hr and consists of cis-α (75%), cis-β (5%), and trans (20%). The equilibria were confirmed by starting from either the cis-α, cis-β, or trans isomers; all topological changes occur with full retention of optical activity.

The *cis*-β-[Co(R,S-tetars)Cl$_2$]ClO$_4$ complex or the chloride salt transforms to the trans complex in boiling water in a few minutes, whereas the same reaction takes about 0.5 hr in boiling methanol. The product, as is characteristic of this ligand, is in either solvent exclusively the *trans*-[Co(R,S-tetars)Cl$_2$]$^+$ ion. We have followed the rate of the cis-β to trans isomerization in dry methanol spectrophotometrically and find a rate constant k = 1.05 ± 0.02 × 10^{-4} sec^{-1} ($t_{1/2}$ = 110 min) at 29.4° over 5 half-lives of reaction. Many of

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(13) N. C. Payne, private communication.

these arsine complexes, particularly those with mildly reducing ligands such as NO_2^-, N_3^-, NCS^-, etc., are highly susceptible to rapid catalytic isomerization because of the production of Co(II) species. We have found these chloro complexes to be free of this complication in dilute water or methanol solutions and we believe the reproducible rate constant given above refers to thermal (uncatalyzed) isomerization. Unlike the chlorotetraamine complexes of cobalt(III), very little solvolysis occurs with these arsine complexes and even at the 10^{-3} *M* aqueous hydrochloric acid solutions used for the equilibration studies, not more than about 2% of the chloro–aquo complexes exist in standing concentrations; the equilibrium proportions are therefore uncomplicated by solvolysis.

In addition to the thermodynamic equilibria, we have also studied the kinetic distribution of isomers during the initial preparations. We find that the meso ligand and cobalt chloride in methanol–ether (2:1) are oxidized by air to give exclusively the *trans*-dichloro complex; there is no detectable cis-β. The racemic ligand under the same conditions gives about 65% cis-α, 35% trans, and a trace of cis-β. For both ligands the time of oxidation varied from 30 to 60 min at 20° with the same results; the thermal equilibration during this time and at this temperature is sufficiently slow as not to affect significantly these kinetic proportions which no doubt to some extent reflect the topological preferences of the Co(II) complexes. In the initial preparation we ensured thermodynamic proportions by boiling the aqueous solutions of the oxidation extract.

Throughout these equilibrations we noted the complete geometric stability of the complexed arsenic atoms, but there are conditions under which inversion of the complexed arsenic ligand will occur. When either the *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Cl_2]Cl or the *trans*-[Co(*R*,*S*-tetars)Cl_2]Cl complexes is refluxed in acetonitrile at concentrations greater than 10^{-2} *M*, equilibrium is achieved after about a day. Starting with either complex the equilibrium consists of *trans*-[Co(*R*,*S*-tetars)Cl_2]$^+$ (60%), *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)-Cl_2]$^-$ (35%), and *cis*-β-[Co(*R*,*R*;*S*,*S*-tetars)Cl_2]$^+$ (5%). If either the *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Br_2]Br or the *trans*-[Co(*R*,*S*-tetars)Br_2]Br complex is used under the same conditions, inversion again occurs in about the same time and a new equilibrium distribution is found, namely, *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Br_2]$^+$ (70%) and *trans*-[Co(*R*,*S*-tetars)Br_2]$^+$ (30%). Of course complete racemization occurs. The equilibrium thus seems to depend on the nature of the free and/or coordinated anion and is a useful preparative method for interconverting from one series of complexes to the other.

With regard to this inversion we have noted the following: (a) no inversion of the free arsine occurs in boiling acetonitrile in the presence or absence of chloride ions after 24 hr, (b) no inversion occurs if either of the [Co(*R*,*R*;*S*,*S*-tetars)$(CH_3CN)_2$]$(ClO_4)_3$ or [Co(*R*,*S*-tetars)$(CH_3CN)_2$]$(ClO_4)_3$ complexes[14] is boiled in acetonitrile for 24 hr, and (c) the rate of approach to equilibrium seems to depend on the concentration of free halide ion, being slower in dilute solutions of the halide salts and increasing in rate as more halide ions are added. These observations and the configurational stability in water and methanol are reminiscent of those Horner[15] reported for the racemization of quaternary arsonium salts. Horner observed concentration-dependent racemization in acetonitrile with Cl^-, Br^-, and I^- salts but not with ClO_4^-; no racemization was observed with any of the salts in water or methanol. This tempts us to suggest, as Horner did for his quaternary salts, that the coordinated arsenic atom (a pseudoquaternary salt?) transiently expands its coordination number to five by accepting a free halide ion which induces rearrangement by pseudorotation leaving, after the expulsion of the halide ion, an inverted arsenic center. Apart from the restrictions to pseudorotation imposed by chelation, the process is certainly more complicated than this.

We have tried to determine the kinetics of these reactions by following the changes in circular dichroism and nmr and visible absorption spectra but have found the velocity constants irreproducible because of catalysis. For the kinetics, we have excluded light and oxygen and have tried to purify both the solvent and the sealed tubes used for containing the reaction solutions, but whatever was tried catalytic arsenic inversion could not be suppressed. The occurrence of catalysis is typically erratic in the sense that some samples displayed little change after a week at 60° while others "triggered-off" after 4 hr. Once the catalysis set in, the inversion was rapid and could either proceed to completion or stop in its progress to be catalyzed again. Catalysis is always accompanied by a sudden production of a small amount of Co(II) and free arsine, but Co(II) complexes in themselves cannot be the catalysts since Co(II) complexes of the arsines in the presence of halide ions do not cause inversion at 60° after a week in acetonitrile. The catalysis may be a result of some internal redox mechanism involving the reduction of Co(III) to Co(II) and the production of a presumably labile arsenic(IV) species. However, halide ions are necessary even if this were the case because the bis(acetonitrile) perchlorate complexes also undergo some reduction to Co(II) and free arsine but no inversion is observed. The equilibrium constants are, of course, not affected by the catalysis but our kinetic measurements of the inversion leave some doubt as to whether even an uncatalyzed thermal inversion will occur in the time and under the conditions of these experiments.

6. Absorption Spectra, Circular Dichroism, and Absolute Configurations

In this section we discuss in some detail the electronic circular dichroism and absorption spectra of these complexes for three important reasons. First, these are the first optically active cobalt(III) arsine complexes reported, and because their spectra are so distinctive, it is important to analyze their circular dichroism spectra in some detail if correlations between absolute configurations and circular dichroism patterns are attempted. Second, the reactivity of cobalt arsine complexes is quite different from those with "hard" donor atom ligands. Such differences in reactivity are usually ascribed to electronic changes at the cobalt atom; the absorption and particularly the circular dichroism

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(14) The bis(acetonitrile) complexes of the racemic ligand exist as the equilibrium mixture cis-α (60%) and cis-β (40%); the same complexes of the meso ligand exist as the equilibrium mixture cis-β (30%) and trans (70%) in acetonitrile at 80°. The proportions vary a little with temperature.

(15) L. Horner and W. Hofer, *Tetrahedron Lett.*, 3281 (1965).

spectra of the d–d bands should be very sensitive to these electronic changes. Third, as we show, the circular dichroism may be useful in determining the conformations of these complexes.

The absorption spectra of the five isomers are shown in Figure 6, together with the associated circular dichroism shown by the resolved complexes of the racemic ligand. It will be seen that the corresponding isomers of the two ligands have very similar visible absorption spectra. There are three identifiable regions which may be characterized in terms of their approximate electronic provenance: the region between about 450 and 800 mμ due mainly to d–d transitions, the region between 290 and 450 mμ dominated by cobalt–arsenic and cobalt–chloride charge transfer transitions, and the region 190 to 290 mμ consisting of other transitions of the system including those localized mainly on the phenyl groups. These classifications are convenient although considerable mixing between levels must be present as evidenced by the high molar extinction coefficients of the d–d bands, over 1000.

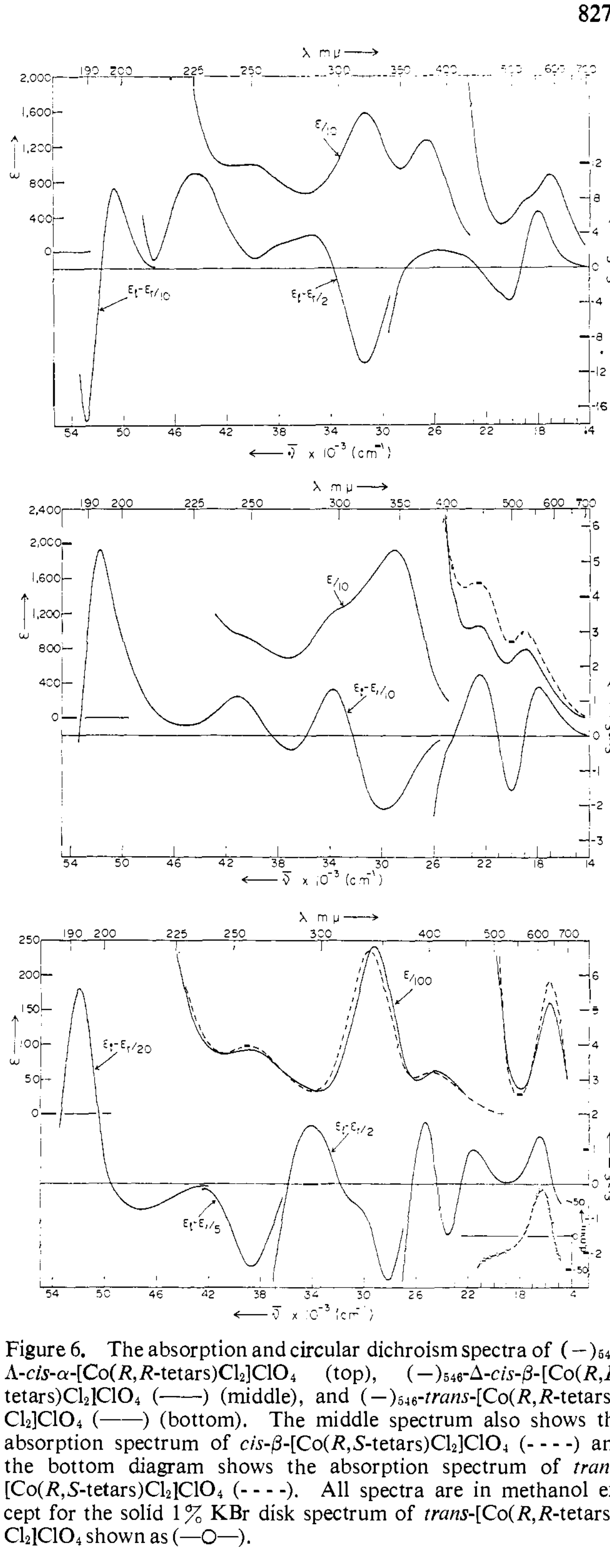

Figure 6. The absorption and circular dichroism spectra of $(-)_{546}$-Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl_2]ClO_4 (top), $(-)_{546}$-Δ-*cis*-β-[Co(*R*,*R*-tetars)Cl_2]ClO_4 (——) (middle), and $(-)_{546}$-*trans*-[Co(*R*,*R*-tetars)-Cl_2]ClO_4 (——) (bottom). The middle spectrum also shows the absorption spectrum of *cis*-β-[Co(*R*,*S*-tetars)Cl_2]ClO_4 (- - - -) and the bottom diagram shows the absorption spectrum of *trans*-[Co(*R*,*S*-tetars)Cl_2]ClO_4 (- - - -). All spectra are in methanol except for the solid 1% KBr disk spectrum of *trans*-[Co(*R*,*R*-tetars)-Cl_2]ClO_4 shown as (—O—).

It has been suggested[16] that the high extinction coefficients of the d–d bands of arsine–cobalt complexes are a reflection of the high covalency of the metal–arsenic bond which in turn will lead to the observed[16b] decrease in the interelectronic repulsion between the crystal field levels. That this is so is readily seen from the absorption and circular dichroism spectra of the cis-β complex. The $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption of $[Co(diars)_3](ClO_4)_3$ (diars = *o*-phenylenebis(dimethylarsine)) occurs at 431 mμ (23,202 cm^{-1});[16b] for the *cis*-$[Co(As)_4(Cl)_2]^+$ chromophore, this $^1A_{1g} \rightarrow {}^1T_{1g}$ transition will be split into essentially two components ($^1A_1 \rightarrow {}^1A_2$, $^1B_2$) and ($^1A_1 \rightarrow {}^1B_1$) both of which will be shifted to lower energies.[17] Using the position of the $[Co(diars)_3]^{3+}$ transition and the spectrochemical shift of the chloro groups,[18] we calculate[17] that the lowest energy component ($^1A_1 \rightarrow {}^1B_1$) should occur at 16,930 cm^{-1} (590 mμ) and the other essentially degenerate[17] two component transition ($^1A_1 \rightarrow {}^1A_2$, $^1B_2$) should occur at 20,070 cm^{-1} (498 mμ). Recognizing the limitations of using overlapping circular dichroism maxima in determining energy positions, there is reasonable agreement if we assign the 17,890 cm^{-1} (559 mμ) positive circular dichroism band to the $^1A_1 \rightarrow {}^1B_1$ transition and the negative band at 20,000 cm^{-1} (500 mμ) to the two component transition ($^1A_1 \rightarrow {}^1A_2$, $^1B_2$) of the cis-β complex. This tendency to have the $^1A_1 \rightarrow {}^1B_1$ transition at somewhat higher than calculated energies has been observed before[19] for cis-β quadridentate amine complexes of cobalt; the corresponding cis-α complexes, however, give good agreement with theory. This may be due to greater ligand–cobalt bond distortions in the cis-β complexes, but whatever the precise details, these calculations clearly indicate that the absorption and corresponding (positive) circular dichroism band at 22,573 cm^{-1} (443 mμ) is a component of the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition. The shoulder seen in the lower absorption spectrum at 24,690 cm^{-1} (405 mμ) may be the other component of the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition. This observation is quite remarkable when these spectra are compared to those involving a cobalt(III) center surrounded by "hard" donor atoms such as oxygen or nitrogen where in, for example, the *cis*-$[Co(en)_2Cl_2]^+$ ion (en = ethylenediamine) the lowest energy component of the $^1A_{1g} \rightarrow {}^1T_{2g}$ manifold occurs at 338 mμ.[18] Thus, as a result of reduced interelectronic repulsion and the spectrochemical shifts of the chloro groups, the $^1T_{2g}$ and $^1T_{1g}$ manifolds have nearly collapsed into one another in these arsine complexes. In addition to this, the usual mag-

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(16) (a) T. M. Dunn, R. S. Nyholm, and S. Yamada, *J. Chem. Soc.*, 1564 (1962). (b) R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, 7, 1154 (1968).

(17) H. Yamatera, *Bull. Chem. Soc. Jap.*, 31, 95 (1958).

(18) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

(19) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 4, 45 (1965).

netic dipole selection rules[20] which are successfully applied to hard donor atom systems also collapse, because, as is evident, the circular dichroism associated with components of the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition are as strong as in the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition. These phenomena will be discussed more fully elsewhere in conjunction with more extensive data; we now turn to the d–d bands of the cis-α complex.

The ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions for the cis-α complex are masked in the absorption spectrum by charge transfer bands, leaving only the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ d–d transition which shows splitting in the absorption spectrum with a maximum at 17,065 cm^{-1} (586 mμ) and a shoulder at 19,230 cm^{-1} (520 mμ). These correspond fairly well to the calculated values 16,930 cm^{-1} (${}^1A_1 \rightarrow {}^1B_1$) and 20,070 cm^{-1} (${}^1A_1 \rightarrow {}^1A_2$, ${}^1B_2$), but the assignment of the positive (at 17,986 cm^{-1}, 556 mμ) and negative (at 20,202 cm^{-1}, 495 mμ) circular dichroism components is not certain. We believe these two circular dichroism bands to represent the ${}^1A_1 \rightarrow {}^1A_2$ and ${}^1A_1 \rightarrow {}^1B_2$ components of the two-component transition for two reasons. First, the lower energy band does not correspond in energy with the lower energy absorption component, and if a roughly gaussian band shape is assumed for either the circular dichroism or absorption bands, the real maximum of the circular dichroism band would be at even higher energies because of overlap with the negative band. Furthermore, the plus–minus couplet is centered about the higher energy absorption component. Second, it is generally observed[21] that the circular dichroism of cis-β complexes of quadridentate ligands is roughly enantiomorphic to those of the corresponding cis-α complexes provided the two isomers are related by a single act of edge displacement of a terminal chelate arm. The circular dichroism spectra shown in Figure 6 refer to the cis-α and cis-β complexes with the same absolute configurations of the arsenic atoms, and their topological absolute configurations are therefore related by a single act of edge displacement of a terminal chelate arm; the signs of the circular dichroism components under the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition, however, are the same. The observation of circular dichroism of two signs for the (${}^1A_1 \rightarrow {}^1A_2$, ${}^1B_2$) transitions is unusual for amine complexes, but we have observed a plus–minus–plus (or the reverse) pattern for the three components of the ${}^1T_{1g}$ manifold in other arsine complexes, for example, the active *cis*-$[Co(diars)_2Cl_2]^+$ ion. The possibility that the Δ-cis-β isomer may have a minus–plus couplet for the (${}^1A_1 \rightarrow {}^1A_2$, ${}^1B_2$) transitions is not ruled out but the close overlap of a ${}^1T_{2g}$ component precludes any decision on the matter. As in the case of the cis-β complex the circular dichroism associated with the ${}^1T_{2g}$ manifold is also strong though heavily overlapped. We assign the negative shoulder at about 21,280 cm^{-1} (470 mμ) to one of these components and possibly the positive hump at around 24,100 cm^{-1} (415 mμ) to the other.

The trans complexes are the simplest to interpret as far as the d–d transitions are concerned. The well isolated band of low intensity at 15,700 cm^{-1} (637 mμ) is assigned to the ${}^1A_{1g} \rightarrow {}^1E_g$ transition derived from the ${}^1T_{1g}$ manifold. The two components of this transition are seen as a circular dichroism couplet. The other component of the ${}^1T_{1g}$ manifold, ${}^1A_{1g} \rightarrow {}^1A_{2g}$, is not resolved in the visible spectrum, but the positive circular dichroism component at around 21,600 cm^{-1} (463 mμ) probably represents this transition; it should occur[17] at around the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ absorption of the $[Co(diars)_3]^{3+}$ ion. The transition, however, is overlapped by components of the ${}^1T_{2g}$ manifold and/or charge transfer bands. We note also that the circular dichroism of the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ band changes sign in the solid but this does not necessarily imply any change in conformation.[22]

The details of the interpretation we have given above for the d–d spectra are subject to some ambiguity. The assignments we have put forward are based on a background knowledge of the spectra of a large number of similar complexes about which we will report elsewhere. These details are important in correlating circular dichroism with absolute configuration. Even with the limited number of examples given here, it is clear that such correlations will be difficult for arsine complexes. But whatever the details, a general observation about the electronic state of the cobalt atom may be made. It is clear from the high intensities of the bands, the enormously reduced interelectronic repulsions, and the extensive mixing of states that the electronic structure of the cobalt atom has been drastically altered from that which exists in the hard donor atom systems. These spectroscopic observations suggest that the d orbitals of the cobalt have lost a large amount of their free-ion character through interaction with the arsenic donor atoms and are, therefore, presumably more diffuse and "softer" (polarizable?) in these systems. This "softness" of the d orbitals may account for the ready reduction of these systems and their organometallic reactivity. We will report on the organometallic chemistry of these systems elsewhere.

The strong absorption bands in the region 290 to 450 mμ are assigned as mainly due to cobalt–arsine and cobalt–chlorine charge transfer bands because these bands only appear when arsenic and chloride are coordinated to cobalt. Some views[23] have been expressed on the "direction" of the charge transfer and we mention them here only to suggest that these intense low lying states are the probable major source of intensity for the d–d bands.

The absolute configurations of the complexes which show the circular dichroism in Figure 6 (all are negative rotatory at 5460 Å) are related to that of $(-)_{5460\text{Å}}$-Δ-*cis*-β-$[Co(R,R\text{-tetars})O_2]ClO_4$ ("sideways" bonded O_2), the absolute configuration of which is known from an absolute crystal structure.[13] This information is necessary in order to interpret the circular dichroism in the 50,000 to 54,000 cm^{-1} region. For the Λ-cis-α complex the circular dichroism is exceedingly strong and shows a typical exciton pattern;[24] our instrument did not allow us to measure much above 53,000 cm^{-1}, but it is clear that the other two complexes are likely to show the same pattern. We believe these two bands to be a result of coupling between the electric transition dipole moments of the phenyl chromophores.

The electric dipole $\pi \rightarrow \pi^*$ transitions of a mono-

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(20) W. Moffit, *J. Chem. Phys.*, **25**, 1189 (1956).

(21) G. R. Brubaker, D. P. Schaeffer, J. H. Worrell, and J. I. Legg, *Coord. Chem. Rev.*, 7, 161 (1971).

(22) B. Bosnich and J. MacB. Harrowfield, *J. Amer. Chem. Soc.*, **94**, 3425 (1972).

(23) S. Yamada, *Coord. Chem. Rev.*, **2**, 83 (1967).

(24) B. Bosnich, *Accounts Chem. Res.*, **2**, 266 (1969).

substituted phenyl chromophore are polarized in the molecular plane and, by symmetry, are directed either along the line joining the substituent and the para position (Figure 7) or at right angles to it. Exciton coupling involving either or both types of transitions can occur between chromophores. However, if, as molecular models indicate, the phenyl chromophores can more or less freely rotate from one chiral disposition to the other, the exciton coupling contribution from the perpendicularly polarized transitions will either vanish or be very small.[25] For a given conformation of the inner five-membered ring, the para directed transition moments are fixed irrespective of rotation and these can couple, under certain geometric circumstances, to give very large exciton couplets.

We have performed a number of such calculations where the conformation of the ring was changed from δ to λ and where a number of bond angles was varied. These calculations are straightforward;[24] tedious and analytic solutions are cumbersome but for the (coordinated) *R*,*R* configurations of the arsenic atoms general conclusions emerge. We have used the bond angles and distances provided by the X-ray structure of *cis*-β-[Co(*R*,*R*-tetars)O_2]ClO although we find the results are not critically dependent on the choice of these within reasonable limits except for one angle which is known to be large[10] for coordinated arsines, namely, the carbon–arsenic–metal angle associated with an arsenic substituent not involved in a chelate arm. In the present case this is the (phenyl) carbon–arsenic–cobalt angle which the X-ray structure shows to be about 120° and is consistent with other observations.[10] When this angle is varied from 109 to 130°, the calculation shows that the exciton coupling gives opposite results for the δ and λ conformation with the same chirality of the arsenic atoms. For the δ conformation, where the phenyl groups are axial for the (coordinated) *R*,*R*-tetars (Figure 2), the exciton circular dichroism is almost zero when the angle is 109° and as this angle is increased a minus (low energy)–plus (higher energy) couplet should appear; the magnitude should increase as the angle is increased to 130°. For the λ conformation, where the phenyl groups are equatorial for the (coordinated) *R*,*R*-tetars (Figure 7), the exciton circular dichroism should give a strong plus (low energy)–minus (higher energy) couplet at 109° which should progressively decrease in magnitude becoming almost zero at around 130°. These results are evident from molecular models. At around 109° for the δ ring and around 130° for the λ ring the magnitude is very small and the sign pattern depends critically on the other angles and bond lengths but, unless there are unreasonably gross distortions of the angles, between 113 and 127° the exciton theory predicts opposite sign patterns for the two conformers.

It will be seen in Figure 6 that all three isomers give the same plus (low energy)–minus (higher energy) patterns which indicates that all three isomers have the same inner ring conformation, namely, λ for the (coordinated) *R*,*R*-tetars. Furthermore, the nmr results indicate that the terminal chelate rings are probably in chair or slightly distorted chair conformations in order to get the high field methyl shifts when the phenyl groups are equatorially disposed.

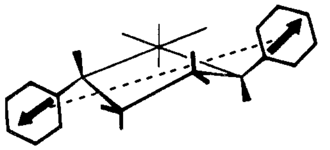

Figure 7. One of the exciton coupling modes involving the para-directed transitions of the phenyl chromophore. The other coupling mode is obtained by reversing the direction of *one* of the arrows. The five-membered ring is in the λ conformation, the arsenic configurations are *R*,*R* (coordinated), and the phenyl groups are equatorially disposed. With this geometry the above coupling gives a positive component at low energies.

This prompts us to make a general observation about the conformational preference of the tetars ligand when coordinated to a metal. We suggest that the terminal chelate rings will prefer chair conformations and the inner ring will adopt a conformation which allows the phenyl groups to be equatorial. This conclusion seems intuitively reasonable; molecular models suggest it and three crystal structures[13] support it.

7. Experimental Section

The nmr spectra were measured on Varian T60 and HA100 spectrometers at 29° using TMS as an internal signal and generally sample concentrations of about 0.1 *M*. Absorption and circular dichroism spectra were obtained using a Unicam SP820 recording spectrophotometer and a Roussell-Jouan Dichrographe II (Xe-lamp), respectively. The conductivities were measured on 10^{-3} *M* solutions using a Yellow Spring Instrument Co. Model 31 conductivity bridge. Optical rotations were obtained using a Perkin-Elmer 141 digital recording polarimeter.

All manipulations of the free tertiary arsines were carried out under pure nitrogen.

$ClCH_2CH_2CH_2AsCl_2$. This compound was prepared by the method of Gough and King[26] except that the initial reaction mixture of trimethylenechlorohydrin and sodium arsenite was required to be stirred for 72 hr at 55°.

$PhClAsCH_2CH_2AsClPh$. The reaction[27] between ethylene dibromide and phenyldichloroarsine[28] gives low yields unless two efficient condensers are used in order to suppress the steam distillation of ethylene dibromide which even under these conditions tends to evaporate off. After the reaction was complete the solid which deposited at pH 7 was collected and regenerated phenyldichloroarsine upon SO_2 reduction in HCl. The solid that came down to Congo Red neutralization was reduced[27] at 20° to give ethylene-1,2-bis(phenylchloroarsine). This was thoroughly dried and extracted with boiling cyclohexane and the filtered pale yellow solution was pumped to dryness to give a mass of pale yellow crystals. No attempt was made to fractionally crystallize this compound which undoubtedly exists in meso and racemic forms.

Meso and Racemic Tetars. The preparation of tetars involves the reaction between the Grignard reagent of $Cl(CH_2)_3As(CH_3)_2$[29] and $PhClAs(CH_2)_2AsClPh$. The Grignard reaction is difficult to initiate and tends to get "stuck," and since the product is not distillable it is important to use excess of the Grignard reagent in order to ensure complete conversion of the bifunctional chloro arsine.

Finely divided magnesium (24.1 g; Anachemia) was covered with dry diethyl ether (40 ml) in a 3-l. three-necked round-bottom flask with an efficient stirrer, condenser, and dropping funnel. A small crystal of iodine was added followed by methyl iodide (0.5 ml). While this initial reaction was proceeding, $(CH_3)_2As(CH_2)_3Cl$ (178 g) in dry ether (55 ml) was slowly added. At first about 40 ml of this solution was added and the mixture was warmed to 50° to initiate the reaction which becomes vigorous and heats up to about

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[25] In principle the rotameric conformations of the two phenyl chromophores must, on the average, prefer chiral dispositions because the phenyl groups are close to the dissymmetry of the rest of the molecule. Molecular models indicate that this contribution to the exciton coupling will be very small.

[26] G. A. Gough and H. King, *J. Chem. Soc.*, 2426 (1928).

[27] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 610 (1939).

[28] G. J. Burrows and E. E. Turner, *J. Chem. Soc.*, 1373 (1920).

[29] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4439 (1961).

80°. Once the Grignard set off it was maintained by the addition of the reagent at a rapid drop rate. After the addition, the reaction may become sluggish, in which case dry ether may be added occasionally, but in any case not more than a total of 100 ml should be added while the reaction is proceeding vigorously. When the reaction subsided the thick product was refluxed for 30 min in a water bath at 80°. The mixture was then cooled in an ice–acetone bath and ether (1200 ml) was added.

To this well stirred solution, $PhClAs(CH_2)_2AsClPh$ (99 g) in dry benzene (550 ml) was added dropwise over a period of 1 hr. The resulting grey-white paste was refluxed and vigorously stirred in order to break up any yellow lumps. The product was then cooled in ice–acetone and carefully (caution!) hydrolyzed by the addition of NH_4Cl (110 g) in water (1100 ml), then 2 *N* HCl (250 ml) and finally 5 *N* HCl (120 ml), to give two clear layers. The lower aqueous layer was run off and extracted twice with ether (2 × 200 ml). The ether extract and the top layer of the reaction mixture were combined, dried ($MgSO_4$), filtered, and pumped to dryness. Reduced pressure distillation (0.01 mm, 150°) of the oily residue (174 g) removed volatile impurities (mainly $CH_3(CH_2)_2As(CH_3)_2$), and two further ether extractions (which removed the solids) and distillations of the volatile materials gave a pale yellow viscous syrup (150 g). *Anal.* Calcd for $C_{24}H_{38}As_4$: C, 46.0; H, 6.1; As, 47.9. Found: C, 46.0; H, 6.0; As, 46.0.

Cobalt(III) Complexes of Tetars: _cis_-α-[Co(_R_,_R_;_S_,_S_-tetars)Cl$_2$]Cl, _cis_-β-[Co(_R_,_R_;_S_,_S_-tetars)Cl$_2$]Cl, and _trans_-[Co(_R_,_S_-tetars)Cl$_2$]Cl. A solution of tetars (30.0 g) in ether (150 ml) was added to $CoCl_2 \cdot 6H_2O$ (11.55 g) in methanol (750 ml) whereupon the solution turned deep brown-green. Hydrochloric acid (9.6 ml; 11 *N*) in methanol (20 ml) was then added to produce a deep green solution which intensified in color as air was drawn through for 3 hr. The solution was then filtered and pumped to dryness to give a deep blue-green semicrystalline residue which was dissolved in boiling water (600 ml) and allowed to digest on a steam bath for 30 min. The cooled aqueous solution (which may deposite blue crystals) was extracted with methylene chloride (7 × 250 ml), leaving a pale yellow aqueous phase which was discarded. (Hydrochloric acid was added toward the end of the extractions to facilitate the extraction of the brown complex which is the last to extract.) The combined extracts were dried ($MgSO_4$), filtered, and taken to dryness giving a residue which consists of the three complexes: *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Cl$_2$]Cl (~55%), *cis*-β-[Co(*R*,*R*;*S*,*S*-tetars)Cl$_2$]Cl (~5 %), and *trans*-[Co(*R*,*S*-tetars)Cl$_2$]Cl (~40%). These were separated as follows. The residue was taken up in boiling water (1500 ml) and HCl (1.5 ml, 11 *N*) was added to the hot filtrate which on standing for 36 hr at room temperature deposited shiny blue-black plates of *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Cl$_2$]Cl. These were collected and first washed with 3 *N* HCl (3 × 25 ml) and the now green filtrate and the HCl wash set aside. The blue crystals were then washed with acetone–ether (1:4, 3 × 25 ml) and finally ether (yield 13.2 g).

To the green filtrate and washings was added HCl (50 ml, 11 *N*) whereupon a fibrous voluminous mass of green crystals formed which on warming to 50° and the slow addition of more HCl (50 ml; 11 *N*) slowly transformed to manageable shiny bright green needles. In order to achieve this crystal transformation properly it is necessary to stir the solution and ensure that the precipitation is nearly complete at 50° before cooling at 0° for 5 hr. The green crystals were filtered and washed with 0.5 *N* HCl (3 × 25 ml) and the brown filtrate set aside. The crystals were then washed with acetone–ether (1:5; 3 × 25 ml) and finally with ether (yield 14.0 g).

trans-[Co(_R_,_S_-tetars)Cl$_2$]Cl. The green crystals were dissolved in absolute ethanol (300 ml), filtered, and ether (800 ml) added. The solution which began depositing green crystals was kept at 5° for 2 hr and then a further 1800 ml of ether was slowly added. After standing at 5° for 12 hr, the large green blocks or needles (depending on the rate of precipitation: slow, blocks; fast, needles) were collected and washed with ether and the blue filtrate set aside. A final crystallization of the green complex from hot water (600 ml) by the addition of excess HCl gave the pure *trans*-[Co(*R*,*S*-tetars)Cl$_2$]Cl complex (12.0 g). $\Lambda = 64.5$ ohm^{-1} cm^2 mol^{-1} (methanol, 10^{-3} *M*). *Anal.* Calcd for $[Co(C_{24}H_{38}As_4)Cl_2]Cl$: Co, 7.4; C, 36.4; H, 4.8; As, 37.9; Cl, 13.4. Found: Co, 7.5; C, 35.9; H, 4.7; As, 37.6; Cl, 13.4.

cis-α-[Co(_R_,_R_;_S_,_S_-tetars)Cl$_2$]Cl. The blue filtrate from the ethanol–ether precipitation of the green complex was pumped to dryness and added to the 13.2 g of blue crystals obtained from water–HCl. These were taken up in boiling water (1200 ml), filtered, and HCl (15 ml; 11 *N*) added to the hot filtrate which was allowed to stand at room temperature for 3 days. The resulting blue crystals were collected and washed as before giving 15.3 g of pure *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Cl$_2$]Cl. The filtrate which was brown was set aside. $\Lambda = 65.0$ ohm^{-1} cm^2 mol^{-1} (methanol, 10^{-3} *M*). *Anal.* Calcd for $[Co(C_{24}H_{38}As_4)Cl_2]Cl$: Co, 7.4; C, 36.4; H, 4.8; As, 37.9; Cl, 13.4. Found: Co, 7.4; C, 36.8; H, 5.1; As, 37.6; Cl, 13.2.

cis-β-[Co(_R_,_R_;_S_,_S_-tetars)Cl$_2$]Cl·H$_2$O. The two brown filtrates, that is the one from the first precipitation of the green complex and the one from the precipitation of the blue complex, were combined and extracted with CH_2Cl_2 (6 × 100 ml). These extracts were dried ($MgSO_4$), filtered, and pumped to dryness. The brown residue was dissolved in methanol (30 ml) and ether (100 ml) was added in portions to give shiny red-brown needles. A further crystallization from methanol–ether gave the pure *cis*-β-[Co(*R*,*R*; *S*,*S*-tetars)Cl$_2$]Cl·H$_2$O complex (1.0 g). $\Lambda = 64.0$ ohm^{-1} cm^2 mol^{-1} (methanol, 10^{-3} *M*). This *cis*-β complex may also be prepared by the method given for its active complex. *Anal.* Calcd for $[Co(C_{24}H_{38}As_4)Cl_2]Cl \cdot H_2O$: Co, 7.3; C, 35.6; H, 5.0; As, 37.0; Cl, 13.1. Found: Co, 7.5; C, 35.5; H, 5.0; As, 37.4; Cl, 12.9.

The brown cis-β complex need not be isolated at this stage and the material can be obtained as the cis-α complex as follows. The brown residue from the CH_2Cl_2 extraction is taken up in boiling water (20 ml), HCl (5 ml; 11 *N*) is added, and after 3 days at room temperature the less soluble blue crystals of the cis-α complex (0.8 g) are collected.

The total yield of complex from 30 g of tetars is 28.3 g.

trans-[Co(_R_,_R_;_S_,_S_-tetars)Cl$_2$]ClO$_4$. *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Cl$_2$]Cl (1 g) in methanol (50 ml) was refluxed for 30 hr and the resulting blue-green solution was pumped to dryness. The *trans*-[Co(*R*,*R*; *S*,*S*-tetars)Cl$_2$]$^+$ may be fractionally crystallized from this mixture but the procedure is long and tedious. It is simplest to pass it down an ion-exchange column as follows.

The residue was dissolved in a minimum amount of methanol and added onto a Dowex 50W-X2 cation exchange resin suspended in methanol (H$^+$ form, 200–400 mesh, 200 g (wet); 30 × 2 cm column). It was eluted slowly with LiCl (0.05 *M* in methanol). The green trans isomer eluted first closely followed by the blue cis-α isomer which, after the green complex was collected, could be rapidly eluted with 1 *M* LiCl and isolated in the usual way. The green eluate was taken down to dryness and taken up in a little acetone, and the green complex precipitated by the addition of excess dilute aqueous sodium perchlorate. This was collected, washed with water, and dried. It was first recrystallized from acetone (45 ml) by the addition of ether and from acetonitrile by the addition of ether and was obtained as deep green blocks (0.12 g) of the perchlorate salt. *Anal.* Calcd for $[Co(C_{24}H_{38}As_4)Cl_2]ClO_4$: C, 33.7; H, 4.5; Cl, 12.4. Found: C, 34.0; H, 4.2; Cl, 12.8.

trans-[Co(_R_,_R_;_S_,_S_-tetars)Cl$_2$]Cl. This was prepared by fractional crystallization of the methanol equilibrated mixture of isomers. It formed shiny apple-green plates from acetone–methanol–ether. $\Lambda = 67$ ohm^{-1} cm^2 mol^{-1} (methanol, 10^{-3} *M*). *Anal.* Calcd for $[Co(C_{24}H_{38}As_4)Cl_2]Cl$: C, 36.4; H, 4.8; Cl, 13.4. Found: C, 36.6; H, 4.9; Cl, 13.4.

cis-β-[Co(_R_,_S_-tetars)CO$_3$]ClO$_4$. Sodium carbonate (0.80 g) was added to a hot solution of *trans*-[Co(*R*,*S*-tetars)Cl$_2$]Cl (5.0 g) in water (450 ml). The solution rapidly turned orange-red and a small amount of gelatinous green material was formed. After heating the solution on a steam bath for 0.75 hr, the solution was filtered, cooled, sodium perchlorate (5 g) added, and the solution filtered again. The resulting clear orange-red solution was extracted into CH_2Cl_2 (10 × 50 ml) which was dried (Na_2SO_4) and evaporated to dryness. The residue was taken up in methanol (20 ml) and acetone (100 ml) and precipitated by the slow addition of ether (600 ml) and cooling at 0° for 12 hr. It was collected and washed with ether. A second crystallization gave pure *cis*-β-[Co(*R*,*S*-tetars)CO$_3$]ClO$_4$ as cherry-red needles (4.0 g). $\Lambda = 72$ ohm^{-1} cm^2 mol^{-1} (methanol, 5.0×10^{-4} *M*). *Anal.* Calcd for $[Co(C_{24}H_{38}As_4)CO_3]ClO_4$: C, 35.6; H, 4.5; Cl, 4.3. Found: C, 35.3; H, 4.8; Cl, 4.3.

cis-β-[Co(_R_,_S_-tetars)Cl$_2$]ClO$_4$. An ice-cold mixture of HCl (50 ml; 11 *N*) and HClO$_4$ (10 ml; 11 *N*) was added to solid *cis*-β-[Co(*R*,*S*-tetars)CO$_3$]ClO$_4$ (5.0 g) in a 250-ml flask held in an ice bath. The slurry was stirred for 5 min as carbon dioxide was liberated and a smooth brown paste developed. Ice-cold methanol (50 ml) was then added whereupon the paste dissolved to give a clear brown solution which soon began to deposit fine brown crystals. These were collected after standing at 0° for 2 hr and were washed with methanol to remove the green trans isomer until the washings turned brown; it was then washed with ether and dried. The brown complex (4.0 g) was dissolved in acetone (600 ml) and methanol (60 ml) and upon the slow addition of ether (1400 ml) shiny brown-black crystals formed; these were collected and washed with cold methanol and then ether. One further crystallization gave the pure *cis*-β-[Co(*R*,*S*-tetars)Cl$_2$]ClO$_4$ complex as shiny brown-black blocks (2.8 g). Λ = 78 ohm^{-1} cm^2 mol^{-1} (methanol, 5.0 × 10^{-4} *M*). *Anal.* Calcd for [Co(C$_{24}$H$_{38}$As$_4$)Cl$_2$]ClO$_4$: Co, 6.9; C, 33.7; H, 4.5; As, 35.0; Cl, 12.4. Found: Co, 7.1; C, 33.8; H, 4.2; As, 35.3; Cl, 12.6.

***cis*-β-[Co(*R*,*S*-tetars)Cl$_2$]Cl·H$_2$O.** Finely ground *cis*-β-[Co(*R*,*S*-tetars)Cl$_2$]ClO$_4$ (0.5 g) in methanol (100 ml) and acetone (100 ml) was shaken with Dowex 2-X8, 20–50 mesh ion-exchange resin (2 g, Cl$^-$ form). The solution was filtered and treated again with 2 g of resin and the chloride salt isolated by the addition of a large volume of ether. It was recrystallized twice from acetone (40 ml) and methanol (40 ml) by the slow addition of ether (900 ml) to give fine brown needles which were collected and washed with ether (0.2 g). *Anal.* Calcd for [Co(C$_{24}$H$_{38}$As$_4$)Cl$_2$]Cl·H$_2$O: C, 35.6; H, 5.0; Cl, 13.1. Found: C, 33.0; H, 4.8; Cl, 13.1.

***trans*-[Co(*R*,*S*-tetars)ClNO$_2$]ClO$_4$, Isomer I.** Sodium nitrite (2.5 g) in water (150 ml) at 0° was slowly added with stirring to *trans*-[Co(*R*,*S*-tetars)Cl$_2$]Cl (2.5 g) in water (800 ml) at 0°. Shiny green plates readily separated on scratching the vessel and after 2 hr at 0°, these were collected, washed with a little ice-water, dried, and recrystallized twice from ethanol by the addition of ether to ensure the removal of any excess sodium nitrite. This material (2.0 g) was dissolved in absolute ethanol (100 ml) and heated on a steam bath for 30 min to produce a brown solution which was poured into sodium perchlorate (5 g) in water (700 ml). The brown solid was collected, taken up in acetone (200 ml), and reprecipitated by the addition of sodium perchlorate (5 g) in water (700 ml). The solid was collected and washed with cold water, then acetone–ether (1:10) and finally ether. This solid consists of a reproducible mixture of *trans*-[Co(*R*,*S*-tetars)Cl$_2$]ClO$_4$ (45%), *trans* [Co(*R*,*S*-tetars)(NO$_2$)$_2$]ClO$_4$ (20%), *trans*-[Co(*R*,*S*-tetars)ClNO$_2$]ClO$_4$, isomer I (30%), and *trans*-[Co(*R*,*S*-tetars)ClNO$_2$]ClO$_4$, isomer II (<5%). These were separated as follows.

The mixture (2.0 g) was taken up in hot methanol (400 ml) and allowed to *slowly* crystallize for 2 days at 0°. Two easily discernible types of crystals were collected (1.05 g): tiny brown needles and tiny plates which contain dinitro and chloronitro isomer I complexes, and very large long brown-black needles which contain the dichloro and (again) chloronitro isomer I. These crystal habits are consistently reproduced and the large long needles were mechanically separated from the tiny needles and plates. The long needles (0.25 g) were thrice recrystallized from hot methanol (50–80 ml) which after standing for a day at 0° gave long deep brown needles (0.15 g) of pure *trans*-[Co(*R*,*S*-tetars)ClNO$_2$]ClO$_4$, isomer I. Λ = 101 ohm^{-1} cm^2 mol^{-1} (methanol, 2.75 × 10^{-4} *M*). *Anal.* Calcd for [Co(C$_{24}$H$_{38}$As$_4$)NO$_2$Cl]ClO$_4$: C, 33.3; H, 4.4; N, 1.62; Cl, 8.1. Found: C, 33.0; H, 4.5; N, 1.61; Cl, 8.4.

***trans*-[Co(*R*,*S*-tetars)ClNO$_2$]ClO$_4$, Isomer II.** Finely ground *trans*-[Co(*R*,*S*-tetars)(NO$_2$)$_2$]ClO$_4$[30] (2.0 g) was stirred into hydrochloric acid (400 ml, 11 *N*) at 90°. After about 25–30 sec a clear orange-brown solution developed and was poured *at once* into cold water (1500 ml) containing sodium perchlorate (5 g). The resulting solid was extracted into CH$_2$Cl$_2$ (4 × 150 ml), dried (Na$_2$SO$_4$), and pumped to dryness (2.2 g). Slow reprecipitation from acetone solution (100 ml) with NaClO$_4$ (3 g) in water (400 ml) gave orange-red needles (2.0 g) which consisted of *trans*-[Co(*R*,*S*-tetars)Cl$_2$]ClO$_4$ (5%), *trans*-[Co(*R*,*S*-tetars)ClNO$_2$]ClO$_4$, isomer I (5%), and the required isomer II (90%). The mixture (2.0 g) was taken up in hot methanol (250 ml) and after cooling at 0° for a day the brown-red needles were collected and washed with ether. A second crystallization from methanol gave the pure *trans*-[Co(*R*,*S*-tetars)ClNO$_2$]ClO$_4$ isomer II complex as large brown-red needles (1.5 g). Λ = 83 ohm^{-1} cm^2 mol^{-1} (methanol, 4.04 × 10^{-4} *M*). *Anal.* Calcd for [Co(C$_{24}$H$_{38}$As$_4$)NO$_2$Cl]ClO$_4$: C, 33.3; H, 4.4; N, 1.62; Cl, 8.1. Found: C, 33.3; H, 4.3; N, 1.63; Cl, 8.4.

***R*,*S*-Tetars from Its Cobalt(III) Complex.** A methanol solution (50 ml) of *trans*-[Co(*R*,*S*-tetars)Cl$_2$]Cl (5.5 g) was added dropwise to a filtered efficiently stirred solution of NaCN (4.5 g) in water (30 ml) under nitrogen at such a rate that there was no build-up of the green complex. The cyanide solution was held at 70° in an oil bath throughout the addition. The green color rapidly faded to yellow and then to light yellow as a clear oil of *R*,*S*-tetars separated. After the addition was complete, water (100 ml) was added and the mixture refluxed for 30 min. On cooling, the arsine was extracted into ether (3 × 100 ml) and the ether extracts were washed with water (5 × 50 ml), dried (Na$_2$SO$_4$), filtered, and the ether was pumped off to give a clear oil (3.8 g). This was taken up in ether (5 ml) diluted with methanol (100 ml), filtered, and rapidly cooled in a Dry Ice–acetone bath. After 15 min the white needles of the pure *R*,*S*-tetars were collected, washed with methanol, and dried *in vacuo* (3.6 g; mp 36°; bp >200° (0.1 mm)). *Anal.* Calcd for C$_{24}$H$_{38}$As$_4$: C, 46.0; H, 6.1; As, 47.9. Found: C, 46.2; H, 6.1; As, 46.0.

***R*,*R*:*S*,*S*-Tetars from Its Cobalt(III) Complex.** A solution of *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Cl$_2$]Cl (5.5 g) in methanol (50 ml) was reacted with cyanide and worked up in the same way as given for the *R*,*S*-tetars. The resulting oil (3.8 g) was purified by dissolution in pure ether (50 ml), drying with MgSO$_4$, and pumping of the ether under high vacuum (2 hr; 60°; 0.05 mm). A clear colorless oil remained (3.6 g) which became solid at Dry Ice–acetone temperatures but melted again as the temperature was raised. *Anal.* Calcd for C$_{24}$H$_{38}$As$_4$: C, 46.0; H, 6.1; As, 47.9. Found: C, 46.1; H, 5.8; As, 47.8.

Resolution of *cis*-α-[Co(*R*,*R*:*S*,*S*-tetars)Cl$_2$]Cl. D-(−)-Dibenzoyl-(+)-tartaric acid monohydrate (10.46 g) was reacted with Na$_2$CO$_3$ (1.47 g) in hot water (1400 ml). When all the acid had dissolved the solution was boiled for a few minutes and filtered. The now clear solution was held at 35° and vigorously stirred as *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Cl$_2$]Cl (20.0 g) in ethanol (250 ml) was added slowly to it dropwise. A microcrystalline blue precipitate formed at once and, when the addition was complete, water (850 ml) was added. The mixture was cooled in ice for 2 hr and the blue precipitate collected, washed with water and then ether, and sucked at the pump. The filtrate is pale blue and consists of the more soluble diastereoisomer which may be extracted with CH$_2$Cl$_2$ (3 × 100 ml) to obtain about 0.5 g of complex. This was set aside.

It is important to obtain the blue solid completely free of solvent for the next step; a quick method of doing this is as follows. After the blue solid was sucked free of loose solvent, it was taken up in boiling methanol (500 ml), filtered, and taken down to a gum; CH$_2$Cl$_2$ (200 ml) was then added and the mixture taken down to dryness giving a dry deep blue powder (27.5 g) of the two diastereoisomers. This was taken up in boiling absolute ethanol (1300 ml), filtered while hot, and allowed to crystallize in a freezer (−5°) for 3 hr; ether (1300 ml) was then added, and the mixture was shaken and allowed to stand at −5° for a further 2 hr. The fine blue-grey needles which deposited were collected, washed with cold ethanol followed by ether, and dried at 100° for 2 hr to give 15.0 g of almost pure Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl$_2$]-D-(−)-DBHT. The deep blue filtrate combined with the 0.5 g of salt obtained from the CH$_2$Cl$_2$ extracts from the original precipitation was pumped to dryness and set aside.

Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl$_2$]-D-(−)-DBHT. The less soluble diastereoisomer (15.0 g) was dissolved in a minimum volume of boiling absolute ethanol and allowed to crystallize at 0° for 12 hr. The blue-grey crystals of the pure Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl$_2$]-D-(−)-DBHT salt were collected and washed with ether (13.0 g): [α]D +378 ± 70° (7.87 × 10^{-5} g/g in methanol). *Anal.* Calcd for Λ-[Co(C$_{24}$H$_{38}$As$_4$)Cl$_2$](C$_{18}$H$_{13}$O$_8$): C, 45.3; H, 4.62; Cl, 6.37. Found: C, 45.4; H, 4.60; Cl, 6.42.

Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl$_2$]ClO$_4$. The less soluble diastereoisomer (13.0 g) was dissolved in methanol (1200 ml) and a cold solution of perchloric acid (85 ml, 11 *N*) in water (2000 ml) was added to it. Deep blue-black needles of Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl$_2$]ClO$_4$ (8.8 g) separated slowly after the mixture was allowed to stand for a day at 0°. The crystals were first washed with ethanol–ether (1:1) and then ether. The rotation of this material does not change upon fractional crystallization from acetonitrile (150 ml) by the slow addition of ether (1500 ml): [α]D +680 ± 80°; [α]$_{546}$ −1286 ± 5° (2.21 × 10^{-4} g/g, methanol). *Anal.* Calcd for [Co(C$_{24}$H$_{38}$As$_4$)Cl$_2$]ClO$_4$: C, 33.7; H, 4.5; Cl, 12.4. Found: C, 34.0; H, 4.3; Cl, 12.7.

Δ-*cis*-α-[Co(*S*,*S*-tetars)Cl$_2$]ClO$_4$. The more soluble diastereoisomer (12.5 g) obtained from pumping down the filtrate of the first ethanol crystallization and the CH$_2$Cl$_2$ extract from the original water precipitation is nearly optically pure and, although possible, it is not economical to crystallize from solution. It is more convenient to convert it to the perchlorate salt in exactly the same way as given for the other diastereoisomer. The perchlorate salt thus obtained is usually more than 95% optically pure and one crystalli-

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[30] This complex was prepared by reaction between the dichloro complex and excess sodium nitrite in hot methanol–water. The reaction is complete after about an hour at 80° and the product may be precipitated with aqueous sodium perchlorate and then recrystallized from hot methanol. The details will be given elsewhere.

zation from acetonitrile by the slow addition of ether gives the pure Δ-*cis*-α-[Co(*S*,*S*-tetars)Cl_2]ClO_4 complex (8.5 g): [α]D −680 ± 80°; $[\alpha]_{546}$ +1286 ± 5° (2.21 × 10^{-4} g/g, methanol).

Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl_2]Cl. Finely divided Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl_2]ClO_4 (9.0 g) in warm methanol (800 ml) was shaken with Dowex 2-X8, 20–50 mesh ion-exchange resin, Cl^- form (40 g); the blue solution was filtered and the procedure repeated with a further 40 g of resin. The solution was taken to dryness and dissolved in hot water (400 ml), HCl (6 ml, 11 *N*) was slowly added, and after several hours at 20°, the shiny blue-black plates of the pure chloride salt (7.7 g) were collected, washed with 0.5 *N* HCl, then acetone–ether (1:2) and finally ether. The brown aqueous filtrate contains the active cis-β isomer and may be extracted by the procedure given presently. The *cis*-α-chloride salt has an identical circular dichroism spectrum to that of the perchlorate salt. *Anal.* Calcd for [Co($C_{24}H_{38}As_4$)Cl_2]Cl: Co, 7.4; C, 36.4; H, 4.8; As, 37.9; Cl, 13.4. Found: Co, 7.4; C, 36.4; H, 4.8; As, 37.5; Cl, 13.2.

Δ-*cis*-α-[Co(*S*,*S*-tetars)Cl_2]Cl. The same procedure as above gave the pure chloride salt of this antipode. *Anal.* Calcd for [Co($C_{24}H_{38}As_4$)Cl_2]Cl: Co, 7.4; C, 36.4; H, 4.8; As, 37.9; Cl, 13.4. Found: Co, 7.4; C, 36.1; H, 5.0; As, 37.5; Cl, 13.4.

Δ-*cis*-β-[Co(*R*,*R*-tetars)Cl_2]Cl·H_2O. The following method may be used for either racemic or active complex; the active complex preparation is described.

Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl_2]Cl (5.0 g) was refluxed in water (600 ml) for 3 hr. The resulting blue-brown solution was filtered hot and HCl (50 ml, 11 *N*) was added, and after cooling at 5° for 0.75 hr the crystals of the cis-α complex (4.1 g) were collected leaving a brown-red filtrate. This was extracted with CH_2Cl_2 (6 × 50 ml), dried ($MgSO_4$), filtered, and pumped to dryness. The residue was taken up in methanol (25 ml) and ether (200 ml) slowly added to the solution which deposited glistening maroon plates after standing at 0° for 12 hr. These were collected and recrystallized from methanol (10 ml) and ether (25 ml) to give the pure Δ-*cis*-β-[Co(*R*,*R*-tetars)Cl_2]Cl complex (0.45 g). *Anal.* Calcd for [Co($C_{24}H_{38}As_4$)Cl_2]Cl·H_2O: C, 35.6; H, 5.0; Cl, 13.1. Found: C, 35.6; H, 5.0; Cl, 12.9.

Δ-*cis*-β-[Co(*R*,*R*-tetars)Cl_2]ClO_4. An aqueous solution of Δ-*cis*-β-[Co(*R*,*R*-tetars)Cl_2]Cl deposits the perchlorate salt by the addition of $NaClO_4$. The perchlorate is not very soluble in methanol and may be recrystallized either from CH_2Cl_2–ether or acetonitrile–ether: [α]D −120 ± 80°; $[\alpha]_{546}$ −500 ± 2°; $[\alpha]_{436}$ −815 ± 1° (1.10 × 10^{-4} g/g, methanol). *Anal.* Calcd for [Co($C_{24}H_{38}As_4$)Cl_2]ClO_4: C, 33.7; H, 4.5; Cl, 12.4. Found: C, 33.4; H, 4.7; Cl, 12.7.

***trans*-[Co(*R*,*R*-tetars)Cl_2]ClO_4.** This compound was prepared from Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl_2]Cl by the same method as given for the racemic salt. After elution from the ion-exchange column the *trans*-chloride salt was converted to the perchlorate which was crystallized from methanol by the slow addition of ether to give fine apple-green needles: [α]D −185 ± 30°; $[\alpha]_{546}$ −382 ± 40°; $[\alpha]_{436}$ +1410 ± 50° (7.58 × 10^{-5} g/g methanol). *Anal.* Calcd for [Co($C_{24}H_{38}As_4$)Cl_2]ClO_4: C, 33.7; H, 4.5; Cl, 12.4. Found: C, 33.9; H, 4.3; Cl, 12.4.

***S*,*S*-Tetars.** The free active arsine may be liberated from Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl_2]Cl in the same way as given for the racemic analog. For the active arsine it is more convenient to start from the perchlorate salt; it was decomposed as follows.

To a well stirred solution of sodium cyanide (3 g) in water (12 ml) and acetonitrile (12 ml) maintained at 65°, was added dropwise a warm solution of Λ-*cis*-α-[Co(*R*,*R*-tetars)Cl_2]ClO_4 (2 g) in acetonitrile (30 ml) at such a rate that there was no build-up of the blue complex. After the addition was complete (∼30 min), water (100 ml) was added, the mixture cooled, and the arsine extracted into ether (2 × 100 ml). The ether extract was washed with water (5 × 50 ml), dried (Na_2SO_4), and taken to dryness leaving a clear oil (1.5 g), which was taken up in pure ether, filtered, and pumped under reduced pressure to leave the pure clear colorless active *S*,*S*-tetars (1.4 g): [α]D +28.7° (2.27 × 10^{-2} g/g, $CHCl_3$). *Anal.* Calcd for $C_{24}H_{38}As_4$: C, 46.0; H, 6.1; As, 47.9. Found: C, 46.0; H, 6.0; As, 46.0.

Oxidation of $CoCl_2$ and *R*,*R*;*S*,*S*-Tetars or *S*,*S*-Tetars. *R*,*R*;*S*,*S*-Tetars or *S*,*S*-tetars (1.2 g) in ether (20 ml) was added to $CoCl_2\cdot 6H_2O$ (0.46 g) in methanol (50 ml). Air was drawn through the solution for 5 min and then HCl (0.5 ml; 11 *N*) was added. Air was drawn through the solution for a further 40 min; the solution was then pumped to dryness and the residue passed down an ion-exchange column. After the usual work-up *trans*-dichloro perchlorate complex (0.3 g) and the *cis*-α-dichloro chloride complex (0.4 g) were obtained.

Oxidation of $CoCl_2$ and *R*,*S*-Tetars. The arsine was reacted with $CoCl_2$ in exactly the same way as given for the racemic arsine. After work-up it gave a quantitative yield of *trans*-[Co(*R*,*S*-tetars)Cl_2]Cl.

Racemization and Isomerization of the Free Arsines. When a dilute solution of either *R*,*S*-tetars, *R*,*R*;*S*,*S*-tetars, or *S*,*S*-tetars in methanol–ether (2:1) is reacted with a few drops of concentrated HCl, the arsines isomerize and racemize within a few minutes. There is no decomposition and starting from any of the arsines an equilibrium mixture consisting of *R*,*S*-tetars (55%) and *R*,*R*;*S*,*S*-tetars (45%) is obtained.

Interconversion of the Complexed Arsines. A solution of either *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Cl_2]Cl (5.0 g) or *trans*-[Co(*R*,*S*-tetars)Cl_2]Cl (5.0 g) in acetonitrile (125 ml) was refluxed for 2 days giving a deep greenish-blue solution which was filtered and pumped to dryness. The residue was washed with ether to remove free arsine and was worked up in the usual way to give *trans*-[Co(*R*,*S*-tetars)Cl_2]Cl (2.0 g) and *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Cl_2]Cl (1.5 g) from either complex.

Starting with either the *trans*-[Co(*R*,*S*-tetars)Br_2]Br or *cis*-α-[Co(*R*,*R*;*S*,*S*-tetars)Br_2]Br complex under the same conditions gave the *cis*-α-dibromo (70%) and *trans*-dibromo (30%) complexes.

Analysis of Isomeric Proportions. The isomeric proportions were analyzed mostly by nmr but sometimes using the absorption and circular dichroism spectra. The first method requires comment. Since all the complexes are insoluble in water but very soluble in CH_2Cl_2 as their perchlorate salts, the conditions were arranged so that the perchlorate salts were extracted from aqueous suspensions into CH_2Cl_2. The extracts were pumped to dryness and the homogenous residue analyzed by nmr integration of the methyl resonances. The accuracy is about 5%.

Kinetics. The kinetics of the *cis*-β-[Co(*R*,*S*-tetars)Cl_2]ClO_4 → *trans*-[Co(*R*,*S*-tetars)Cl_2]ClO_4 isomerization were studied in dry methanol (Mg) at 29.4° using a Cary 14 manual spectrophotometer equipped with constant temperature cells. Measurements were made at two wavelengths (540 mμ, ε(cis-β) = 940 M^{-1} cm^{-1}, ε(*trans*) = 34 M^{-1} cm^{-1}; 570 mμ, ε(cis-β) = 640 M^{-1} cm^{-1}, ε(*trans*) = 36 M^{-1} cm^{-1}) using 1-cm cells and 1.00 × 10^{-3} *M* concentrations of the perchlorate salt. The results were quite reproducible and a continuous scan revealed an isobestic point throughout the reaction at 645 mμ (ε = 186 M^{-1} cm^{-1}) in agreement with prediction, *i.e.*, 645 mμ (ε = 190 M^{-1} cm^{-1}).

Coordinated Arsenic Inversions. Our attempts to measure the kinetics of coordinated arsenic inversion were carried out in dry acetonitrile (P_2O_5) using usually 2.00 × 10^{-2} *M* solutions in sealed ampoules under nitrogen. The ampoules were protected from light and submerged in a constant temperature water bath at 60.0°. The meso, racemic, and active arsine cobalt(III) complexes were used and analyzed by nmr, visible absorption, and circular dichroism in the usual way. The equilibrium constants thus obtained were accurate to within about 2%.

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