

Contribution from the Department of Physical and Inorganic Chemistry,  
The University of Adelaide, Adelaide 5001, Australia

## Homogeneous and Charcoal-Catalyzed Isomerizations of the (Diethylenetriamine)(methyldiethylenetriamine)cobalt(III) and Bis(diethylenetriamine)cobalt(III) Ions

GRAEME H. SEARLE,\* F. RICHARD KEENE, and STEPHEN F. LINCOLN

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Each of the *s-fac* and *u-fac* isomers of  $[\text{Co}(\text{dien})(\text{medien})](\text{ClO}_4)_3$  isomerizes in homogeneous aqueous solution to the same equilibrium mixture of the three geometric isomers, with no other products detectable. Proportions after 2 days at 90 °C were *s-fac:u-fac:mer* = 81:10:9. This reaction is the basis for obtaining on a preparative scale the new *u-fac* and *mer* isomers which have been characterized by  $^{13}\text{C}$  NMR spectra. Over catalytic charcoal disproportionation occurs to a mixture of seven complexes which can be mostly separated on SP-Sephadex C-25 cation-exchange resin. Equilibrium molar proportions after 4 h at 80 °C were  $\text{Co}(\text{dien})_2^{3+}$  *s-fac:u-fac:mer*: $\text{Co}(\text{dien})(\text{medien})^{3+}$  *s-fac:u-fac*: $\text{Co}(\text{medien})_2^{3+}$  *s-fac* = 5:~23:19 [which includes a little nonseparable *mer*- $\text{Co}(\text{dien})(\text{medien})^{3+}$ ]:~23:4:26. The charcoal reactions must involve complete dissociations of ligands, and by comparison the homogeneous reactions must involve intramolecular processes. In the homogeneous isomerizations at least two rearrangement processes must be involved, and probably three rearrangements occur. Similar experimental results have been obtained for the catalyzed and uncatalyzed reactions of the three isomers of  $\text{Co}(\text{dien})_2^{3+}$ . All the homogeneous reactions are base-catalyzed and probably involve conjugate-base intermediates (deprotonated at the secondary amine nitrogens of coordinated dien). All the experimental data for the homogeneous reactions are most satisfactorily accommodated by the proposal of transient five-coordinated intermediates, formed by bond rupture, rearranging. The possibility of twisting mechanisms occurring through trigonal-prismatic transition states is also considered. Racemizations of  $\text{Co}(\text{en})_3^{3+}$  under both charcoal-catalyzed and homogeneous conditions are also base catalyzed.

### Introduction

Intramolecular rearrangements in octahedral complexes,<sup>1</sup> manifested as isomerization or racemization processes, can occur by two major pathways: nondissociative, involving the twisting of one octahedral face relative to the opposite face about a  $C_3$  (or a pseudo- or imaginary- $C_3$ ) axis via an idealized trigonal-prismatic transition state, and bond rupture via idealized trigonal-bipyramidal or square-pyramidal transition states. In rearrangement reactions where the processes have been established to be intramolecular, the choice between the nondissociative and bond-rupture alternatives has seldom been unambiguous, particularly for complexes of bidentate ligands on which almost all of these studies have been made.<sup>1-3a</sup>

Since the initial proposals of twist mechanisms<sup>4-7</sup> there have been considerable efforts to establish experimentally their existence, and the work has been reviewed.<sup>1,2,8</sup> Only recently have twist mechanisms for isomerization and racemization processes in some octahedral complexes been definitely demonstrated and several approaches have been used.

Conventional kinetic approaches involving exchange and competition rate measurements do not in general provide sufficient data to distinguish the two intramolecular alternatives. However, the complexes *cis*- and *trans*-tetracarbonyl(methoxymethylcarbene)(trialkylphosphine)chromium(0),  $(\text{CO})_4\text{Cr}[\text{C}(\text{OCH}_3)\text{CH}_3](\text{PR}_3)$ ,  $\text{R} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_{11}$ , provide an interesting instance where the *cis*-*trans* isomerization was assigned as a twist process.<sup>9</sup> For these complexes, with exclusively monodentate ligands, all possible dissociative processes were eliminated by the kinetic data leaving an intramolecular process, that is, a twist in this particular instance, as the only plausible mechanism.

Dynamic  $^1\text{H}$  NMR spectroscopy<sup>2</sup> has been employed to establish twist mechanisms for the dynamic inversions  $\Delta \rightleftharpoons \Lambda$  of some tris(tropolonato) complexes of cobalt(III) and aluminium by Holm and co-workers<sup>10,11</sup> and of some tris(dithiocarbamate) complexes of iron(III) and ruthenium(III) by Pignolet and co-workers.<sup>12,13</sup> Lawrence and Stranks<sup>14</sup> have recently demonstrated that volumes of activation, obtained from rate-pressure measurements, may provide a general criterion to distinguish the bond-rupture and twist mechanisms with some stereochemically rigid complexes. By this means

the racemizations of  $\text{Cr}(\text{phen})_3^{3+}$ ,  $\text{Cr}(\text{bpy})_3^{3+}$ ,  $\text{Cr}(\text{ox})(\text{phen})_2^+$ , and  $\text{Cr}(\text{ox})(\text{bpy})_2^+$ <sup>15</sup> were shown to proceed by twist mechanisms, whereas  $\text{Cr}(\text{ox})_3^{3-}$ ,  $\text{Cr}(\text{ox})_2(\text{phen})^-$ , and  $\text{Cr}(\text{ox})_2(\text{bpy})^-$  involved bond ruptures. These methods have limitations. The dynamic  $^1\text{H}$  NMR method is restricted to stereochemically nonrigid complexes, and diastereotopic substituent groups on the chelate ligands are required as probes to detect the changes in chirality around the metal centers. The activation volume approach may not be easily applicable to complexes of primary and secondary amines where there is the possibility of deprotonation followed by rearrangement of a deprotonated species. Thus the generality of twist mechanisms is still unknown.

It was hoped that the use of complexes of multidentate ligands in mechanistic studies of intramolecular rearrangements might offer more opportunity of distinguishing between the bond-rupture and twist alternatives, since the coupled chelate rings restrict the number of different possible interconversions and because such molecules possess more distinguishable points of reference by which to trace the paths of specific rearrangements. We now describe experiments on the isomerizations of the geometric isomers of  $[\text{Co}(\text{dien})(\text{medien})](\text{ClO}_4)_3$ .<sup>15</sup> These hexamine-type complexes are useful for such mechanistic studies because the isomerizations are relatively uncomplicated by competing hydrolysis reactions and because they are closely related to other complexes like  $\text{Co}(\text{en})_3^{3+}$  for which racemization mechanisms are still unclear. Although the experiments demonstrate that the isomerizations in homogeneous solution proceed by intramolecular mechanisms, the bond-rupture and twist possibilities are not readily distinguished. However, the bond-rupture route is supported by observations on some similar systems.

### Results

**Identification of the Three  $\text{Co}(\text{dien})(\text{medien})^{3+}$  Isomers by  $^{13}\text{C}$  NMR Spectroscopy.** The complexes  $\text{Co}(\text{dien})(\text{medien})^{3+}$ ,  $\text{Co}(\text{dien})_2^{3+}$ , and  $\text{Co}(\text{medien})_2^{3+}$  can each exist in three possible geometric isomers as shown in Figure 1. In two of these geometric forms the two secondary or tertiary amine groups are disposed *trans* to each other, but in the *u-fac* isomer these groups are in *cis* positions.

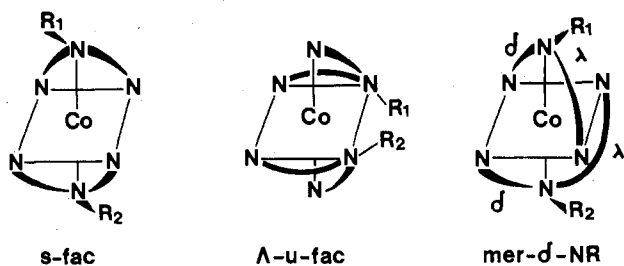


Figure 1. Possible geometric isomers of  $\text{Co}(\text{dien})_2^{3+}$  ( $R_1 = R_2 = \text{H}$ ),  $\text{Co}(\text{medien})_2^{3+}$  ( $R_1 = R_2 = \text{Me}$ ), and  $\text{Co}(\text{dien})(\text{medien})^{3+}$  ( $R_1 = \text{H}$ ,  $R_2 = \text{Me}$ ). One optical isomer is shown for each of the *u-fac* and *mer* forms.

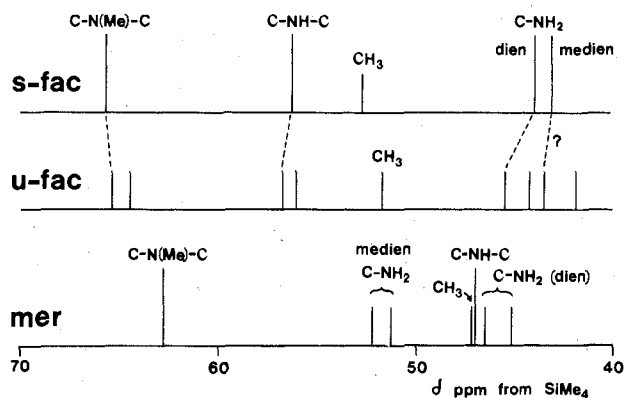


Figure 2.  $^{13}\text{C}$  NMR spectra in  $\text{D}_2\text{O}$  of the geometric isomers of  $[\text{Co}(\text{dien})(\text{medien})](\text{ClO}_4)_3$ .

The compounds *s-fac*- $[\text{Co}(\text{dien})(\text{medien})]^{3+}$  and *s-fac*- $[\text{Co}(\text{medien})_2]^{3+}$  are the major products from the reaction of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  with dien and medien, and their geometric configurations were assigned previously from comparisons of their  $^{13}\text{C}$  NMR spectra with the spectra of the three isomers of  $\text{Co}(\text{dien})_2^{3+}$ .<sup>16</sup>

The *u-fac* and *mer* isomers of  $\text{Co}(\text{dien})(\text{medien})^{3+}$  are formed by isomerization of *s-fac*- $[\text{Co}(\text{dien})(\text{medien})](\text{ClO}_4)_3$  in aqueous solution as described below, and their identities follow from their  $^{13}\text{C}$  NMR spectra (Figure 2). In each of these two isomers the nine carbon atoms are, in principle, in stereochemically different environments (each isomer has symmetry  $C_1$ ). However, the two methylene carbons adjacent to the secondary amine nitrogen of dien in *mer*- $[\text{Co}(\text{dien})(\text{medien})]^{3+}$  are evidently in closely similar environments since they give a single resonance peak ( $\delta$  47.0 ppm from  $\text{SiMe}_4$ ) just as for *mer*- $[\text{Co}(\text{dien})_2]^{3+}$ . Similarly, the two methylene carbons adjacent to the tertiary amine group of *meridionally* coordinated medien give a single peak ( $\delta$  62.8). Thus the four methylene carbons in each ligand in a *mer* complex give a characteristic 2:1:1 peak pattern. There are no equivalences for *u-fac* isomers, so that the *u-fac*- $[\text{Co}(\text{dien})(\text{medien})]^{3+}$  isomer must be that which gives the nine peaks, all of similar magnitude (Figure 2).

**Reactions of *s-fac*- and *u-fac*- $\text{Co}(\text{dien})(\text{medien})^{3+}$  in Homogeneous Aqueous Solution.** When *s-fac*- $[\text{Co}(\text{dien})(\text{medien})](\text{ClO}_4)_3$  was heated in water at  $90^\circ\text{C}$ , and the resulting solution was separated chromatographically on a column of SP-Sephadex cation-exchange resin, three bands of the geometric isomers of  $\text{Co}(\text{dien})(\text{medien})^{3+}$  separated as the only products (Figure 3A). The rates of formation of the two new minor isomers *u-fac* and *mer* seemed to be variable in different runs in water (pH  $\sim$  5–5.5). We therefore carried out two parallel reactions of the *s-fac* isomer, one in 0.01 M perchloric acid and one in sodium hydroxide solution adjusted to pH 10.5. After 2 days at  $90^\circ\text{C}$ , chromatography of the solutions showed that the *s-fac* had remained completely unchanged in the

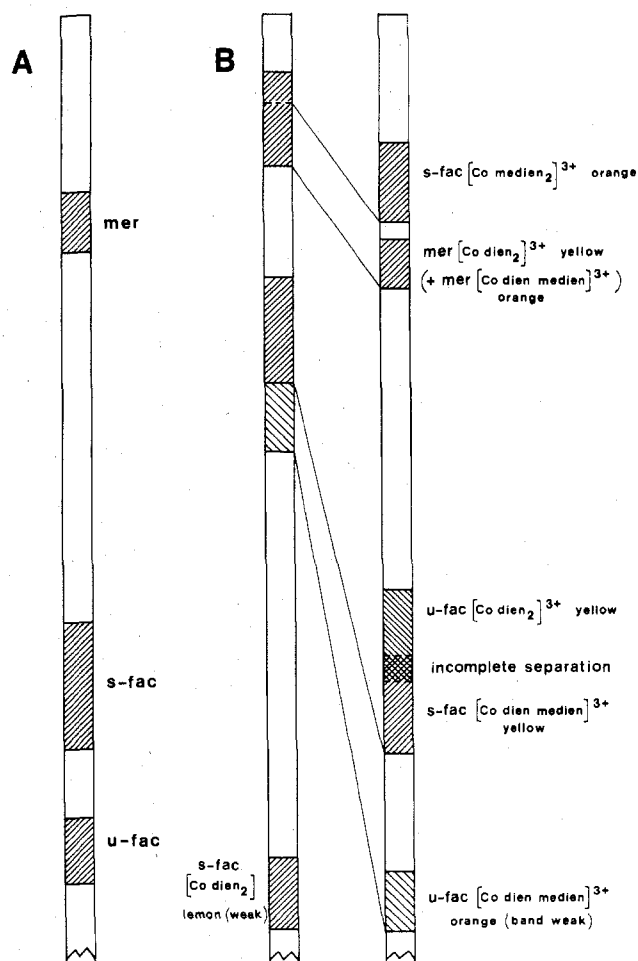


Figure 3. Chromatographic separations on Sephadex columns ( $\text{Na}_3\text{PO}_4$  eluent): (A) equilibrium mixture of  $\text{Co}(\text{dien})(\text{medien})^{3+}$  isomers, from *s-fac*- $[\text{Co}(\text{dien})(\text{medien})](\text{ClO}_4)_3$  in aqueous buffer, pH  $\sim$  8; (B) products from *s-fac*- $[\text{Co}(\text{dien})(\text{medien})](\text{ClO}_4)_3$  on charcoal in water.

perchloric acid but had substantially isomerized in the sodium hydroxide solution (pH now 7.5), so that it was clear that the isomerization reactions were inhibited by acid and were apparently base catalyzed. The reactions were subsequently carried out in a buffer solution, 0.05 M 2,4,6-trimethylpyridine-perchloric acid adjusted to pH 8.0 at  $25^\circ\text{C}$ , although the actual pH at the elevated reaction temperatures would be substantially less than this, probably around 7.

Separate solutions of *s-fac*- and *u-fac*- $[\text{Co}(\text{dien})(\text{medien})](\text{ClO}_4)_3$  in the buffer solution were allowed to react at  $90^\circ\text{C}$ . Samples from the two solutions at this temperature gave apparently similar proportions of the three constituent isomers after 2 days so that each mixture had essentially reached equilibrium by this time. At 3 days, analysis of the proportions gave identical results from the two solutions of starting *s-fac* and *u-fac*. These equilibrium proportions of  $\text{Co}(\text{dien})(\text{medien})^{3+}$  were *s-fac*:*u-fac*:*mer* =  $(81 \pm 2)$ : $(10 \pm 1)$ : $(9 \pm 1)$  at  $90^\circ\text{C}$ .

Chromatography of a solution of *u-fac*- $[\text{Co}(\text{dien})(\text{medien})](\text{ClO}_4)_3$  in 0.01 M perchloric acid, which had reacted for 2.5 days at  $90^\circ\text{C}$ , showed that some isomerization to *s-fac* had occurred (*s-fac*:*u-fac*  $\sim$  1:10 by visual estimate), but *mer* was not detectable. The formation of both of the other isomers from *u-fac* was clearly acid retarded.

The isomerization of the more stable *s-fac* isomer under the above conditions provides the most convenient means of obtaining the *u-fac* and *mer* isomers. Not only are the yields better than from other reactions we have studied (the dis-

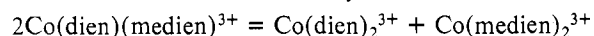
proportionation of *s-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> on charcoal as described below, and [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> + dien + medien) but these other reactions produce the Co(dien)<sub>2</sub><sup>3+</sup> isomers also and it is almost impossible to separate *mer*-[Co(dien)(medien)]<sup>3+</sup> from *mer*-[Co(dien)<sub>2</sub>]<sup>3+</sup> and difficult to separate *s-fac*-[Co(dien)(medien)]<sup>3+</sup> from *u-fac*-[Co(dien)<sub>2</sub>]<sup>3+</sup> by chromatography on Sephadex.<sup>17</sup>

**Reactions of *s-fac*- and *u-fac*-[Co(dien)(medien)]<sup>3+</sup> over Charcoal.** In water with catalytic charcoal, *s-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> gave a mixture of seven complexes which were separated chromatographically into six bands on SP-Sephadex cation-exchange resin using Na<sub>3</sub>PO<sub>4</sub> eluent (Figure 3B). The reaction was studied at 80 °C because some information on the equilibrium proportions of the three Co(dien)<sub>2</sub><sup>3+</sup> isomers is available for that temperature.<sup>18</sup> Equilibrium was established within 4 h. The identities of the six yellow or orange complexes were established from their relative orders of separation on Sephadex with Na<sub>3</sub>PO<sub>4</sub>, compared with those of the authentic complexes determined separately<sup>17</sup> and which have been characterized by <sup>13</sup>C NMR spectroscopy.<sup>16</sup>

The molar proportions of these six products were determined (atomic absorption) to be as follows: *s-fac*-[Co(dien)<sub>2</sub>]<sup>3+</sup>:*u-fac*-[Co(dien)<sub>2</sub>]<sup>3+</sup>:*mer*-[Co(dien)<sub>2</sub>]<sup>3+</sup> (+*mer*-[Co(dien)(medien)]<sup>3+</sup>):*s-fac*-[Co(dien)(medien)]<sup>3+</sup>:*u-fac*-[Co(dien)(medien)]<sup>3+</sup>:*s-fac*-[Co(medien)<sub>2</sub>]<sup>3+</sup> = 5:~23:19:~23:4:26. Clearly *s-fac*-[Co(dien)(medien)]<sup>3+</sup> had undergone disproportionation (in the ligand sense) so that the above proportions should represent the relative stabilities of the various species corresponding to equimolar amounts of the two ligands. Some orange *mer*-[Co(dien)(medien)]<sup>3+</sup> was undoubtedly formed, but this complex chromatographs with yellow *mer*-[Co(dien)<sub>2</sub>]<sup>3+</sup> in a single band<sup>17</sup> so that the proportions of these two species could not be directly assessed. However from the yellow color of this band and the proportion arguments below, we believe that the proportion of *mer*-[Co(dien)(medien)]<sup>3+</sup> was small (<4% of the total products).

The above proportions of the Co(dien)<sub>2</sub><sup>3+</sup> isomers (5:~23:~19 for perchlorates) are in accord with the previously measured equilibrium proportions at the same temperature, *s-fac*:*u-fac*:*mer* = 6:19:22 (for chlorides).<sup>18</sup> There is also reasonable agreement between the above proportions of the Co(dien)(medien)<sup>3+</sup> isomers, *s-fac*:*u-fac*:*mer* = ~23:4:small, and the equilibrium proportions of these isomers as determined for homogeneous solution (81:10:9, although these were at 90 °C). Of the three possible Co(medien)<sub>2</sub><sup>3+</sup> isomers, there has been no evidence for the formation of the *u-fac* and *mer* isomers in detectable quantities from several reactions studied.<sup>19</sup>

From the reaction stoichiometry



the molar amounts of Co(dien)<sub>2</sub><sup>3+</sup> (three isomers) and Co(medien)<sub>2</sub><sup>3+</sup> were expected to be equal, but their proportion as measured above, ~47:26, shows a deficiency of medien. This proportion is only approximate because *s-fac*-[Co(dien)(medien)]<sup>3+</sup> and *u-fac*-[Co(dien)<sub>2</sub>]<sup>3+</sup> were incompletely separated in the chromatography (Figure 3B) and were estimated visually to be in similar amounts and because any *mer*-[Co(dien)(medien)]<sup>3+</sup> formed is included in the *mer*-[Co(dien)<sub>2</sub>]<sup>3+</sup> figure. Nevertheless to give a 1:1 ratio of dien:medien over the total chromatographed products, proportions of *s-fac*-[Co(dien)(medien)]<sup>3+</sup> and *mer*-[Co(dien)(medien)]<sup>3+</sup> in the respective incompletely separated bands would be required which would be too high to satisfy simultaneously the following three requirements: (1) the experimental observations (albeit approximate) of the compositions of these two bands; (2) the equilibrium proportions of the three Co(dien)<sub>2</sub><sup>3+</sup> isomers as determined separately (though

for chlorides); (3) the equilibrium proportions of the three Co(dien)(medien)<sup>3+</sup> isomers as determined separately (though at 90 °C). Further, it is improbable that any significant amounts of *u-fac* and *mer* Co(medien)<sub>2</sub><sup>3+</sup> have escaped detection. It seems clear therefore that the amount of Co(medien)<sub>2</sub><sup>3+</sup> formed is less than stoichiometric. This probably reflects the lower stability of the coordination between cobalt(III) and medien than between cobalt(III) and dien. This may be viewed alternatively as a greater propensity toward decomposition by Co(medien)<sub>2</sub><sup>3+</sup>, probably to cobalt(II) (with charcoal, water, or OH<sup>-</sup> as possible reductants) and free ligand, than by the Co(dien)<sub>2</sub><sup>3+</sup>. A significant amount of cobalt(II) was present (thiocyanate test) in the solution at 48 h despite an oxygen atmosphere being maintained above the solution. Some demethylation of *s-fac*-[Co(medien)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> to *s-fac*-[Co(dien)(medien)]<sup>3+</sup> on the charcoal, as observed in separate experiments,<sup>19</sup> would also raise the dien:medien ratio.

The *u-fac* isomer of [Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> disproportionated on charcoal to give the same products in similar proportions as from the *s-fac* isomer above. In this instance the extent of isomerization *u-fac* → *s-fac*-[Co(dien)(medien)]<sup>3+</sup> was considerable, and again the amount of the *mer* isomer formed was probably small.

## Discussion

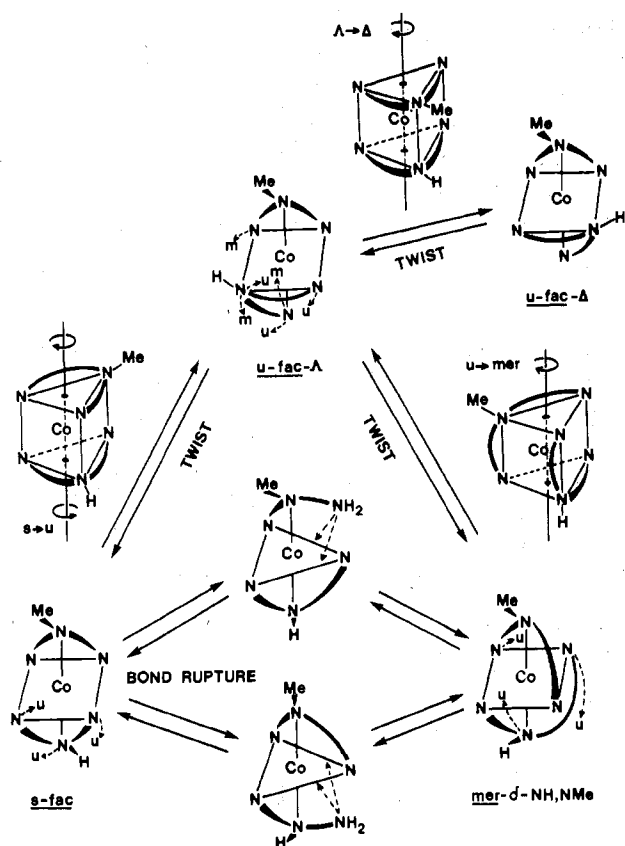
**Isomerization Reactions of Co(dien)(medien)<sup>3+</sup> in Homogeneous Aqueous Solution.** In aqueous solution without charcoal, isomerization of both *s-fac*- and *u-fac*-Co(dien)(medien)<sup>3+</sup> occurred slowly to give the same mixture of the three Co(dien)(medien)<sup>3+</sup> isomers, *s-fac*:*u-fac*:*mer* = 81:10:9. That no other products were observed under these conditions implies that the reactions could not have involved ligand dissociation, since this should lead to disproportionation as in the charcoal reaction. Certainly any *s-fac*-[Co(medien)<sub>2</sub>]<sup>3+</sup> would be readily detectable in the chromatographic separations (Figure 3B). Thus the isomerizations must involve entirely intramolecular pathways.

Figure 4 proposes reaction pathways between each pair of isomers. Since all three isomers are involved in the isomerizations, at least two of these three rearrangement pathways must occur, and the experimental observations give no reason to exclude any of the three interconversions between isomer pairs.

The reaction directly linking *s-fac* and *mer* involves no gross rearrangement (the secondary and tertiary amine nitrogens remain trans), and a bond rupture (one-ended dissociation) proceeding through a trigonal-bipyramidal intermediate as sketched in Figure 4 is the simplest possible process for this conversion.

In the *u-fac* isomer the secondary and tertiary amine nitrogens are cis. Thus any change from *u-fac* to either of the other two isomers involves changing the relative positions of these nitrogens from cis to trans so that gross rearrangements are necessary. Two possibilities for these rearrangements can be envisaged: (1) intramolecular twists proceeding through trigonal-prismatic transition states and (2) bond ruptures to five-coordinate intermediates followed by rearrangement within each intermediate and subsequent recoordination of the -NH<sub>2</sub> group. This latter sequence is similar to the "twist-with-rupture" mechanism as described by Eaton and co-workers.<sup>10</sup>

Figure 4 shows the two twist processes proceeding through different trigonal-prismatic transition states which can account for the interconversions from *u-fac*. These two twists differ in that one, for *u-fac* ⇌ *s-fac*, is envisaged as a trigonal twisting of one coordinated ligand relative to the other ligand by 120° around an axis (imaginary C<sub>3</sub>) through the centers of the faces of the octahedron containing each of the ligands as in Figure 4. The other twist, for *u-fac* ⇌ *mer*, involves the



**Figure 4.** Possible intramolecular twist (and bond-rupture) pathways for interconversions of  $\text{Co}(\text{dien})(\text{medien})^{3+}$  isomers. The particular enantiomers shown of the two possible geometrically different trigonal-bipyramidal intermediates linking *s-fac* and *mer* are those corresponding to the *mer- $\delta$*  optical isomer only. The trigonal-prismatic transition state for racemization of the *u-fac* is symmetrical (plane). The enantiomers shown of the other two trigonal prisms correspond to the particular optical isomers drawn for *u-fac* ( $\Delta$ ) and *mer* ( $\delta$ -NH, NMe). The small dashed arrows indicate movements of donor atoms around octahedron faces by trigonal twisting to give products designated as *s* (*s-fac*), *u* (*u-fac*), and *m* (*mer*).

trigonal twisting by  $120^\circ$  around an octahedral face of two donor nitrogen atoms of one ligand (one primary amine, one secondary or tertiary amine) and one nitrogen (primary amine) of the other ligand. Both of the trigonal-prismatic transition states are dissymmetric, so that the *u-fac*  $\rightleftharpoons$  *mer* change should be stereospecific as indicated in Figure 4. It is conceivable that in any reactions of cobalt(III), particularly those conducted at higher temperatures and in basic conditions as in the present instance, some cobalt(II) species could be formed.<sup>20-22</sup> Cobalt(II) was not detectable in the product solutions by the thiocyanate test, so that the concentration of any cobalt(II) must have been small ( $<10$  ppm). Formation of any cobalt(II) would appear to provide a mechanism for the observed rearrangements by slow electron transfer between a cobalt(III) complex and labile cobalt(II),<sup>23</sup> but this mechanism should lead to some concomitant disproportionation, albeit at a slow rate if the cobalt(II) concentration was extremely small, and this was not observed. Such an electron-transfer mechanism for the equilibrations can thus be discarded, but this does not eliminate the possibility that the rearrangement processes (twist or bond rupture) might occur via transient labile  $\text{Co}(\text{dien})(\text{medien})^{2+}$  intermediates. However to be consistent with the experimental observations, this mechanistic route would require that the rate of dissociation of the ligands from the transient  $\text{Co}(\text{dien})(\text{medien})^{2+}$  be relatively slow compared with the rates of both the rearrangement and the electron-transfer acts. The electron transfer

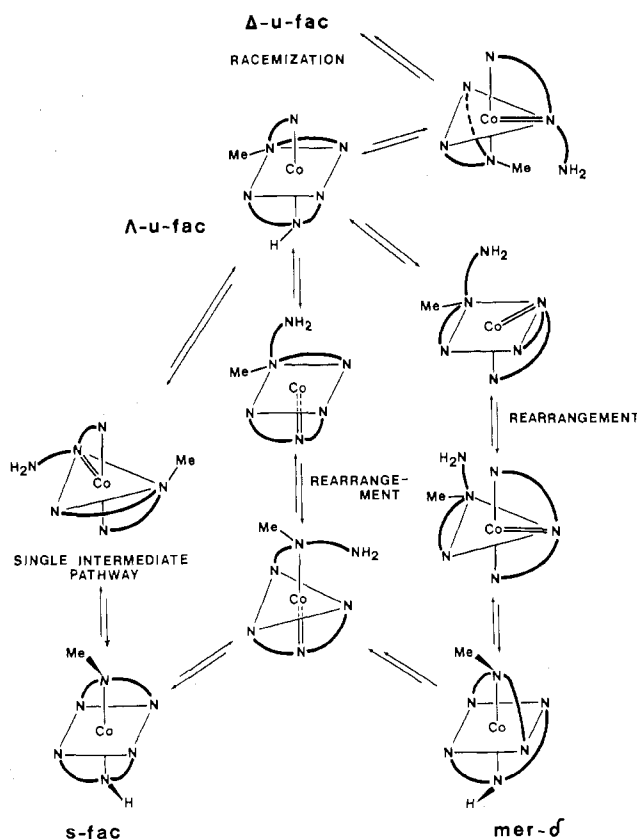
between  $\text{Co}(\text{en})_3^{3+}$  and  $\text{Co}(\text{en})_3^{2+}$  is quite slow, however,<sup>23</sup> and since this is a cobalt(III)-hexamine system of the same general type as  $\text{Co}(\text{dien})(\text{medien})^{3+}$ , the possibility of the above suggested cobalt(II)-rearrangement mechanism occurring without any observed dissociation of the  $\text{Co}(\text{dien})(\text{medien})^{2+}$  seems remote. The experimental observations are therefore entirely consistent with at least one rearrangement occurring in the cobalt(III) species, *u-fac*  $\rightleftharpoons$  *s-fac* and/or *u-fac*  $\rightleftharpoons$  *mer*, and the presence of cobalt(II) need not be invoked as a participant in these slow isomerization reactions. We consider the present demonstration of an intramolecular mechanism for isomerization of  $\text{Co}(\text{dien})(\text{medien})^{3+}$  significant because it represents one of the few cases of rearrangements of cobalt(III)-hexamine-type complexes having five-membered chelate rings where the possibility of an electron-transfer-promoted mechanism can be discounted.

**The Effect of pH on the Isomerizations of  $\text{Co}(\text{dien})(\text{medien})^{3+}$ .** Acid retardation is a characteristic of these intramolecular isomerization processes, which include at least two rearrangements. Acid retardation (or base catalysis) implies that the rearrangement processes might proceed through conjugate base species, and the most likely sites of the deprotonations would be the secondary amines of the coordinated dien rather than any of the coordinated primary amines. The relative acidities of the amine protons in the corresponding three isomers of  $\text{Co}(\text{dien})_2^{3+}$ , based on the relative rates of N-H exchange,<sup>24-26</sup> are *sec*-NH (*mer*)  $>$  *sec*-NH (*s-fac* and *u-fac*)  $\gg$  -NH<sub>2</sub> (all three isomers),<sup>27,28</sup> and the secondary amine protons should be the most acidic in the closely similar  $\text{Co}(\text{dien})(\text{medien})^{3+}$  complexes also. We now consider how deprotonation might facilitate either twist or bond-rupture processes.

Twists of deprotonated species would pass through the same dissymmetric trigonal-prismatic transition-state geometries as those shown in Figure 4 (but deprotonated at the *sec*-NH), so that for the *u-fac*  $\rightarrow$  *mer* change the twist act itself should remain stereospecific and optical activity should be retained. However some inversion will occur at the deprotonated *sec*-N center (coordinated dien) of the *mer* structure,<sup>29</sup> and under the conditions of the isomerization experiments the final *mer* product after reprotonation would not be expected to be optically active. For this *u-fac*  $\rightarrow$  *mer* change we see some possibility of nitrogen to cobalt  $p\pi-d\pi$  bonding. Although  $\pi$  stabilization has not been considered to be a dominating feature in the racemization (through NH exchange) of *mer*- $[\text{Co}(\text{dien})_2]^{3+}$ <sup>29</sup> nor in the base hydrolysis of *sym*- $[\text{Co}(\text{tren})\text{Cl}]^{2+}$ <sup>15,26</sup> some degree of  $\pi$  bonding could be the factor which promotes the *u-fac* (deprotonated)  $\rightarrow$  *mer* (deprotonated) twist act.

An alternative view is that deprotonation facilitates the adjustments of the bond angles at the *sec*-amine sites which necessarily accompany stereo change. The required adjustments of bond angles would probably be greatest for the *u-fac*  $\rightarrow$  *mer* twist change where a facial dien ligand becomes meridional, and this situation is analogous to the base-catalyzed isomerization *cis*  $\rightarrow$  *trans*- $[\text{Co}(\text{cyclam})(\text{OH}_2)_2]^{3+}$ <sup>15</sup> in which proton abstraction from a coordinated *sec*-amine group was associated with *fac* to *mer* change of coupled chelate rings in the cyclam ligand.<sup>30</sup> However such deprotonation requirement should be less stringent, in terms either of  $\pi$  bonding or of facilitating nitrogen bond angle adjustments, for the possible *s-fac*  $\rightleftharpoons$  *u-fac* twist where each ligand remains facial.

Our observations on the acid retardations of the isomerizations of  $\text{Co}(\text{dien})(\text{medien})^{3+}$  are in accord with the suggested bond angle adjustments. After 2.5 days at  $90^\circ\text{C}$  in 0.01 M perchloric acid the *u-fac* isomer had undergone some isomerization to *s-fac* ( $\sim 10\%$ ) but no *mer* was detected, and this suggests that the *u-fac*  $\rightarrow$  *s-fac* twist was less retarded by



**Figure 5.** Possible intramolecular pathways for interconversions of  $\text{Co}(\text{dien})(\text{medien})^{3+}$  isomers involving bond ruptures to five-coordinate intermediates. Only the central pathway may be stereospecific  $\Lambda$ -*u-fac*  $\rightarrow$  *mer- $\delta$* .

acidic conditions than were the other two processes. Under identical conditions the *s-fac* isomer showed no change, and the nonobservance of any *s-fac*  $\rightarrow$  *u-fac* probably reflects the equilibrium position being heavily in favor of *s-fac*.

Acidic conditions may inhibit a bond-rupture process by the protonation of the dissociated amine group preventing its recoordination to the metal, as with the racemization of  $\text{Fe}(\text{bpy})_3^{2+}$ .<sup>3a</sup> However, for the present complexes with acidic *sec*-amine sites (*dien*), the base catalysis of the possible bond-rupture pathways is more satisfactorily accounted for in terms of  $\pi$  stabilization of the five-coordinate conjugate-base intermediates (Figure 5). The apparent greater rate for *u-fac*  $\rightarrow$  *s-fac* than for *u-fac*  $\rightarrow$  *mer* and *s-fac*  $\rightarrow$  *mer* referred to above is consistent with the single intermediate pathway for *u-fac*  $\rightarrow$  *s-fac* being preferred over the others. In this single trigonal-bipyramid intermediate  $\pi$ -bonding overlap is likely to be more efficient as a consequence of the flexibility of the detached arm of the *dien*;<sup>26</sup> the other two pathways involve intermediates with facial *dien*.

Figure 4 also shows that a third twist process of the *u-fac* isomer could lead to its racemization, the transition state in this instance possessing a plane of symmetry. Similarly a bond-rupture process through a symmetrical trigonal-bipyramid intermediate (Figure 5) could lead to direct racemization of *u-fac*. The possible routes involving either twists or bond ruptures by which optical activity could be lost from the *u-fac* isomer are numerous: (1) direct racemization; (2) the symmetrical *s-fac*; (3) mutarotation to *mer* deprotonated intermediate by twist, followed by inversion of the intermediate; (4) the nonstereospecific *u-fac*  $\rightarrow$  *mer* bond-rupture pathway; (5) any active *mer* product formed being subsequently racemized by hydrogen exchange at the *sec*-NH of the coordinated *dien*.<sup>29</sup> This complexity would preclude an analysis of the kinetics of loss of optical activity from active

*u-fac*- $[\text{Co}(\text{dien})(\text{medien})]^{3+}$  in terms of possible processes, and in any case the twist and bond-rupture possibilities could probably not be distinguished. Isomerization and racemization in the isomers of  $\text{Co}(\text{medien})_2^{3+}$  should be somewhat simpler, since racemization by direct inversion of the *mer* isomer should be avoided with the two methyl substituents.

A third possible interpretation of the base catalysis of the isomerizations of  $\text{Co}(\text{dien})(\text{medien})^{3+}$  is that  $\text{OH}^-$  is involved in the transition state in an  $\text{S}_{\text{N}}2$  process. This kind of mechanism was proposed by Cooke, Im, and Busch for the base-catalyzed racemization of  $\text{Co}(\text{edta})^{-15}$  by a twist process, with the  $\text{OH}^-$  suggested to be coordinated to the cobalt at a rectangular face of the trigonal prism.<sup>31</sup> Deprotonation is not possible with  $\text{Co}(\text{edta})^-$ , and with our present amine complexes we favor the conjugate-base interpretation.

On the basis of the above conjugate-base twist and bond-rupture proposals, it becomes of considerable interest to know whether the  $\text{Co}(\text{medien})_2^{3+}$  isomers would isomerize at all in homogeneous solution, since deprotonations analogous to those at the coordinated *sec*-NH centers of the  $\text{Co}(\text{dien})(\text{medien})^{3+}$  isomers are not possible with the  $\text{Co}(\text{medien})_2^{3+}$  compounds. A reluctance of  $\text{Co}(\text{medien})_2^{3+}$  to isomerize might confirm that deprotonations at *sec*-nitrogens are necessary preludes for twist or bond-rupture processes with cobalt(III)-amine complexes in aqueous solution and enable the  $\text{S}_{\text{N}}2$  mechanism to be discounted. Unfortunately the *s-fac* is the most stable isomer of  $\text{Co}(\text{medien})_2^{3+}$ , and we have not been able to obtain the *u-fac* and *mer* isomers in detectable amounts in the presence of charcoal.<sup>19</sup> Thus at present the crucial experiment of examining the  $[\text{OH}^-]$  dependence of the isomerization  $u\text{-fac-}[\text{Co}(\text{medien})_2]^{3+} \rightarrow s\text{-fac-}[\text{Co}(\text{medien})_2]^{3+}$  cannot be carried out.

**Isomerizations in the  $\text{Co}(\text{dien})_2^{3+}$  System.** Isomerization experiments we have carried out with the  $\text{Co}(\text{dien})_2^{3+}$  isomers are relevant to the work already described. Due to the close similarity between the  $\text{Co}(\text{dien})_2^{3+}$  and  $\text{Co}(\text{dien})(\text{medien})^{3+}$  complexes, we would expect that isomerizations would proceed by similar mechanisms in both systems. For the homogeneous isomerizations of  $\text{Co}(\text{dien})_2^{3+}$  the mechanisms could be confirmed as intramolecular only by comparing ligand-exchange and isomerization rates. Nevertheless intermolecular mechanisms for these homogeneous processes of  $\text{Co}(\text{dien})_2^{3+}$  and  $\text{Co}(\text{dien})(\text{medien})^{3+}$  under the concentrations of complexes employed are considered quite unlikely, as complete dissociations of tridentate ligands would be expected to result in considerable amounts of hydrolysis products from the reactions in water, and these were not evident.

The three  $\text{Co}(\text{dien})_2^{3+}$  isomers as the acetate salts have been interconverted under a variety of conditions of solvent (water, dimethyl sulfoxide, alcohols up to *tert*-butyl alcohol, glacial acetic acid, *dien*), the presence or absence of charcoal for reactions in water, pH for aqueous solutions (varied by addition of 2,4,6-trimethylpyridine-hydrochloric acid buffer pH 8,<sup>32</sup> hydrochloric acid, or sodium hydroxide), and temperature (25 and 82 °C). The experimental methods were similar to those used for the  $\text{Co}(\text{dien})(\text{medien})^{3+}$  compounds. Samples taken from a run at various times were chromatographed on Sephadex columns, and the proportions of the three separated isomers were determined spectrophotometrically.<sup>18,33</sup>

The results can be summarized as follows, one set of experimental data being given in Table I: (1) Each isomer gives a mixture of all three isomers. The reaction rates depend on the starting isomer, being greatest for the *mer* (Table I). (2) The isomerizations in water are catalyzed by base (pH range 5–9) and do not occur at pH < 3. No reaction was detectable in glacial acetic acid. The complex (*s-fac*) decomposed in 0.1 M sodium hydroxide at 80 °C. (3) The *mer* equilibrium proportion is always established relatively rapidly, and the two

**Table I.** Isomerization Reactions of the  $[\text{Co}(\text{dien})_2](\text{CH}_3\text{COO})_3$  Isomers in Water at 82 °C

starting isomer <sup>a</sup>	sampling time	isomer proportions <sup>b</sup>		
		<i>s-fac</i>	<i>u-fac</i>	<i>mer</i>
<i>s-fac</i>	1 day	69	7	24
	3 days	32	24	44
	7 days	18	37	45
	14 days	15	41	44
<i>u-fac</i>	3 h	6	84	10
	1 day	7	62	31
	3 days	9	49	42
	7 days	12	45	43
<i>mer</i>	14 days	14	44	42
	3 h	4	7	89
	1 day	9	33	58
	3 days	13	40	47
	7 days	13	44	43
	14 days	13	43	44
proportions on charcoal at 82 °C (12 h)		15	42	43

<sup>a</sup> Complex concentration  $\sim 0.02$  M. <sup>b</sup> Values given are subject to experimental error of  $\pm 2$ .

*fac* forms continue to adjust more slowly to their equilibrium proportions (Table I). The final product distribution is the same from each starting isomer under a given set of conditions and in water is identical with that obtained by the rapid equilibration of any of the isomers on activated charcoal (Table I). This confirms that charcoal effects true thermodynamic equilibration between the isomers. (4) In all instances where isomerization occurred, a small amount of a reddish purple species was detected. It is likely that this was a monoquo species whose formation competes with isomerization in a bond-rupture process. Some cobalt(II) was evident in the reactions in alcohols, particularly in the most reducing alcohol, methanol.

The significant result here is the variation in the rates of reaction and formation of the three geometric isomers. If intramolecular mechanisms may be assumed for these processes, this observation is consistent with the reactions proceeding through three (rather than two) intramolecular pathways.

From the relative N-H exchange rates in the three isomers (given earlier), the deprotonated (at *sec*-N) *mer* species would be the most rapidly formed and would be in the greatest concentration. This probably accounts for the *mer* complex isomerizing the most rapidly and the equilibrium proportion of this isomer being attained relatively quickly.

The experimental observations on the homogeneous Co(dien)(medien)<sup>3+</sup> isomerizations have not allowed a decision between the twist and bond-rupture intramolecular mechanisms. However the bond-rupture route for these reactions of cobalt(III)-amine complexes is supported by the following facts: (1) decomposition of Co(dien)<sub>2</sub><sup>3+</sup> and *s-fac*-Co(medien)<sub>2</sub><sup>3+</sup> complexes in alkali at 80 °C; (2) the presence of [Co(dien)<sub>2</sub>OH]<sub>2</sub><sup>3+</sup> or [Co(dien)<sub>2</sub>OH]<sub>2</sub><sup>2+</sup> in the reaction products in small amounts; (3) a recently observed reaction of the same type with *u-fac*-[Co(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>]<sup>3+</sup> which with alkali gives [Co(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>OH]<sub>2</sub><sup>2+</sup>.<sup>34</sup> All the data for the homogeneous systems can be rationalized by transient five-coordinate intermediates rearranging. If the twisting hypothesis is adopted the [Co(dien)<sub>2</sub>OH]<sub>2</sub><sup>2+</sup> product and the decomposition have to be produced by an independent path. On the basis of the "principle of parsimony" we prefer the former analysis.

**Charcoal-Catalyzed Equilibrations of Cobalt(III)-Amine Complexes, and the Catalyzed and Uncatalyzed Racemization of Co(en)<sub>3</sub><sup>3+</sup>.** The catalytic effect of charcoal in promoting

equilibrations of cobalt(III)-amine complexes has been widely attested, but uncertainty remains as to the mechanism involved.<sup>3b,35</sup> Most of the kinetic and mechanistic studies have been on the racemizations of Co(en)<sub>3</sub><sup>3+</sup> salts, and since Co(en)<sub>3</sub><sup>3+</sup> and the Co(dien)(medien)<sup>3+</sup> isomers are all CoN<sub>6</sub><sup>3+</sup> complexes with five-membered saturated rings, similar mechanistic features might reasonably be expected for the isomerization reactions in these two systems.

Dwyer and Sargeson demonstrated the involvement of cobalt(II) in the catalyzed racemization of [Co(en)<sub>3</sub>]Cl<sub>3</sub> ( $\sim 0.06$  M complex in water)<sup>36</sup> and proposed<sup>22,36</sup> that the catalytic equilibration and racemization reactions of cobalt(III) complexes occur by two routes: (1) labilization through a high-spin activated state of cobalt(III), one suggested role of the carbon being to catalyze the conversion of a small amount of spin-paired cobalt(III) to the activated spin-free state (rearrangements and ligand dissociation would be facilitated); (2) rapid electron-transfer, charcoal catalyzed, between labile cobalt(II) species—generated by charcoal reduction of the activated high-spin cobalt(III) arising by (1)—and high-spin cobalt(III).

It has been shown subsequently<sup>37</sup> that with Co(pn)<sub>3</sub><sup>3+</sup> isomers on charcoal  $\Delta \rightleftharpoons \Lambda$  interconversions occur much more rapidly than ligand exchange. In these interconversions, the major role of the charcoal thus appears to be catalysis of intramolecular processes.

Mureinik and Spiro have recently shown that in more dilute solutions ( $\sim 0.002$  M [Co(en)<sub>3</sub>]I<sub>3</sub> in water) a different mechanism, which does not involve a cobalt(II) intermediate, must obtain.<sup>35</sup> The deduced third-order rate law implied that the reaction proceeded by interaction on the carbon surface between two adsorbed Co(en)<sub>3</sub><sup>3+</sup> ions and one adsorbed iodide. The halide apparently played a crucial although undefined role, since the perchlorate salt did not racemize at all on charcoal under similar conditions.

The mechanism for the disproportionations of the isomers of [Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> over charcoal to give Co(dien)<sub>2</sub><sup>3+</sup> and Co(medien)<sub>2</sub><sup>3+</sup> clearly must involve complete dissociations of ligands, and any charcoal catalysis of intramolecular processes is obscured. In comparison with Mureinik and Spiro's work, it is significant that our present results were obtained using perchlorate salts, so that we tested the effect of our charcoal on (+)-[Co(en)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>. Under a particular set of conditions (concentration, amount of charcoal, and time) in neutral water at 19 °C little if any racemization of (+)-[Co(en)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub> nor of (+)-[Co(en)<sub>3</sub>]I<sub>3</sub> was evident (percent decrease in optical rotation approximately equals decrease in visible absorption). However under similar conditions in 0.01 M sodium hydroxide we found that substantial racemization of (+)-[Co(en)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub> occurred. Clearly the effects of added bases on this catalyzed reaction merit further attention.<sup>38</sup>

It appears therefore that different mechanisms dominate for charcoal-catalyzed equilibrations under different conditions of complex concentration. The concentrations (usually  $\sim 0.08$  M) employed in our present charcoal-catalyzed isomerizations of [Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> were comparable with those in Dwyer and Sargeson's work,<sup>36</sup> and we prefer to interpret our charcoal-catalyzed reactions as occurring essentially by electron transfer between the cobalt(III) complexes and labile cobalt(II) (both the proposed steps (1) and (2) outlined above). Our observations of significant amounts of cobalt(II) being formed in the Co(dien)(medien)<sup>3+</sup> reactions accords with observations on other cobalt(III) complex systems with charcoal.<sup>22,35,36</sup>

For the isomerization of Co(dien)(medien)<sup>3+</sup> in homogeneous alkaline solution, the rearrangement process might require the complex to be in an activated state as proposed

in process (1) above for the catalyzed isomerizations of cobalt(III)-amine complexes. In the homogeneous conditions the activated high-spin state of the deprotonated cobalt(III) could be attained thermally.<sup>39</sup> In contrast, (+)-[Co(en)<sub>3</sub>]<sup>3+</sup> salts are highly optically stable, undergoing no change in neutral water (nor in dilute acid) even at 100 °C.<sup>22,35,36,38,40</sup> However the difference may well be associated with the higher acidities of the Co(dien)(medien)<sup>3+</sup> isomers due to the coordinated secondary amines, whereas (+)-[Co(en)<sub>3</sub>]<sup>3+</sup> has only coordinated primary amines as sites for deprotonation.

In homogeneous solution in the presence of added [Co(en)<sub>3</sub>]Cl<sub>2</sub> and ethylenediamine, racemization of (+)-[Co(en)<sub>3</sub>]Cl<sub>3</sub> occurs by a second pathway in addition to the slow electron-transfer reaction.<sup>23</sup> The rates closely fit the proposed two-term rate law  $R = k[\text{Co(III)}][\text{Co(II)}] + k'[\text{Co(III)}][\text{en}]$ , and the second term has been attributed to the formation of a seven- or eight-covalent intermediate between the complex and ethylenediamine.<sup>22,23,36,38</sup> In the light of our finding that the rates of the homogeneous isomerizations of [Co(dien)<sub>2</sub>](CH<sub>3</sub>COO)<sub>3</sub> and [Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> are enhanced by added base, it now seems possible that the ethylenediamine functioned as a base to abstract a proton from the thermally activated Co(en)<sub>3</sub><sup>3+</sup> species in the second pathway, so that the mechanism could be S<sub>N</sub>1CB as with Co(dien)(medien)<sup>3+</sup>.

## Experimental Section

The complex *s-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> was obtained from reaction of [Co(NH<sub>3</sub>)<sub>2</sub>Cl]Cl<sub>2</sub> with dien and medien.<sup>16</sup> The details of its isolation along with other products from this reaction will be described in a subsequent article.

**Reactions of *s-fac*- and *u-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> Isomers on Charcoal.** A solution of *s-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> (0.60 g) in water (12 mL) was stirred with charcoal (0.20 g of freshly ground BDH granulated charcoal for gas absorption) in a 50-mL stoppered flask with an oxygen atmosphere and maintained at 80 °C in an oil bath. Samples (~1 mL) were removed, and the charcoal was immediately filtered off, at five different times from 4 to 48 h. These solutions were chromatographed on columns (1.2 × 40 cm) of SP-Sephadex C-25 cation-exchange resin, Na<sup>+</sup> form, with 0.1 M Na<sub>3</sub>PO<sub>4</sub> when five clear yellow or orange bands separated (Figure 3B). The chromatographed patterns on the five columns appeared all identical. The five band effluents were collected separately and made up to standard volumes with water, and the cobalt concentrations were determined on a Varian-Techtron Model 1200 atomic absorption spectrophotometer using the emission line 240.7 nm. Values obtained for the bands (in order of their elution) from one particular aliquot were as follows: *s-fac*-[Co(dien)<sub>2</sub>]<sup>3+</sup> in 25 mL, 11.6 ppm; *u-fac*-[Co(dien)(medien)]<sup>3+</sup> in 25 mL, 8.3 ppm; *s-fac*-[Co(dien)(medien)]<sup>3+</sup> + *u-fac*-[Co(dien)<sub>2</sub>]<sup>3+</sup> in 200 mL, 12.8 ppm; *mer*-[Co(dien)<sub>2</sub>]<sup>3+</sup> in 100 mL, 11.3 ppm; *s-fac*-[Co(medien)<sub>2</sub>]<sup>3+</sup> in 100 mL, 15.6 ppm. Mean values of the cobalt ratios in the five bands, from the five separations, were (5 ± 1):(4 ± 1):(46 ± 2):(19 ± 1):(26 ± 2), respectively. The separation of the complexes *s-fac*-[Co(dien)(medien)]<sup>3+</sup> and *u-fac*-[Co(dien)<sub>2</sub>]<sup>3+</sup> within the one band was sufficient to gauge visually that these complexes were present in roughly comparable amounts (Figure 3B), so that the molar proportions of the six complexes (in order of their elution) were 5:4:~23:~23:19:26.

*u-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> was similarly equilibrated (0.10 g in 10 mL of water) over charcoal (0.04 g) for 2 days at 80 °C. Sephadex chromatography then gave a pattern of bands apparently identical in every respect (visual comparison) with the pattern starting from the corresponding *s-fac* isomer above.

**Reactions of *s-fac*- and *u-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> Isomers in Homogeneous Solution.** In test reactions, solutions of 1.00 g of *s-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> in 20 mL of water, 0.01 M HClO<sub>4</sub>, or buffer solution (0.05 M 2,4,6-trimethylpyridine-perchloric acid adjusted to pH 8.0 at 25 °C),<sup>32</sup> in stoppered flasks were maintained at 90 °C in an oil bath. At appropriate times, samples (~1 mL) were taken and applied directly to columns (1.2 × 40 cm) of Sephadex cation-exchange resin. On elution with 0.1 M Na<sub>3</sub>PO<sub>4</sub> three bands separated as in Figure 3A from the reactions in water or buffer, but only the single band of *s-fac* was obtained from the reaction in HClO<sub>4</sub>.

The effect of acid on isomerization of *u-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> was determined by chromatographing samples from two small-scale reactions, 0.10 g of complex in 4 mL of 0.01 M HClO<sub>4</sub> or buffer solution, run concurrently at 90 °C for 2.5 days.

The determination of the equilibrium proportions of the three Co(dien)(medien)<sup>3+</sup> isomers was carried out on separate reactions of the *s-fac* and *u-fac* perchlorates in the buffer solution (1.00 g in 20 mL) run concurrently at 90 °C. After 3 days, samples from each reaction were chromatographed in duplicate. The three effluents containing the separated isomers from each column were collected and made up to appropriate standard volumes (*s-fac* to 250 mL, *u-fac* and *mer* each to 25 mL), and the cobalt concentrations were determined by atomic absorption. A typical result was *s-fac* 9.9 ppm, *u-fac* 11.9 ppm, and *mer* 11.3 ppm, from where the proportions follow as 81:10:9, respectively. Remaining solutions were combined and worked up for isolation of the three isomers as described below.

On a preparative scale *s-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> (2.055 g) in the buffer solution (40 mL) was reacted at 90 °C as above. After 3 days the now orange solution was diluted (200 mL) and applied to a large Sephadex column (4.5 × 44 cm), which was then eluted with 0.1 M Na<sub>3</sub>PO<sub>4</sub>. The separate effluents of the three isomers were diluted threefold and adsorbed on appropriately sized columns of BIO-REX 70 weak-acid cation-exchange resin, 50-100 mesh, Li<sup>+</sup> form (column sizes 3 cm diameter × 2 cm for *s-fac*, 1.2 cm × 3 cm for *u-fac* and *mer*). After washing the columns with water, the complexes were eluted off with 0.1 M HClO<sub>4</sub>. These effluents were evaporated to dryness or sludge on a rotary evaporator, ethanol was added, and the flasks were cooled at 0 °C. The ethanol (containing NaClO<sub>4</sub>) was sucked off and each crystalline product was suspended in fresh ethanol. The ethanol suspensions of the orange *u-fac* and *mer* perchlorates were transferred to weighing bottles, most of the ethanol was sucked off, and the remaining ethanol was then removed in a vacuum desiccator. The yellow *s-fac* product was filtered off and washed with ethanol, and finally all three products were dried at 70 °C to constant weight. Amounts of the [Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> isomers obtained were *s-fac* 1.556 g, *u-fac* 0.183 g, and *mer* 0.192 g, representing 94.0% recovery, and giving *s-fac*:*u-fac*:*mer* = 81:9:10 in satisfactory agreement with the proportions determined above.

Anal. Calcd for [Co(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)(C<sub>5</sub>H<sub>15</sub>N<sub>3</sub>)](ClO<sub>4</sub>)<sub>3</sub>: C, 18.7; H, 4.9; N, 14.6; Cl, 18.4; (N)CH<sub>3</sub>, 2.6. Found for *u-fac*: C, 18.2; H, 4.8; N, 14.8; Cl, 18.3; (N)CH<sub>3</sub>, 3.1. Found for *mer*: C, 18.3; H, 4.8; N, 14.3; Cl, 18.7.

The <sup>13</sup>C NMR spectra of the [Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> isomers in D<sub>2</sub>O were obtained as described previously.<sup>16</sup> The methyl carbon resonances were identified by rerunning the spectra under off-resonance proton-decoupled conditions when methylene carbon resonances appeared as triplets (centered at the broad-band proton-decoupled single frequencies) and methyl carbons gave quartets. Chemical shifts δ, from SiMe<sub>4</sub>, for the isomers of [Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub> isolated from the isomerization of the *s-fac* perchlorate in aqueous buffer solution at 90 °C are as follows: *s-fac* 65.7, 56.3, 52.7 (methyl), 43.9, 43.0 (these are almost identical with those reported previously<sup>16</sup> for the chloride salt); *u-fac* 65.4, 64.5, 56.7, 56.1, 51.7 (methyl), 45.5, 44.2, 43.5, 41.9; *mer* 62.8, 52.2, 51.3, 47.2 (methyl), 47.0, 46.5, 45.1. The number of scans accumulated for *u-fac* and *mer* were 63 000 for 0.10 g in 2 mL of D<sub>2</sub>O, and for *s-fac*, 10 600 scans for 0.20 g.

**[Co(dien)<sub>2</sub>](CH<sub>3</sub>COO)<sub>3</sub> Isomers.** These were obtained by shaking the separated isomers of [Co(dien)<sub>2</sub>]Br<sub>3</sub><sup>33</sup> with stoichiometric silver acetate in methanol solution, filtering, and evaporating the filtrates to dryness. The hygroscopic acetate salts were stored in a desiccator.

**Registry No.** *u-fac*[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub>, 67049-22-3; *mer*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub>, 65608-69-7; *s-fac*-[Co(dien)(medien)](ClO<sub>4</sub>)<sub>3</sub>, 63566-67-6; Co(dien)<sub>2</sub><sup>3+</sup>, 18703-28-1.

## References and Notes

- N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).
- R. H. Holm in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, pp 317-376.
- F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed. Wiley, New York, N.Y., 1967: (a) p 316; (b) pp 330-332.
- P. C. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).
- W. G. Gehman, Ph.D. Thesis, Pennsylvania State University, 1954; L. Seiden, Ph.D. Thesis, Northwestern University, 1957; J. C. Bailar, *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).
- C. S. Springer and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).
- J. E. Brady, *Inorg. Chem.*, **8**, 1208 (1969).
- J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 331 (1971).

- (9) H. Fischer, E. O. Fischer, and H. Werner, *J. Organomet. Chem.*, **73**, 331 (1974).
- (10) S. S. Eaton, J. R. Hutchinson, R. H. Holm, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 6411 (1972).
- (11) S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *J. Am. Chem. Soc.*, **95**, 1116 (1973).
- (12) D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, **11**, 2843 (1972).
- (13) D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, **13**, 2045 (1974).
- (14) G. A. Lawrance and D. R. Stranks, *Inorg. Chem.*, **16**, 929 (1977).
- (15) Abbreviations used: phen = 1,10-phenanthroline; bpy = 2,2'-bipyridyl; ox = oxalate; dien = diethylenetriamine =  $H_2N-CH_2CH_2-NHCH_2-CH_2-NH_2$ ; medien = 4-methyldiethylenetriamine = 2,2'-methyliminobis(ethylamine) =  $H_2N-CH_2CH_2-NMe-CH_2CH_2-NH_2$ ; en = ethylenediamine; pn = propane-1,2-diamine; trenen = 4-(aminoethyl)-1,4,7,10-tetraazadecane; cyclam = 1,4,8,11-tetraazacyclotetradecane; edta = ethylenediaminetetraacetate.
- (16) G. H. Searle, S. F. Lincoln, F. R. Keene, S. G. Teague, and D. G. Rowe, *Aust. J. Chem.*, **30**, 1221 (1977).
- (17) G. H. Searle, *Aust. J. Chem.*, **30**, 2625 (1977).
- (18) F. R. Keene and G. H. Searle, *Inorg. Chem.*, **13**, 2173 (1974).
- (19) G. H. Searle, S. F. Lincoln, F. R. Keene, S. G. Teague, and D. G. Rowe, unpublished work.
- (20) R. D. Gillard, *J. Chem. Soc. A*, 917 (1967).
- (21) F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **81**, 5269 (1959).
- (22) F. P. Dwyer in "Advances in the Chemistry of the Coordination Compounds", S. Kirschner, Ed., Macmillan, New York, N.Y., 1961, p 21.
- (23) F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, **65**, 1892 (1961).
- (24) M. Eigen, *Angew. Chem., Int. Ed., Engl.*, **3**, 1 (1964).
- (25) E. Grunwald and E. K. Ralph, *Acc. Chem. Res.*, **4**, 107 (1971).
- (26) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **8**, 1595 (1969).
- (27) Y. Yoshikawa and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, **45**, 179 (1972).
- (28) F. R. Keene, Ph.D. Thesis, University of Adelaide, 1972, pp 143, 167.
- (29) G. H. Searle and F. R. Keene, *Inorg. Chem.*, **11**, 1006 (1972).
- (30) C. K. Poon and M. L. Tobe, *Inorg. Chem.*, **7**, 2398 (1968). The gross mechanism for the base-catalyzed isomerization *cis*  $\rightarrow$  *trans*-[Co(cyclam)(OH)<sub>2</sub>]<sup>3+</sup> was intermolecular involving attack of water and not intramolecular.
- (31) D. W. Cooke, Y. A. Im, and D. H. Busch, *Inorg. Chem.*, **1**, 13 (1962).
- (32) R. M. C. Dawson, D. C. Elliott, W. H. Elliott, and K. M. Jones, "Data for Biochemical Research", 2nd ed, Oxford University Press, London, 1969, p 491.
- (33) F. R. Keene and G. H. Searle, *Inorg. Chem.*, **11**, 148 (1972).
- (34) E. Larsen, private communication.
- (35) R. J. Mureinik and M. Spiro, *J. Chem. Soc., Dalton Trans.*, 2480, 2493 (1974).
- (36) F. P. Dwyer and A. M. Sargeson, *Nature (London)*, **187**, 1022 (1960).
- (37) S. E. Harnung, S. Kallesoe, A. M. Sargeson, and C. E. Schaffer, *Acta Chem. Scand., Ser. A*, **28**, 385 (1974).
- (38) W. H. Gehman and W. C. Fernelius, *J. Inorg. Nucl. Chem.*, **9**, 71 (1959).
- (39) D. Sen and W. C. Fernelius, *J. Inorg. Nucl. Chem.*, **10**, 269 (1959).
- (40) B. E. Douglas, *J. Am. Chem. Soc.*, **76**, 1020 (1954).

Contribution from the Department of Chemistry,  
Vanderbilt University, Nashville, Tennessee 37235

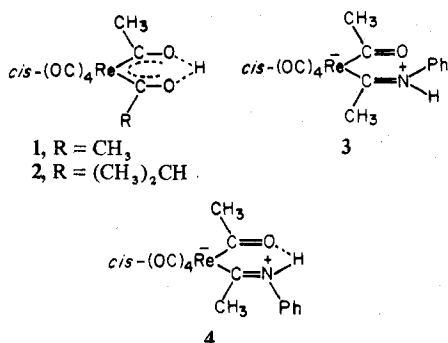
## Reactions of Coordinated Molecules. 16. Preparation and Characterization of Several Metalla- $\beta$ -ketoimine Molecules as the Ketamine Tautomers

C. M. LUKEHART\* and JANE V. ZEILE

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The reaction of the metalla- $\beta$ -diketone molecules *cis*-(OC)<sub>4</sub>Re[C(CH<sub>3</sub>)O...H...OC(R)], where R is either methyl or isopropyl, with anhydrous ammonia or with several primary aliphatic or aromatic amines H<sub>2</sub>NR', where R' is phenyl, *p*-tolyl, methyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, cyclohexyl, or benzyl, or with ethylenediamine or propylenediamine affords the metalla- $\beta$ -ketoimine molecules *cis*-(OC)<sub>4</sub>Re[RC(O)][CH<sub>3</sub>CN(R')(H)] as the ketamine tautomers. Seventeen such complexes are reported. The structure and chemical reactivity of these molecules is discussed. Both structural and geometrical isomerism is observed.

We reported recently the reaction of the metallaacetylacetone molecule, **1** (3,3,3,3-tetracarbonyl-3 $\lambda^6$ -rhena-2,4-



pentanedione), with aniline and *p*-toluidine affording the metalla analogues of the corresponding  $\beta$ -ketoimine molecules.<sup>1,2</sup> The X-ray structure of the *N*-phenyl complex, **3**, indicates that the molecule is described best as the zwitterionic ketamine tautomer.<sup>1</sup> Two geometrical isomers, **3** and **4**, of this molecule are observed. Isomer **3** is isolated by crystallization from ether solution as an extended intermolecular hydrogen-bonded structure. When **3** is dissolved in CDCl<sub>3</sub> solution at 34 °C, it isomerizes slowly and nearly completely (6:94) to another isomer, **4**, which is presumed to be the isomer

having intramolecular hydrogen bonding. Isomer **4** can be isolated pure by crystallization from hexane solution.

In this paper we report the preparation and characterization of 17 metalla- $\beta$ -ketoimine molecules. In many cases the geometrical isomerization about the C-N multiple bond is observed. When the unsymmetrical metalla- $\beta$ -diketone, **2**, is used, the condensation reaction of the amine occurs predominantly at the acetyl ligand, although the other structural isomer is observed for some molecules. Both the presence of coupling between the  $\alpha$  protons of the R' group and the enolic NH proton and the facile deuterium exchange of the enolic NH proton further substantiate the solution-phase structures of these molecules. These metalla- $\beta$ -ketoimine complexes represent a new class of compounds which are derivatives of well-known organic molecules.

### Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25 °C. Diethyl ether and pentane were dried over Na-K alloy with added benzophenone, and methylene chloride was dried over P<sub>2</sub>O<sub>5</sub>. These solvents were dried under a nitrogen atmosphere and were freshly distilled before use. Cyclohexylamine was distilled over calcium hydride before use. Other amines were used as purchased.

Infrared spectra were recorded on a Perkin-Elmer 727 spectrophotometer as solutions in 0.10-mm sodium chloride cavity cells using the solvent as a reference and a polystyrene film as a calibration