cis-β-[Co(*R*,*S*-tetars)Cl_2]$^+$, 50803-99-1; *cis*-β-[Co(*R*,*S*-tetars)$(NO_2)_2$]$^+$, 50804-00-7; *cis*-β-[Co(*R*,*S*-tetars)$(NCS)_2$]$^+$, 50804-01-8; *trans*-[Co(*R*,*S*-tetars)$(NCS)_2$]$^+$, 50804-02-9; *trans*-[Co(*R*,*S*-tetars)Cl(NO_2)]$^+$, 50804-03-0; *trans*-[Co(*R*,*R*-tetars)Cl_2]$^+$, 50804-04-1; *trans*-[Co(*R*,*R*-tetars)$(N_3)_2$]$^+$, 50804-05-2; Λ-*cis*-α-[Co(*R*,*R*-tetars)$(OH)_2$]$^+$, 50804-06-3; Δ-*cis*-β-[Co(*R*,*R*-tetars)$(OH)_2$]$^+$, 50804-07-4.

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Dissymmetric Arsine Complexes. Synthesis, Chemistry, and Configurational Stability of *cis*-Bis(*o*-phenylenebis(dimethylarsine))cobalt(III) Complexes

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Systematic methods for preparing *cis*-[Co(diars)$_2X_2$]$^{n+}$ (diars = *o*-phenylenebis(dimethylarsine)) complexes are given. The *cis*-[Co(diars)$_2Cl_2$]$^+$ ion has been resolved into its pure optical isomers and from these the optical isomers of the diaquo, carbonato, dinitrato, dinitro, and hydroxoaquo complexes have been isolated. It is shown by chemical interconversion reactions that all are optically pure and substitution of the diaquo complex proceeds with complete chiral retention. In the absence of catalysis all these complexes are remarkably inert to racemization. The rate constant for loss of optical activity of the *cis*-[Co(diars)$_2Cl_2$]ClO_4 complex in dilute dry methanol at 54.9° is found to be 30% faster than that for cis → trans isomerization.

In the preceding paper[1] we described the preparation of an extensive series of dissymmetric cobalt(III)–arsine complexes derived from a stereospecific quadridentate tetra(tertiary arsine) ligand. As we shall see in subsequent papers, the circular dichroism that these complexes show is exceedingly complex. We therefore sought a simpler model system to investigate so that the general characteristics of the circular dichroism spectra of dissymmetric arsine complexes could be analyzed as a prelude to the more complicated systems. Of all the arsine ligand complexes that are conveniently prepared, the bis(*o*-phenylenebis(dimethylarsine))cobalt(III) complexes (Figure 1) seemed to present themselves as the least complicated as well as having the electronic features necessary for a nonempirical determination of their absolute configurations.

The first reported[2] complexes of this ligand coordinated to a cobalt(III) center were of the type [Co(diars)$_2X_2$]$^+$, $X^- = Cl^-, Br^-, I^-$, and NCS^-, and all had the trans configuration. Subsequently, two reports[3,4] described the preparations of some *cis*-[Co(diars)$_2X_2$]$^+$ complexes which involved the use of Ag^+ ions to remove the halogens from the complexes. These methods of entry into the cis complexes, however, amount to little more than recipes and are devoid of the necessary systematic preparative features necessary for dealing with a series of optically active complexes and interrelating their configurations. On the basis of our previous experience,[1] it occurred to us that the reason the silver method worked was that solvento complexes were produced and these were stable in the cis geometry and anated with retention. These previous reports also noted that the stability of these cis species was capricious in the sense that although cis species were isolated, they, without apparent inducement, quickly and erratically reverted to the trans isomers. Thus the problem of using diars as a model compound in the study of the optical activity of its cobalt(III) complexes is not a simple one.

It is the purpose of this paper to describe systematic preparative methods which give both the racemic and optically active complexes with full retention of geometry and chirality. In addition we offer an explanation and supporting evidence for the capricious instability of the cis complexes.

1. Preparations

The green *trans*-[Co(diars)$_2Cl_2$]Cl complex is easily prepared by the addition of hydrochloric acid to an aerially oxidized aqueous alcohol solution of cobalt acetate and 2 mol of diars. This complex reacts with lithium carbonate in aqueous methanol to give a high yield of the very water-soluble orange *cis*-[Co(diars)$_2CO_3$]Cl salt which is unstable in water in the presence of chloride ions and tends to revert to the *trans*-dichloro complex. It was obtained as the perchlorate salt after extraction into methylene chloride. Upon the addition of concentrated perchloric acid to this carbonato complex, crystals of the *cis*-[Co(diars)$_2(OH_2)_2$]$(ClO_4)_3$ complex deposit.

The nmr spectrum of the *cis*-diaquo ion in dilute aqueous perchloric acid solutions shows the characteristic four-line methyl proton spectrum and there is no evidence for the *trans*-diaquo isomer after 1 month at room temperature. The addition of 1 equiv of hydroxide ions to an aqueous solution of the *cis*-diaquo complex deposits the rather insoluble *cis*-[Co(diars)$_2OH(OH_2)$]$(ClO_4)_2$ complex. These two complexes are starting materials which give easy entry into the preparations of cis complexes.

The aquo group of the *cis*-hydroxoaquo complex is very much more labile than the hydroxo group and it thus may be possible selectively to substitute the cis octahedral positions one at a time by simply adjusting the pH of the solution. We have not pursued this problem of preparing *cis*-[Co(diars)$_2$XY]$^{n+}$ complexes except for the *cis*-[Co(diars)$_2OH(CH_3CN)$]$(ClO_4)_2$ complex which is prepared by dissolving the *cis*-hydroxoaquo complex in acetonitrile. The orange product shows an nmr pattern typical of a *cis*-[Co(diars)$_2$XY]$^{n+}$ species (Table I).

The aquo groups of the *cis*-diaquo species are also very labile and, in all cases, appear to be substituted with steric retention. Thus, in acetonitrile, the *cis*-diaquo complex

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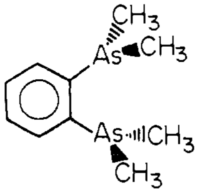
Table I. Methyl Resonances[a] of Bis(diarsine)cobalt(III) Complexes

Compd	Solvent	δ, ppm
trans-$[Co(diars)_2Cl_2]ClO_4$	$(CD_3)_2SO$	1.93
cis-$[Co(diars)_2Cl_2]Cl\cdot{}^1/_2HCl\cdot 4H_2O$	CD_3OD	2.20, 2.08, 1.60, 1.20
cis-$[Co(diars)_2Cl_2]ClO_4$	CD_3CN	2.13, 2.04, 1.55, 1.13
cis-$[Co(diars)_2CO_3]ClO_4\cdot CH_2Cl_2$	$(CD_3)_2SO$	2.22, 1.67, 1.62, 1.18
cis-$[Co(diars)_2(OH_2)_2](ClO_4)_3$	D_2O[b]	2.95, 2.72, 2.18, 1.68
cis-$[Co(diars)_2(NO_2)_2]ClO_4$	CD_2Cl_2	2.28, 2.10, 1.72, 1.18
cis-$[Co(diars)_2(NO_3)_2]ClO_4$	CD_3NO_2	2.40, 2.25, 1.62, 1.03
cis-$[Co(diars)_2C_2O_4]B(C_6H_5)_4$	$(CD_3)_2SO$	2.20, 1.65, 1.57, 1.13
cis-$[Co(diars)_2(CH_3CN)_2](ClO_4)_3\cdot CH_3CN$	$(CD_3)_2SO$	2.54, 2.37, 1.90, 1.32, 2.74,[c] 2.05[d]
cis-$[Co(diars)_2(OH)(CH_3CN)](ClO_4)_2$[e]	$(CD_3)_2SO$	2.34, 2.29, 1.88, 1.77, 1.53, 1.53, 1.22, 1.02

[a] All spectra recorded on a 60-MHz instrument; resonances are reported relative to internal TMS standard, unless otherwise noted. [b] Relative to external TMS standard. [c] Methyl resonance of coordinated acetonitrile. [d] Methyl resonance of free acetonitrile. [e] Integration indicates that two of the arsine methyl resonances are accidentally degenerate at 1.53 ppm and that a third coincides with the resonance of the coordinated acetonitrile molecule 1.77 ppm. These assignments have been confirmed by comparison of this spectrum with that of the hydroxoaquo complex in CD_3CN.



diars

Figure 1.

reacts rapidly to produce the yellow *cis*-bis(acetonitrile) ion exclusively. There is no trans product although a much slower isomerization may be induced in acetonitrile to give an equilibrium mixture consisting of 95% cis and 5% trans at 80°. With anionic unidentate ligands the initial acts of substitution undoubtedly proceed with retention of geometry, but in some cases, we have not found it possible to suppress the catalytic isomerization even under very mild conditions.

All the compounds are subject to catalytic substitution and/or isomerization to a greater or lesser degree. Starting with pure compounds catalysis is more prevalent in concentrated than in dilute solutions, is more likely in reducing solvents such as dimethyl sulfoxide, and can always be induced by prolonged boiling of the solutions. Substitution of the diaquo complex with mildly reducing anions such as Br^-, I^-, N_3^-, NCS^-, and NO_2^- generally leads to partial or complete isomerization. It was only with the NO_2^- substitution that an uncatalyzed reaction could be achieved and only then in very dilute solutions. In the cases of the Br^-, I^-, N_3^-, and NCS^- substitutions, samples of the complexes could be obtained which were at least 90% cis and the rest trans. But attempts to recrystallize these complexes from acetone or acetonitrile led to rapid and apparently spontaneous isomerization. For the *cis*-dibromo compound, we treated the carbonato complex with concentrated hydrobromic acid under mild conditions and obtained the brown *cis*-dibromo isomer nearly pure but attempts at recrystallization again gave the green *trans*-dibromo complex. Ion-exchange chromatography separated the trans and cis isomers of the dibromo complex by elution with $LiClO_4$ in methanol but, without changing the conditions, the brown cis isomer suddenly isomerized to the green trans isomer.

We suppose that, in all cases, the catalyst is a labile Co(II) species which causes the equilibration to the thermodynamically more stable trans complexes *via* an electron-transfer mechanism. The high sensitivity of the mildly reducing anions is undoubtedly related to their ability to reduce the Co(III) complexes during the substitution process. It is also probable that, even if this production of the catalyst could be suppressed during substitution, the cis complexes containing Br^-, I^-, N_3^-, NCS^-, and, to a lesser extent, NO_2^- ligands are intrinsically isomerically unstable in solution because of internal reduction of the cobalt atom and the simultaneous oxidation of the coordinated ligand. All the complexes containing two Br^-, I^-, N_3^-, NCS^-, or NO_2^- ligands are exclusively trans at equilibrium. It is therefore not surprising that previous attempts[2-4] at obtaining cis complexes with reducing ligands were unsuccessful, but these observations do suggest that cis complexes should be stable with ligands which are not easily oxidized. In general this has proved to be the case and, for example, we encountered little difficulty in preparing the *cis*-dichloro and *cis*-dinitrato complexes from the diaquo ion.

2. Resolution and Optical Stability

For the purposes of resolution, the *cis*-dichloro complex seemed to present the most promising starting material and we have developed a large-scale preparative method which involves the reaction between the carbonato complex and hydrochloric acid. The *cis*-$[Co(diars)_2Cl_2]^+$ ion is readily resolved with sodium arsenyltartrate. The optically active *cis*-dichloro complex was converted to the optically active *cis*-$[Co(diars)_2(OH_2)_2]^{3+}$ ion with full retention of optical activity by reaction with mercuric perchlorate in perchloric acid and was readily isolated. The diaquo complex reacts with chloride ions to regenerate the *cis*-dichloro complex with full retention of optical activity.

Using the optically active diaquo ion the *cis*-dinitrato, -dinitro, -carbonato, and -hydroxoaquo complexes have been isolated and these, too, were obtained optically pure because they can be converted to the *cis*-dichloro complex with full retention of activity (Figure 2).

In 0.1 *M* sodium hydroxide solution the diaquo species generates the *cis*-dihydroxo complex which gives a constant visible and circular dichroism spectrum for about 1 hr at 25°. After about 3 hr the circular dichroism changes slightly (~5%), possibly due to dimer formation, but in either case acidification with perchloric acid regenerates the fully active *cis*-diaquo complex. The *cis*-hydroxoaquo complex shows a similar stability; its rotation remains unchanged after 3 hr in water. The *cis*-diaquo is the most remarkable in that its rotation does not change in dilute perchloric acid after 1 month at 25°. There seems little doubt that the aquo groups of this complex are exchanging completely in a matter of hours because all the anation reactions in dilute solutions (10^{-4} *M*) occur in this time and approximately at the same rate. The optical stability of these arsine complexes can be compared with those of the corresponding bis(ethylenediamine) analogs where the racemization half-lives at 25° are as

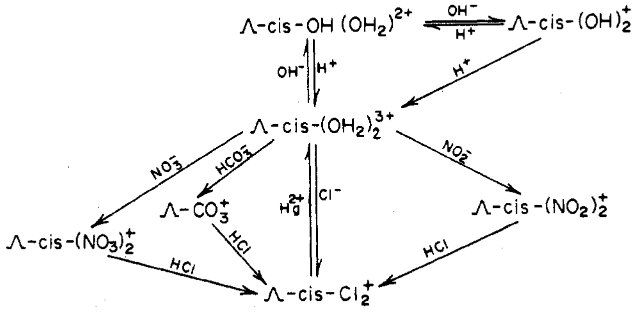


Figure 2. Chemical interconversions involving the optically active diars complexes. All conversions can be carried out with full retention of optical activity.

follows: *cis*-$[Co(en)_2(OH_2)_2]^{3+}$, $t_{1/2}$ = 50 days;[5,6] *cis*-$[Co(en)_2OH(OH_2)]^{2+}$, $t_{1/2}$ = 6.6 min;[7] *cis*-$[Co(en)_2(OH)_2]^+$, $t_{1/2}$ = 20.6 hr.[8] In the absence of catalysis, therefore, these arsine complexes are remarkably inert to stereochemical change.

In dilute solution the active *cis*-diaquo complex reacts rapidly with oxalic acid to give an absorption spectrum identical with that of the characterized racemic oxalato complex and the resultatnt circular dichroism spectrum remains constant for 5 hr. In acetonitrile solution the diaquo complex is rapidly substituted by acetonitrile to give a stable (5 hr) circular dichroism spectrum. However, attempts to isolate the active oxalato and *cis*-bis(acetonitrile) complexes were unsuccessful; only racemic products were obtained. In both these cases, the active species are difficult to isolate and the catalyst is produced during the work-up. We have obtained nearly pure solids of both these but the final purification step led to the production of the much less soluble racemic compounds.

In dilute solutions Br^- and NCS^- substitution proceeds rapidly to produce circular dichroism spectra which probably represent essentially those of the active *cis*-dibromo and *cis*-diisothiocyanto complexes but within 5 min both the spectra fade to zero. It is worth noting, in this respect, that the loss of activity is not smooth and tends to start and stop and start again. Thus for the thiocyanate reaction the circular dichroism sometimes decreases for 5 min, stops at a constant value for 1 hr, and then suddenly decays to zero. This erratic behavior is characteristic of all the catalytic reactions.

Our preparation of the fully active *cis*-dinitro complex is perhaps surprising in view of the possibility of internal reduction. It is not obvious why it should be less prone to reduction than the dibromo and diisothiocyanato complexes. The *cis*-dinitro complex is quite stable in dilute water solution for at least 2 days at room temperature.

All the complexes are less stable in alcohols than in water but this is undoubtedly related to the ability of these solvents to reduce the cobalt(III) complexes to the cobalt(II) state.

3. Kinetics

The rate of isomerization of *cis*-$[Co(diars)_2Cl_2]ClO_4$ to the thermodynamically stable trans complex has been measured in dilute methanol.[9] In view of the high optical stability of these complexes under noncatalytic conditions, it was of interest to compare the rate of loss of optical activity with the isomerization rate.

We have measured the rate of loss of optical activity and the rate of isomerization of *cis*-$[Co(diars)_2Cl_2]ClO_4$ at 2×10^{-4} *M* in dry methanol at 54.9°. These are conditions identical with those used previously[9] and we confirm that the reaction is uncatalyzed for 2 half-lives (227 hr) under these conditions and that the spectrophotometrically determined rate constant for cis → trans isomerization is 1.7×10^{-6} sec^{-1}. The rate of loss of activity was measured by the decay of the circular dichroism spectrum at 473 and 414 mμ; zero isodichroic points were observed throughout the reaction. The rate constant for the loss of activity was found to be 2.2×10^{-6} sec^{-1}. Both rate constants are accurate to ±5%. Thus, the rate constant for loss of optical activity is made up of cis → trans isomerization (80%) and cis racemization (20%). These results are strikingly similar to those observed for *cis*-$[Co(en)_2Cl_2]ClO_4$ in methanol at 35° where the cis → trans isomerization constitutes 70% of the loss of activity rate constant.[10]

4. Stereochemistry

The structures of these complexes are, in principle, easily determined from the nmr methyl proton resonances. Thus, the complexes, *trans*-X_2, *trans*-XY, *cis*-X_2, and *cis*-XY should show, one, two, four, and eight methyl proton resonances respectively based simply on the symmetry of the complexes. Table I lists the observed proton resonances of these complexes and it will be seen that the assignments are unambiguous.

We will report and discuss the circular dichroism spectra of the active complexes elsewhere but we note here that the (+)D-*cis*-$[Co(diars)_2Cl_2]^+$ ion shows a strong exciton couplet at around 200 mμ which is very similar in position and half the intensity[11] of that observed for the tris(catecholato)arsenate(V) ion.[12] If we assume that the exciton couplet arises from coupling between $\pi \rightarrow \pi^*$ transitions of the benzene rings and that the transition moments are directed along the octahedral edges, then the plus (lower energies)-minus (higher energies) couplet observed for the (+)D-dichloro and (+)D-diaquo ions suggests that these complexes have the Λ absolute configuration.[11] It therefore follows from the interconversions shown in Figure 2 that the (+)D-dichloro, (+)D-carbonato, (+)D-diaquo, (+)D-hydroxoaquo, (−)D-dinitro, and (+)D-dinitrato complexes all have the Λ absolute configuration.

Experimental Section

Materials and Analyses. The ligand *o*-phenylenebis(dimethylarsine) was prepared by a recently described new method,[13] using sodium cacodylate trihydrate. Reagent grade *o*-dichlorobenzene was distilled before use. Other chemicals, with the exception of bulk solvents, were reagent grade. Sodium (+)-arsenyltartrate was prepared.[14]

Physical Measurements. Proton magnetic resonance spectra were measured on a Varian T-60 instrument. Visible and ultraviolet absorption spectra were recorded on a Unicam SP-800A spectrophotometer, using 1-cm silica cells. CD spectra were obtained on a Roussel-Jouan Dichrographe II, using 1-, 0.1-, and 0.05-cm silica cells. Rotations were measured on a Perkin-Elmer Model 141 electric polarimeter with a 1-dm cell; the values quoted for the rotations are corrected for the density of the solvent used. Conductivity measurements (on 10^{-3} to 10^{-4} *M* solutions at 20°) were made with a Yellow Springs

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Instrument Co. Model 31 conductivity bridge equipped with a Model 3401 "DIPE" type cell. For the kinetics experiment the optical densities of the sample solutions were measured on a Cary 16 manual spectrophotometer, using 5-cm silica cells. Light was excluded from the reaction vessel.

***trans*-[Co(diars)$_2$Cl$_2$]Cl.** A solution of diarsine (5.7 g) in ethanol (25 ml) was added to a solution of cobaltous acetate tetrahydrate (2.5 g) and glacial acetic acid (1 ml) in water (10 ml) and ethanol (50 ml). Air was bubbled through this solution for 1 min to give a dark brown solution; concentrated hydrochloric acid (5 ml) was then added and aeration continued for another 5 min, as a fine green precipitate formed. The addition of water (75 ml) and slight heating gave a deep green solution which was aerated for a further 0.5 hr. The ethanol was then evaporated off at reduced pressure, and golden green flakes of the trans complex separated from solution. The crystals were filtered from the pale orange aqueous supernatant layer and were washed with 1 *M* HCl solution, a mixture of ethanol and ether (1:10 by volume), and then with ether and were dried in air; yield 6.3 g (85%). This product is sufficiently pure for the subsequent reactions described below but can be recrystallized from a mixture of methanol and dichloromethane by the addition of ether.

***cis*-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O.** *trans*-[Co(diars)$_2$Cl$_2$]Cl (5.0 g) was slurried in hot methanol (15 ml) and lithium carbonate (2.0 g) and water (50 ml) were added. This mixture was heated on a steam bath for 15 min, after which the liquid phase was a clear deep red. The methanol was then removed by rotary evaporation at reduced pressure, *with only very gentle warming* (water bath at 40°). (If any green trans isomer is observed during this operation, it is necessary to reheat the solution to reconvert the *trans*-dichloro complex to the carbonato complex.) The flask was then cooled in an ice bath for a few minutes; the mixture in the flask usually formed a solid mass. Concentrated hydrochloric acid (50 ml) was added quickly, with vigorous stirring to combat the considerable frothing. The mixture was heated for 2–3 min on a steam bath and methanol (15 ml) was added. The mixture was filtered by gravity to remove *trans*-[Co(diars)$_2$Cl$_2$]Cl and the methanol was evaporated, under reduced pressure, from the deep red filtrate. The aqueous residue was left to stand at 5° for 12 hr. The dark red needles of *cis*-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O were filtered off and washed with cold 3 *M* HCl solution, a mixture of acetone and ether (1:5 by volume), and finally ether; yield 3.0 g.

The cis complex prepared in this manner sometimes contains a small amount of *trans*-dichloro impuritiy. This can be removed by the following recrystallization procedure. The complex (3.0 g) was dissolved in hot (90°) 0.2 *N* hydrochloric acid (225 ml). The solution was allowed to cool to 60° before filtering through paper and concentrated hydrochloric acid (75 ml) was added to the filtrate. The solution was filtered through paper again, just as the first dark crystals of cis complex started to form. These two filtrations removed any *trans*-dichloro impurity present. On standing at 5° for 15–20 hr, the dark red solution deposited large lustrous needles of pure *cis*-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O, which were filtered off and washed in the manner described above. *Anal.* Calcd for $C_{20}H_{40.5}As_4Cl_{3.5}CoO_4$: C, 29.0; H, 4.9; Cl, 15.0. Found: C, 29.2; H, 4.6; Cl, 15.3.

***cis*-[Co(diars)$_2$CO$_3$]ClO$_4$·CH$_2$Cl$_2$.** *trans*-[Co(diars)$_2$Cl$_2$]Cl (5.0 g) was suspended in methanol (15 ml); the methanol was brought to the boiling point and lithium carbonate (2.0 g) and water (50 ml) were added. This mixture was heated on a steam bath for 15 min, at which point the liquid phase was a clear deep orange-red. The methanol was then removed by rotary evaporation at reduced pressure at 40°, as described in the *cis*-dichloro preparation. After removal of the methanol, a solution of sodium perchlorate (0.95 g) in water (30 ml) was added, and the orange-red aqueous solution was filtered by gravity to remove residual lithium carbonate and also any *trans*-[Co(diars)$_2$Cl$_2$]ClO$_4$ present. A solution of a further 5.0 g of sodium perchlorate in water (40 ml) was added to the filtrate, which was then extracted repeatedly with dichloromethane. The combined dichloromethane extractions were dried (Na$_2$SO$_4$) and evaporated to dryness. The orange oily residue was redissolved in about 100 ml of dichloromethane by addition of a few drops of methanol. The solution was filtered and ether was slowly added until faint cloudiness developed. Crystallization proceeded rapidly, and after 20 min, the flask was placed in a refrigerator at 5° for 12 hr. The large orange crystals were filtered off and washed with a mixture of dichloromethane and ether (2:1 by volume) and then ether and dried in an oven at 140°; yield 4.7 g. By concentrating the filtrate, a further 0.3 g of the complex was obtained; total yield 5.0 g (84%). The complex can be recrystallized from dichloromethane by the procedure described for the initial crystallization. The presence of 1 mol of loosely held dichloromethane, suggested by microanalysis results, was confirmed by nmr. *Anal.* Calcd for $C_{22}H_{34}As_4Cl_3CoO_7$: C, 30.2; H, 3.9; Cl, 12.2. Found: C, 30.7; H, 4.2; Cl, 11.9. $\Lambda_M = 80.4$ ohm^{-1} mol^{-1} cm^2 (methanol).

***cis*-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$.** Concentrated perchloric acid[15] (8 ml) was cautiously poured over solid *cis*-[Co(diars)$_2$CO$_3$]ClO$_4$·CH$_2$Cl$_2$ (1.6 g) in a large test tube. The carbonato complex reacted, with effervescence, and a very deep red solution resulted. This solution was filtered through a finely sintered glass frit into a small flask and was diluted with an equal volume of water. Crystals started to form almost immediately; better crystals were obtained if the solution was gently heated for about 1 min. The solution was allowed to cool to room temperature and then left to stand for 6 hr at 5°. The beautiful burgundy plates were filtered off and washed quickly with cold 6 *M* perchloric acid, followed immediately by repeated washings with ether. The crystals were dried in air; yield 1.65 g (84%). The complex can be recrystallized, if desired, by dissolving it in warm perchloric acid and then adding an equal volume of warm water. On standing and cooling, the solution deposits large crystals. *Anal.* Calcd for $C_{20}H_{36}As_4Cl_3CoO_{14}$: C, 24.9; H, 3.8; Cl, 11.0. Found: C, 24.7; H, 4.0; Cl, 10.9. Conductivity in water: $\Lambda_M =$ 347 ohm^{-1} mol^{-1} cm^2. This complex can also be prepared in good yield by the method described for the synthesis of the optically active diaquo complex.

***cis*-[Co(diars)$_2$Cl$_2$]ClO$_4$. Method 1.** Cold concentrated hydrochloric acid (10 ml) was added, with swirling, to a chilled flask containing crystals of *cis*-[Co(diars)$_2$CO$_3$]ClO$_4$·CH$_2$Cl$_2$ (1.0 g). Within 5 min, the resultant dark red solution of *cis*-[Co(diars)$_2$Cl$_2$]$^+$ began to deposit crystals. The flask was removed from the ice bath after 5 min, and after a further 15 min, water (20 ml) and perchloric acid (0.5 ml) were added. Fifteen minutes later, the dark reddish brown crystals of *cis*-[Co(diars)$_2$Cl$_2$]ClO$_4$ were filtered off and washed with water, ethanol, and ether; yield 0.8 g.

Method 2. *cis*-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$ (0.5 g) was dissolved in cold water (10 ml). Cold 6 *M* hydrochloric acid (20 ml) was filtered into this solution, which was allowed to warm up to room temperature. The color of the solution darkened slightly, and on standing at 5° overnight, it deposited small reddish brown crystals of *cis*-[Co(diars)$_2$Cl$_2$]ClO$_4$, which were filtered off and washed as described above.

Method 3. *cis*-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O is readily converted to the perchlorate salt by dissolution in water and addition of aqueous sodium perchlorate solution.

The perchlorate salt of the *cis*-dichloro complex is practically insoluble in water and much less soluble in methanol than is the chloride salt. The crude products prepared by methods 1–3 above were recrystallized from a minimum volume of acetonitrile by careful addition of aqueous sodium perchlorate solution until permanent cloudiness developed. On standing at 5° for several hours, the solutions deposited shiny reddish brown plates of *cis*-[Co(diars)$_2$Cl$_2$]ClO$_4$. *Anal.* Calcd for $C_{20}H_{32}As_4Cl_3CoO_4$: C, 30.0; H, 4.0; Cl, 13.3. Found: C, 29.8; H, 4.0; Cl, 13.2. $\Lambda_M = 79.4$ ohm^{-1} mol^{-1} cm^2 (methanol).

***cis*-[Co(diars)$_2$C$_2$O$_4$]B(C$_6$H$_5$)$_4$.** A solution of oxalic acid dihydrate (0.2 g) in water (5 ml) was filtered into a previously filtered solution of *cis*-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$ (0.2 g) in water (10 ml). The mixture was warmed to 50° for 1 min; the color changed from red-orange to a lighter yellow-orange. The solution was then cooled, and sodium tetraphenylborate (0.1 g) in water (5 ml) was filtered into it, with stirring. The desired product separated quantitatively as fine yellow crystals, which were redissolved by the slow addition of acetone (~25 ml). After refiltering this solution, water was slowly added until cloudiness was observed. On standing at room temperature, well-formed yellow crystals began to separate. The total volume of this solution was slowly made up to 200 ml with water, and after 0.5 hr of standing at room temperature, the solution was cooled at 5° for 1 hr. The crystals were filtered, washed with water and then with ether, and dried in air; yield 0.25 g. This product was recrystallized from acetonitrile (12 ml) by the addition of ether (60 ml) and cooling at 5° overnight. The product separated as very long orange needles which were washed with a 1:5 mixture of acetonitrile and ether and then with ether. The crystals were oven dried at 120° for 1 hr; yield 0.2 g. *Anal.* Calcd for $C_{46}H_{52}As_4BCoO_4$: C, 53.2; H, 5.1. Found: C, 53.1; H, 5.0. $\Lambda_M = 46.2$ ohm^{-1} mol^{-1} cm^2 (methanol).

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(15) This procedure can be dangerous. The perchloric acid should be checked for Cl$^-$ ions and the presence of any organic matter. If either are present, it is advisable to use a fresh bottle of perchloric acid.

cis-[Co(diars)$_2$(NO$_3$)$_2$]ClO$_4$. *cis*-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$ (0.2 g) was dissolved in cold 8 *M* nitric acid (5 ml). This solution was filtered, and to it was added concentrated perchloric acid (1 ml). The solution was left to stand in the dark at 5° for several days; well-formed red plates deposited. These crystals were filtered off, washed with water and then ether, and dried in an oven at 100°; yield 0.15 g. If necessary, the product can be recrystallized from nitromethane by the addition of ether. It is also quite soluble in acetonitrile but only slightly soluble in water, acetone, and methanol. *Anal.* Calcd for $C_{20}H_{32}As_4ClCoN_2O_{10}$: C, 28.1; H, 3.8; Cl, 4.2; N, 3.4. Found: C, 28.7; H, 3.8; Cl, 3.8; N, 3.6. $\Lambda_M = 86.2$ ohm^{-1} mol^{-1} cm^2 (nitromethane).

cis-[Co(diars)$_2$(NO$_2$)$_2$]ClO$_4$. A solution of sodium nitrite (0.15 g) in water (20 ml) was added, with stirring, to a filtered solution of *cis*-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$ (0.2 g) in water (180 ml). The orange-red diaquo solution turned darker initially, but after standing in the dark at room temperature for several minutes, the solution was clear yellow. This solution was filtered and it deposited a small quantity of yellow blocks on standing overnight. The remainder of the product was isolated by addition of a concentrated aqueous solution of sodium perchlorate (2 g) and cooling at 5° for 1 hr. The fine yellow needles were filtered and washed with a small amount of cold water and then with ether. The product was oven-dried for 1 hr at 100°; yield 0.15 g. *Anal.* Calcd for $C_{20}H_{32}As_4ClCoN_2O_8$: C, 29.2; H, 3.9; Cl, 4.3; N, 3.4. Found: C, 28.7; H, 4.1; Cl, 4.5; N, 3.6. $\Lambda_M =$ 76.1 ohm^{-1} mol^{-1} cm^2 (methanol).

cis-[Co(diars)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_3$·CH$_3$CN. A solution of *cis*-[Co(diars)$_2$(H$_2$O)$_2$](ClO$_4$)$_3$ (0.3 g) in acetonitrile (25 ml) was heated on a steam bath for 5 min to give a yellow solution. This solution was filtered through a paper which was then washed with acetonitrile (15 ml). Ether (~30 ml) was slowly filtered in until cloudiness was observed and the solution was left to stand at 5°. The small bright yellow crystals were filtered off, washed with a 1:1 mixture of acetonitrile and ether and then with ether, and dried in air. This product was recrystallized from acetonitrile (50 ml) by the addition of ether, as before, and cooling for several hours at 5°. The yellow crystals, which have a slight greenish tinge when larger, were filtered off and washed as before; yield 0.2 g. The presence of 1 mol of uncoordinated acetonitrile, suggested by microanalysis data, is confirmed by nmr. *Anal.* Calcd for $C_{26}H_{41}As_4Cl_3CoN_3O_{12}$: C, 29.6; H, 3.9; N, 4.0; Cl, 10.1. Found: C, 28.9; H, 4.4; N, 3.8; Cl, 10.0. $\Lambda_M = 347$ ohm^{-1} mol^{-1} cm^2 (acetonitrile).

Resolution of the _cis_-[Co(diars)$_2$Cl$_2$]$^+$ Ion. Racemic *cis*-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O (2.0 g) was slurried with methanol (2 ml); water (75 ml) was then added to dissolve all the complex. To this solution, sodium (+)-arsenyltartrate (2.0 g) in water (25 ml) was added dropwise, with efficient stirring. Following this addition, the flask was cooled in an ice bath for about 15 min; crystallization of the less soluble diastereomer was induced by scratching the sides of the flask with a glass rod. The less soluble diastereomer, *cis*-(+)-[Co(diars)$_2$Cl$_2$]AsOC$_4$H$_4$O$_6$, was filtered off and washed with two 10-ml portions of water; the filtrate and these aqueous washings were set aside. The brown granular crystals of the less soluble diastereomer were then washed with a mixture of ethanol and ether (1:5 by volume) and with ether and dried in air; yield 1.05 g. This product can be recrystallized from methanol by addition of ether, but partial decomposition to a green compound (probably the *trans*-dichloro isomer) often occurs. The optically active chloride salt obtained from this diastereomer is more easily recrystallized to obtain optical purity. A small sample of the less soluble diastereomer was recrystallized for microanalysis. *Anal.* Calcd for $C_{24}H_{36}As_5Cl_2CoO_7$: C, 30.6; H, 3.9; Cl, 7.5. Found: C, 30.0; H, 3.8; Cl, 8.0. Rotations (in methanol, $c = 2.53 \times 10^{-4}$ g/ml): $[\alpha]^{34}\mathrm{D}$ 146° ± 5%, $[\alpha]^{34}{}_{546}$ 670° ± 2%.

cis-(+)-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O. *cis*-(+)-[Co(diars)$_2$Cl$_2$]AsOC$_4$H$_4$O$_6$ (1.0 g) was dissolved in a minimum volume of methanol at room temperature and an equal volume of 3 *M* hydrochloric acid was added. The methanol was then gently removed at reduced pressure; the remaining aqueous acid solution was filtered and then left to stand at 5° for 12 hr. Fine crystals of *cis*-(+)-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O separated from the solution and were filtered off. The crystals were washed with cold 3 *N* hydrochloric acid, a mixture of acetone and ether (1:5 by volume), and then ether; yield 0.8 g. This enantiomer was obtained in optically pure form by one recrystallization as described for the chloride salt of the racemic *cis*-dichloro complex. *Anal.* Calcd for $C_{20}H_{40.5}As_4Cl_{3.5}CoO_4$: C, 29.0; H, 4.9; Cl, 15.0. Found: C, 29.2; H, 4.6; Cl, 15.3. Rotations (in methanol, $c = 9.4 \times 10^{-5}$ g/ml): $[\alpha]^{31}\mathrm{D}$ 203° ± 5%, $[\alpha]^{34}{}_{546}$ 887° ± 2%.

cis-(−)-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O. The solution of the more soluble diastereomer, obtained as described above, was evaporated at reduced pressure to remove the methanol present, made up to 3 *N* in chloride ion with concentrated hydrochloric acid, and left to stand at 5° for 12 hr. The resultant crystals of *cis*-(−)-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O were filtered off and washed in the usual manner; yield 0.7 g. The sample was fractionally recrystallized a total of four times by dissolving it in hot 0.1 *N* HCl solution (50–100 ml), filtering, and increasing the chloride ion concentration to 3 *N* with concentrated hydrochloric acid; the first fraction from each successive recrystallization was more optically active until optical purity was attained. Rotations (in methanol, $c = 1.02 \times 10^{-4}$ g/ml): $[\alpha]^{34}\mathrm{D}$ −226° ± 5%, $[\alpha]^{34}{}_{546}$ −880° ± 2%.

cis-(+)-[Co(diars)$_2$Cl$_2$]ClO$_4$. This complex was prepared from the optically pure *cis*-(+)-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O by the procedure described for the conversion of the racemic *cis*-dichloro chloride to the perchlorate salt. Rotations (in methanol, $c = 1.62 \times 10^{-4}$ g/ml): $[\alpha]^{28}\mathrm{D}$ 166° ± 5%, $[\alpha]^{29}{}_{546}$ 741° ± 2%.

cis-(−)-[Co(diars)$_2$Cl$_2$]ClO$_4$. Similarly, the optically pure *cis*-(−)-[Co(diars)$_2$Cl$_2$]Cl·$^1/_2$HCl·4H$_2$O was converted to the perchlorate salt. *Anal.* Calcd for $C_{20}H_{32}As_4Cl_3CoO_4$: C, 30.0; H, 4.0. Found: C, 30.3; H, 4.1. Rotations (in methanol, $c = 1.69 \times 10^{-4}$ g/ml): $[\alpha]^{28}\mathrm{D}$ −150° ± 5%, $[\alpha]^{28}{}_{546}$ −760° × 2%.

cis-(+)-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$. A solution of mercury(II) perchlorate was prepared as follows. Yellow mercuric oxide (21.7 g) was dissolved in a mixture of water (25 ml) and concentrated perchloric acid (25 ml). This solution was filtered twice through a double thickness of paper. Finely ground *cis*-(+)-[Co(diars)$_2$Cl$_2$]ClO$_4$ (1.0 g) in a large test tube was treated with 20 ml of this solution, with stirring and slight heating. A homogeneous solution was not obtained, because the desired diaquo complex began to crystallize from the deep red supernatant solution before all of the *cis*-dichloro complex had reacted. When the crystals appeared homogeneous, the mixture was left to stand at 5° for 1 hr. The wine red crystals were filtered off, washed with cold 6 *M* perchloric acid and then with ether, and dried in air; yield 1.1 g. The product was recrystallized in the manner described for the racemic *cis*-diaquo complex without change in optical activity. *Anal.* Calcd for $C_{20}H_{36}As_4Cl_3CoO_{14}$: C, 24.9; H, 3.8; Cl, 11.0. Found: C, 25.0; H, 3.7; Cl, 11.1. Rotations (in 0.1 *M* HClO$_4$, $c = 1.1 \times 10^{-4}$ g/ml): $[\alpha]^{28}\mathrm{D}$ 115° ± 5%, $[\alpha]^{28}{}_{436}$ 1480° ± 2%.

cis-(−)-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$. Similarly, the *cis*-(−)-diaquo complex can be prepared from *cis*-(−)-[Co(diars)$_2$Cl$_2$]ClO$_4$. Rotations (in 0.1 *M* HClO$_4$, $c = 1.0 \times 10^{-4}$ g/ml): $[\alpha]^{28}\mathrm{D}$ − 106° ± 5%, $[\alpha]^{28}{}_{436}$ −1520° ± 2%.

cis-(+)-[Co(diars)$_2$CO$_3$]ClO$_4$·CH$_3$CN. Sodium bicarbonate (0.15 g) in water (5 ml) was added to a solution of *cis*-(+)-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$ in water (10 ml). The color changed immediately from deep orange-red to yellow-orange. This solution was filtered, and to it was added a filtered solution of sodium perchlorate (2 g) in water (5 ml). The orange solution was extracted with four 15-ml portions of dichloromethane (ACS). The combined extractions were dried (Na$_2$SO$_4$) and evaporated to dryness. The orange residue was redissolved in dichloromethane (11 ml) and methanol (1 ml), the solution was filtered, and enough ether was gradually added to precipitate quantitatively the complex as an oil. The colorless supernatant liquid was decanted, and the oily residue was dissolved in 15 ml of acetonitrile. Ether (30 ml) was added to the filtered solution and it was left to stand at 5°. When crystallization had commenced, a further 15 ml of ether was added and the mixture was left at 5° for 15 hr. The lustrous orange plates were filtered off, washed with a 1:5 mixture of acetonitrile and ether and then with ether, and oven-dried. *Anal.* Calcd for $C_{23}H_{35}As_4CoNO_7$: C, 33.2; H, 4.2. Found: C, 33.3; H, 4.9. Rotations (in methanol, $c = 8.0 \times 10^{-5}$ g/ml): $[\alpha]^{27}\mathrm{D}$ 380° ± 2%, $[\alpha]^{27}{}_{546}$ 950° ± 2%.

cis-(+)-[Co(diars)$_2$(NO$_3$)$_2$]ClO$_4$. The complex was prepared from *cis*-(+)-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$ by the procedure described for the synthesis of the racemic compound. *Anal.* Calcd for $C_{20}H_{32}As_4ClCoN_2O_{10}$: C, 28.1; H, 3.8; Cl, 4.2. Found: C, 28.5, H, 4.0; Cl, 3.8. Rotations (in nitromethane, $c = 1.2 \times 10^{-4}$ g/ml): $[\alpha]^{30}\mathrm{D}$ 85° ± 10%, $[\alpha]^{30}{}_{546}$ 2030° ± 2%.

cis-(−)-[Co(diars)$_2$(NO$_2$)$_2$]ClO$_4$. This complex was prepared from *cis*-(+)-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$ by the procedure described for the synthesis of the racemic *cis*-dinitro complex. *Anal.* Calcd for $C_{20}H_{32}As_4ClCoN_2O_8$: C, 29.2; H, 3.9; N, 3.4. Found: C, 29.7; H, 4.2; N, 3.3. Rotations (in methanol, $c = 9.4 \times 10^{-5}$ g/ml): $[\alpha]^{27}\mathrm{D}$ −92° ± 5%, $[\alpha]^{27}{}_{436}$ 660° ± 2%.

Interconversion Experiments. _cis_-(+)-[Co(diars)$_2$(OH$_2$)$_2$]$^{3+}$ → _cis_-(+)-[Co(diars)$_2$Cl$_2$]$^+$. *cis*-(+)-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$ (0.01 g) was dissolved in HCl (1 *N*; 10 ml) at room temperature. The solution rapidly changed to a deep brown and after 2 days at 25° all the *cis*-(+)-[Co(diars)$_2$Cl$_2$]ClO$_4$ complex had precipitated as fine needles leaving a completely colorless supernatant solution. The crystals were collected and found to be optically pure.

***cis*-(+)-[Co(diars)$_2$CO$_3$]$^+$ → *cis*-(+)-[Co(diars)$_2$Cl$_2$]$^+$.** *cis*-(+)-[Co(diars)$_2$CO$_3$]ClO$_4$ (0.01 g) was dissolved in water (10 ml) and 2 drops of concentrated HCl was added. Carbon dioxide was quickly liberated and the solution turned brown and after 2 days at 25° deposited the *cis*-(+)-[Co(diars)$_2$Cl$_2$]ClO$_4$ salt quantitatively. It was collected and found to be optically pure.

***cis*-(+)-[Co(diars)$_2$OH(OH$_2$)]$^{2+}$ → *cis*-(+)-[Co(diars)$_2$(OH$_2$)$_2$]$^{3+}$.** A 10^{-3} *M* solution of the *cis*-(+)-[Co(diars)$_2$OH(OH$_2$)](ClO$_4$)$_2$ salt was made up in 1.0 *N* HClO$_4$. The circular dichroism spectrum was the same as that of the pure diaquo complex.

***cis*-(−)-[Co(diars)$_2$(NO$_2$)$_2$]$^+$ → *cis*-(+)-[Co(diars)$_2$Cl$_2$]$^+$.** *cis*-(−)-[Co(diars)$_2$(NO$_2$)$_2$]ClO$_4$ (0.009 g) was dissolved in HCl (10 ml; 5 M) containing a few crystals of urea. The solution slowly turned brown and after it stood at room temperature for 20 hr, 2 drops of concentrated HClO$_4$ was added. After a further 2 days the crystals of the *cis*-dichloro complex were filtered from the colorless supernatant solution. The product was optically pure.

***cis*-(+)-[Co(diars)$_2$(NO$_3$)$_2$]$^+$ → *cis*-(+)-[Co(diars)$_2$Cl$_2$]$^+$.** Exactly the same procedure was used for interconverting the dinitrato complex as that described for the dinitro complex except that urea was not added. The product was optically pure.

***cis*-(+)-[Co(diars)$_2$(OH$_2$)$_2$]$^{3+}$ → *cis*-[Co(diars)$_2$(OH)$_2$]$^+$.** When the diaquo complex is dissolved in 0.1 *M* NaOH solution, a constant absorption and circular dichroism spectrum is obtained of the pink dihydroxo complex. Addition of HClO$_4$ regenerates the diaquo species with full retention of activity.

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Registry No. *trans*-[Co(diars)$_2$Cl$_2$]Cl, 14170-33-3; *cis*-[Co(diars)$_2$Cl$_2$]Cl, 50804-93-8; *cis*-[Co(diars)$_2$CO$_3$]ClO$_4$, 51017-98-2; *cis*-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$, 50804-95-0; *cis*-[Co(diars)$_2$Cl$_2$]ClO$_4$, 14170-34-4; H$_2$C$_2$O$_4$, 144-62-7; *cis*-[Co(diars)$_2$C$_2$O$_4$]B(C$_6$H$_5$)$_4$, 51017-99-3; *cis*-[Co(diars)$_2$(NO$_3$)$_2$]ClO$_4$, 50804-97-2; *cis*-[Co(diars)$_2$(NO$_2$)$_2$]ClO$_4$, 51014-57-4; CH$_3$CN, 75-05-8; *cis*-[Co(diars)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_3$, 50804-99-4; *cis*-(+)-[Co(diars)$_2$Cl$_2$]AsOC$_4$H$_4$O$_6$, 51050-98-7; *cis*-(+)-[Co(diars)$_2$Cl$_2$]Cl, 51050-99-8; *cis*-(−)-[Co(diars)$_2$Cl$_2$]Cl, 51051-00-4; *cis*-(+)-[Co(diars)$_2$Cl$_2$]ClO$_4$, 51051-01-5; *cis*-(−)-[Co(diars)$_2$Cl$_2$]ClO$_4$, 50805-01-1; *cis*-(+)-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$, 51018-01-0; *cis*-(−)-[Co(diars)$_2$(OH$_2$)$_2$](ClO$_4$)$_3$, 51020-04-3; *cis*-(+)-[Co(diars)$_2$CO$_3$]ClO$_4$, 51018-03-2; *cis*-(+)-[Co(diars)$_2$(NO$_3$)$_2$]ClO$_4$, 51063-05-9; *cis*-(−)-[Co(diars)$_2$(NO$_2$)$_2$]ClO$_4$, 50805-03-3; *cis*-[Co(diars)$_2$(OH)(CH$_3$CN)](ClO$_4$)$_2$, 50805-05-5.

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Small Cobalt and Nickel Metallocarboranes from 2,3-$C_2B_4H_8$ and 1,6-$C_2B_4H_6$. Sandwich Complexes of the Cyclic $C_2B_3H_7^{2-}$ and $C_2B_3H_5^{4-}$ Ligands

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The reaction of Na$^+$C$_2$B$_4$H$_7^-$ with CoCl$_2$ and NaC$_5$H$_5$ followed by exposure to air, water, and acetone gives (π-2,3-C$_2$B$_4$H$_6$)Co(π-C$_5$H$_5$), (π-2,3-C$_2$B$_3$H$_7$)Co(π-C$_5$H$_5$), and (π-2,3-C$_2$B$_3$H$_5$)Co$_2$(π-C$_5$H$_5$)$_2$. *C*-Methyl and *C,C'*-dimethyl derivatives are obtained by analogous reactions of Na$^+$CH$_3$C$_2$B$_4$H$_6^-$ and Na$^+$(CH$_3$)$_2$C$_2$B$_4$H$_5^-$. Work-up of the parent metallocarborane products in 1 *M* HCl increases the yield of the four-boron species. Bridge deprotonation of (π-2,3-C$_2$B$_3$H$_7$)Co(π-C$_5$H$_5$) by NaH gives the (C$_2$B$_3$H$_6$)Co(C$_5$H$_5$)$^-$ anion, which on reaction with CoCl$_2$ and NaC$_5$H$_5$ yields (π-2,3-C$_2$B$_3$H$_5$)Co$_2$(π-C$_5$H$_5$)$_2$; treatment of the anion with HCl regenerates (C$_2$B$_3$H$_7$)Co(C$_5$H$_5$). Reduction of 1,6-C$_2$B$_4$H$_6$ with sodium naphthalide followed by reaction with CoCl$_2$, NaC$_5$H$_5$, air, and water gives (π-2,4-C$_2$B$_3$H$_5$)Co$_2$(π-C$_5$H$_5$)$_2$, (π-C$_2$B$_4$H$_6$)Co$_2$(π-C$_5$H$_5$)$_2$, and [σ-5-(1-C$_{10}$H$_7$)(π-2,4-C$_2$B$_4$H$_5$)]Co(π-C$_5$H$_5$), but only a trace of (π-2,4-C$_2$B$_4$H$_6$)Co(π-C$_5$H$_5$). The yield of the latter compound is improved by shorter reaction time. A similar reaction employing 2,3-C$_2$B$_4$H$_8$ in place of 1,6-C$_2$B$_4$H$_6$ gives the same products as in the reaction of Na$^+$C$_2$B$_4$H$_7^-$ described above, except that only a trace of (π-2,3-C$_2$B$_4$H$_6$)Co(π-C$_5$H$_5$) is obtained. The reaction of 2,4-C$_2$B$_5$H$_7$ with sodium naphthalide and CoCl$_2$ gives a probable (π-2,4-C$_2$B$_4$H$_6$)$_2$Co$^-$ anion which was isolated as the tetramethylammonium salt. Reaction of Na$^+$C$_2$B$_4$H$_7^-$ with bis(diphenylphosphino)ethanenickel(II) chloride gives (π-2,3-C$_2$B$_4$H$_6$)Ni[(C$_6$H$_5$)$_2$PCH$_2$]$_2$. Reaction of Na$^+$C$_2$B$_4$H$_7^-$ with NiBr$_2$, NaC$_5$H$_5$, HCl, and air yields (π-C$_2$B$_5$H$_7$)Ni$_2$(π-C$_5$H$_5$)$_2$ which is postulated to have an opened or distorted tricapped trigonal-prismatic structure.

Introduction

Previous work has shown that a variety of small cobalt[1,2] and iron[3-6] metallocarboranes can be synthesized from the lower carboranes *nido*-2,3-$C_2B_4H_8$ and *closo*-$C_2B_5H_7$, and a manganese[7] species has been obtained from *nido*-$CH_3C_3B_3H_6$. Several of these syntheses[1,5] utilized methods previously applied to the large carboranes, particularly the opening of a polyhedral cage by electron transfer with subsequent metal insertion (polyhedral expansion) as developed extensively by Hawthorne and coworkers.[8-10] In other cases, metallocarboranes have been obtained from the small carboranes by new preparative routes such as the gas-phase incorporation of metals into closo[5,6] and nido[3,5,7,11,12] cages. Our interest in further exploration of the small metallocarboranes has been stimulated by the discovery of the cyclocarboranyl sandwich complexes,[2,3,5] which contain cyclic planar boron-carbon ligands analogous to the cyclopentadienyl system. The prototype compound, (π-$C_2B_3H_7$)Fe(CO)$_3$, was pre-

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