ence of iodide. The same feature was common to some earlier reported reactions.[1] The second product was $C_5H_5Fe(CO)_2CN$, also known.[4] This compound was shown by infrared analysis not to be present as an impurity in the starting material. Hence its origin would appear to be by a demethylation reaction of an unspecified nature.

As has been so often the case in these reactions, the total yield of low-valent complexes is small. This is a disappointment, of course, but it suggests that an adequate explanation should be sought. We are inclined to consider the possibility that many neutral complexes formed in these reactions are themselves susceptible to attack by (fairly brutal) reagents such as organolithium compounds; in turn the anionic complexes would be lost in subsequent work-up either by air oxidation or by failure to elute from alumina on chromatography. This result does preclude an estimation of the reactivities of various positions in the molecule and its correlation with bonding theory, which ultimately is one goal in this study.

In summary, we have succeeded in further substantiating the nonselectivity of this kind of reaction. The isocyanide ligand, like carbonyls, is clearly susceptible to attack by a nucleophilic reagent. We find most intriguing, at this time, the potential isocyanide–carbonyl analogies which appear to be possible; we are especially interested in carbonylation–decarbonylation reaction analogies. Some of our present efforts are being directed in this area.

CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON W.C.1, ENGLAND

The Relationship between Chelate Ring Size and the Stereochemistry of Some Cobalt(III) Complexes Containing Quadridentate Ligands

By B. BOSNICH, W. R. KNEEN, AND A. T. PHILLIP

The three homologous open-chain quadridentate ligands 1,8-diamino-3,6-dithiaoctane (EEE), 1,9-diamino-3,7-dithianonane (ETE), and 1,10-diamino-4,7-dithiadecane (TET) have been used to prepare a number of isomeric dichlorocobalt(III) complexes. It was found that the EEE ligand gave only the blue cis-α-CoEEECl$_2$$^+$ isomer and the ETE ligand gave the green $trans$-CoETECl$_2$$^+$ and the red-violet cis-β-CoETECl$_2$$^+$ isomers while the TET ligand gave the red-violet cis-β-CoTETCl$_2$$^+$ and the blue cis-α-CoTETCl$_2$$^+$ isomers. In addition, a series of cobalt(III) complexes of the type CoEEEX$_2$$^{n+}$ (where X$^-$ = Br$^-$, N$_3$$^-$, NCS$^-$, NO$_2$$^-$, oxalate, and 2,2'-bipyridyl) has been prepared and investigated. These latter complexes all appear to have the cis-α configuration. The equilibria $trans$-CoETECl$_2$$^+$ $\rightleftharpoons$ cis-β-CoETECl$_2$$^+$ and cis-β-CoTETCl$_2$$^+$ $\rightleftharpoons$ cis-α-CoTETCl$_2$$^+$ have been studied and the relationship between chain length and stereochemistry is discussed in terms of the conformations of the chelate rings.

It is well known that[1] five-membered chelate rings formed by bidentate ligands containing only single bonds are the most stable and that, with the saturated ligands, these five-membered rings adopt the stable staggered *(gauche)* conformation.[2] In multidentate ligand systems a new problem arises by the circumstance that the ligand may adopt a number of arrangements about an octahedral metal ion. Thus, for example, the terdentate ligand diethylenetriamine may coordinate either in a planar or vicinal arrangement about an octahedral atom and the question arises as to which of the two arrangements is the most stable. It seems probable that two of the important considerations in deciding the outcome are the size of the individual chelate rings and the conformations which can be adopted. We have discussed this problem recently in relation to the quadridentate ligands triethylenetetramine and 1,4,8,11-tetraazaundecane (the latter contains an extra methylene group between the two secondary nitrogen atoms).[3] It was found that the former ligand tended to give *cis*-octahedral complexes[4] whereas the latter tended to give *trans* isomers. In this paper we wish to pursue this problem further and for this purpose we describe the results of our investigation of the stereochemistries adopted by the three homologous quadridentate ligands 1,8-diamino-3,6-dithiaoctane (EEE), 1,9-diamino-3,7-dithianonane (ETE), and 1,10-diamino-4,7-dithiadecane (TET) (Figure 1) about a cobalt(III) atom.

1. General Considerations

Octahedral metal complexes formed by the ligands EEE, ETE, and TET can be envisaged as existing in potentially three isomeric forms: the *cis*-α, *cis*-β, and *trans* isomers (Figure 2). In deciding which geometries will be the most stable for the quadridentate EEE ligand we shall consider only two factors: (a) that each che-

(1) H. Irving, R. J. P. Williams, D. F. Fenett, and A. E. Williams, *J. Chem. Soc.*, 3494 (1954).
(2) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).
(3) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc., A*, 1331 (1966).
(4) A. M. Sargeson and G. Searle, *Nature*, **200**, 356 (1963).
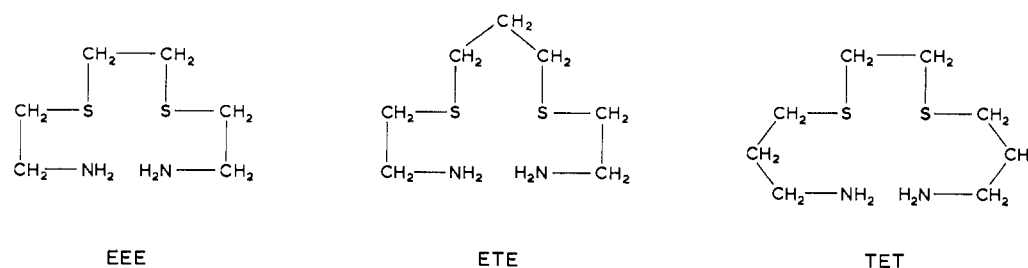
Figure 1. The three ligands 1,8-diamino-3,6-dithiaoctane (EEE), 1,9-diamino-3,7-dithianonane (ETE), and 1,10-diamino-4,7-dithia-decane (TET).
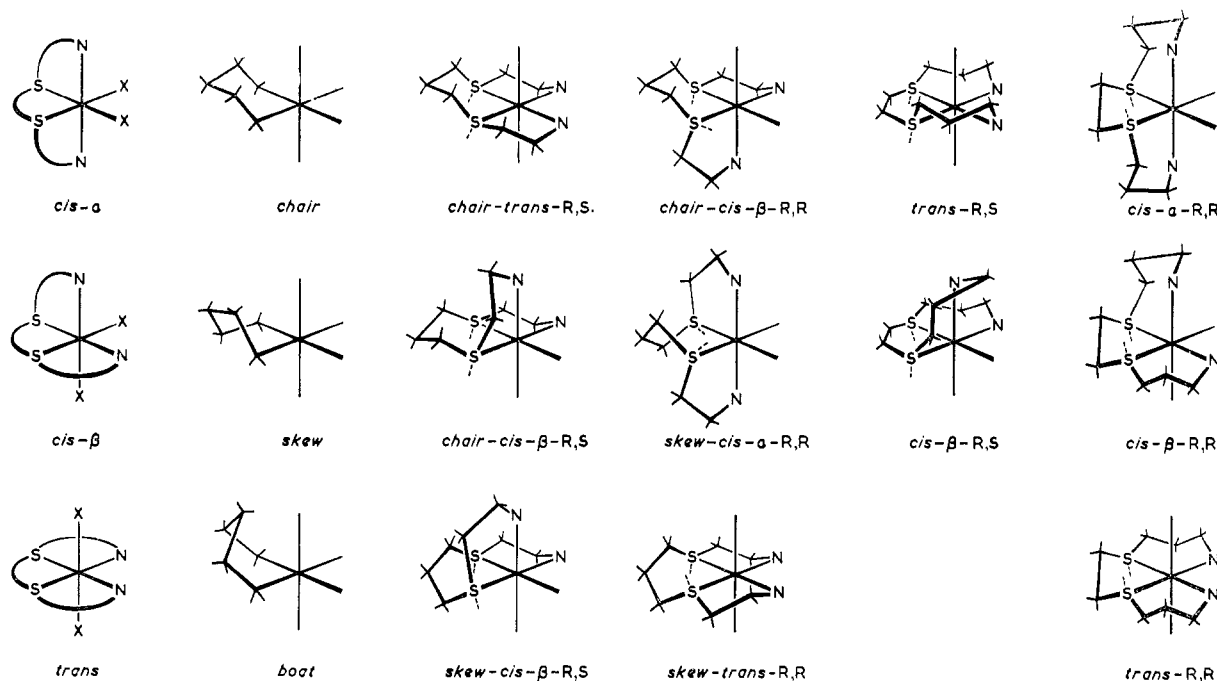

Figure 2.—Diagrammatic representations of the possible isomers and conformers formed by complexes of the three ligands EEE, ETE, TET. Column 1 shows the three isomeric forms; column 2 shows the three conformers of a six-membered chelate ring; columns 3 and 4 show the possible geometric and conformational isomers formed by the ETE ligand; and columns 5 and 6 show the possible geometric and conformational isomers of the TET ligand. The dotted lines emanating from the sulfur atoms indicate the direction of the lone-pair electrons.

late ring will adopt a staggered (*gauche*) conformation[2] and (b) that the atoms will approximately retain their normal trigonal, tetrahedral, and octahedral bond angles. Although there are undoubtedly other factors[3] which may influence the stereochemical outcome, it seems probable that in the present system, these two considerations will be of major importance. Molecular models indicate that the only configuration which satisfies both these criteria is the *cis-α* isomer. In either the *cis-β* or *trans* stereochemistry there is considerable strain engendered in the system, the *trans* isomer being more strained than the *cis-β* isomer. Thus if the above considerations predominate, we would expect the EEE ligand to give mainly *cis-α* octahedral complexes.

The situation with regard to the ETE ligand is more complicated because of the presence of the central six-membered chelate ring. In this discussion it is convenient to focus on two partly contingent aspects of the six-membered ring system. The first is related to the

fact that the two coordinated secondary sulfur atoms are asymmetric, and thus the total ring system can be in either the optically inactive *meso* (*R,S*) configuration or in the optically active forms (*R,R* or *S,S*). It is known that in platinum(II) complexes the asymmetric sulfur atom is relatively optically stable[5] and there is strong evidence to suggest that the same is true for cobalt complexes.[6] The second aspect is related to the conformation of the six-membered chelate ring which can adopt either a pseudochair or a number of pseudoboat conformations. The three conformations which we call chair, boat, and skew are shown in Figure 2. It should be noted that the skew conformation can exist in enantiomeric forms and that in the chair and skew conformations the hydrogen atoms are not eclipsed. We assume that the order of decreasing stability for these three conformers is chair > skew > boat for the following reasons. In the boat conformation the hy-

(5) F. G. Mann, *J. Chem. Soc.*, 1745 (1930).
(6) B. Bosnich and A. T. Phillip, *J. Am. Chem. Soc.*, **90**, 6352 (1968).

drogen atoms cannot arrange themselves in a proper staggered configuration, and furthermore, a hydrogen atom bonded to the central carbon atom of the trimethylene chain is in close proximity to an apical octahedral position (Figure 2). Both these effects will contribute to the instability of the boat conformation. The chair and skew forms appear to be devoid of serious nonbonding repulsions except that the chair conformer has a somewhat less crowded structure than the skew conformer. We assume that the chair conformer is more stable than the skew conformer because a recent X-ray determination of the conformation of the 1,3-diaminopropanecobalt ring in the tris(1,3-diaminopropane)cobalt(III) ion shows it to have a chair conformation.[7] However, the isolation[8] of two conformational isomers of the *trans*-dichloro-1,4,8,11-tetraazaundecanecobalt(III) ion suggests that the chair and skew conformers are of comparable stability. Thus, for our consideration of the stereochemistries adopted by the ETE ligand we shall make the assumptions (a) that the sulfur atoms can coordinate in three stable geometries, namely, the *meso* (R,S) form and the two optical isomers $(R,R$ and $S,S)$ and (b) that, *ceteris paribus*, within any given geometry of the coordinate sulfur atoms the chair conformation will be preferred over the skew conformation and the boat conformation is unlikely to occur under equilibrium conditions. Within these restrictions Figure 2 shows the possible isomers which can be obtained from the ETE ligand. Except for the chair *cis-β-R,S* isomer which is slightly strained, all of the stereochemistries are without strain, all can arrange the hydrogen atoms of all of the chelate rings in a staggered configuration, and there appears to be little congestion between neighboring ring systems in any of the isomers. It is evident from molecular models that when the coordinated sulfur atoms have an R,S geometry, the chair *cis-α* stereoisomer cannot be obtained whereas the R,R and S,S geometries allow for all three isomers.

For the TET ligand we focus attention on the central (*gauche*) ethanedithiacobalt ring in which the sulfur atoms can either be R,S or either R,R or S,S. If the sulfur atoms are in the R,S geometry, the ligand can take up the somewhat strained and crowded *trans* geometry and the strain-free *cis-β* geometry but not the *cis-α* stereochemistry, whereas if the sulfur atoms are R,R or S,S, all three forms are possible (Figure 2). In all these cases the six-membered rings can adopt the *chair* conformation and, except for the *trans-R,S* stereoisomer, there appears to be little strain and the nonbonding interactions appear to be small.

Finally, it should be noted for all three ligands that the asymmetry of the coordinated sulfur atoms is intimately connected with the chirality of all of the chelate rings and with the chirality of the over-all stereochemistry—all three must be compatible.

2. Chemistry and Stereochemistry

When air is passed through a methanol solution containing the EEE ligand and cobalt chloride, a rapid reaction occurs to produce a deep brown solution containing the sparingly (methanol) soluble oxygen adduct (peroxo complex). This complex is decomposed by hydrochloric acid to give to the deep blue $CoEEECl_2^+$ ion. Under similar conditions the ETE and TET ligands do not consistently give the desired dihalogenocobalt(III) complexes. The complexes of these latter two ligands were prepared as the dinitro derivatives which were then converted to the dichloro complexes. The ETE ligand gave a mixture of green and red-violet $CoETECl_2^+$ isomers while the TET ligand gave a mixture of red-violet and blue $CoTETCl_2^+$ isomers. All of these complexes were separated by fractional crystallization of their perchlorate salts. The stereochemistries were inferred from their visible absorption and nmr spectra in deuterated dimethyl sulfoxide solution.

The *cis-α-*, *cis-β-*, and *trans*-dichloro complexes should have different visible absorption spectra. In particular the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition should split differently for each of the isomers. The expected splittings can be calculated semiempirically[9] in terms of the spectrochemical effects of the donor atoms which are arranged differently in the three isomers. The results of such a calculation for the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition are shown in Table I. In this table the effect of π bonding has been neglected and only the σ-bonding contributions to the spectral shifts are given. It is readily shown, however, that the effect of π bonding will not alter these splitting patterns.

TABLE I

Transition	*cis-α*	*cis-β*	*trans*
$d_{xz} \rightarrow d_{x^2-z^2}$	$\frac{1}{4}\delta_s + \frac{1}{4}\delta_{Cl}$	$\frac{1}{4}\delta_s + \frac{1}{4}\delta_{Cl}$	$\frac{1}{4}\delta_s + \frac{1}{2}\delta_{Cl}$
$d_{yz} \rightarrow d_{y^2-z^2}$	$\frac{1}{4}\delta_s + \frac{1}{4}\delta_{Cl}$	$\frac{1}{4}\delta_s + \frac{1}{2}\delta_{Cl}$	$\frac{1}{4}\delta_s + \frac{1}{2}\delta_{Cl}$
$d_{xy} \rightarrow d_{x^2-y^2}$	$\frac{1}{2}\delta_s + \frac{1}{2}\delta_{Cl}$	$\frac{1}{2}\delta_s + \frac{1}{4}\delta_{Cl}$	$\frac{1}{2}\delta_s$

In constructing Table I we have used the position of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the $Co(NH_3)_6^{3+}$ ion as reference and δ_s and δ_{Cl} refer, respectively, to the differences in energy between this transition of $Co(NH_3)_6^{3+}$ and that of the complexes $Co(SR_2)_6^{3+}$ and $CoCl_6^{3-}$. The effect of the sulfur and chloride groups will be to shift the components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band to the red region compared to $Co(NH_3)_6^{3+}$; the shift due to chloride will be greater than that due to sulfur.[10]

Thus we expect that, of the three isomers, the *cis-α* isomers should have one component shifted most to the red region and the *trans* isomer should have one component closest to the transition of the reference compound. The amount of splitting between the components for the *cis-α* and *trans* isomers will be about the same and is greater than the spread of splitting of the *cis-β* isomer. This latter complex is expected to have the components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition occurring between the most displaced component of the *cis-α*

(7) Y. Saito, T. Nomura, and F. Marumo, *Bull. Chem. Soc. Japan*, **41**, 530 (1968).

(8) H. G. Hamilton and M. D. Alexander, *J. Am. Chem. Soc.*, **89**, 5065 (1967).

(9) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

(10) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London, 1962.
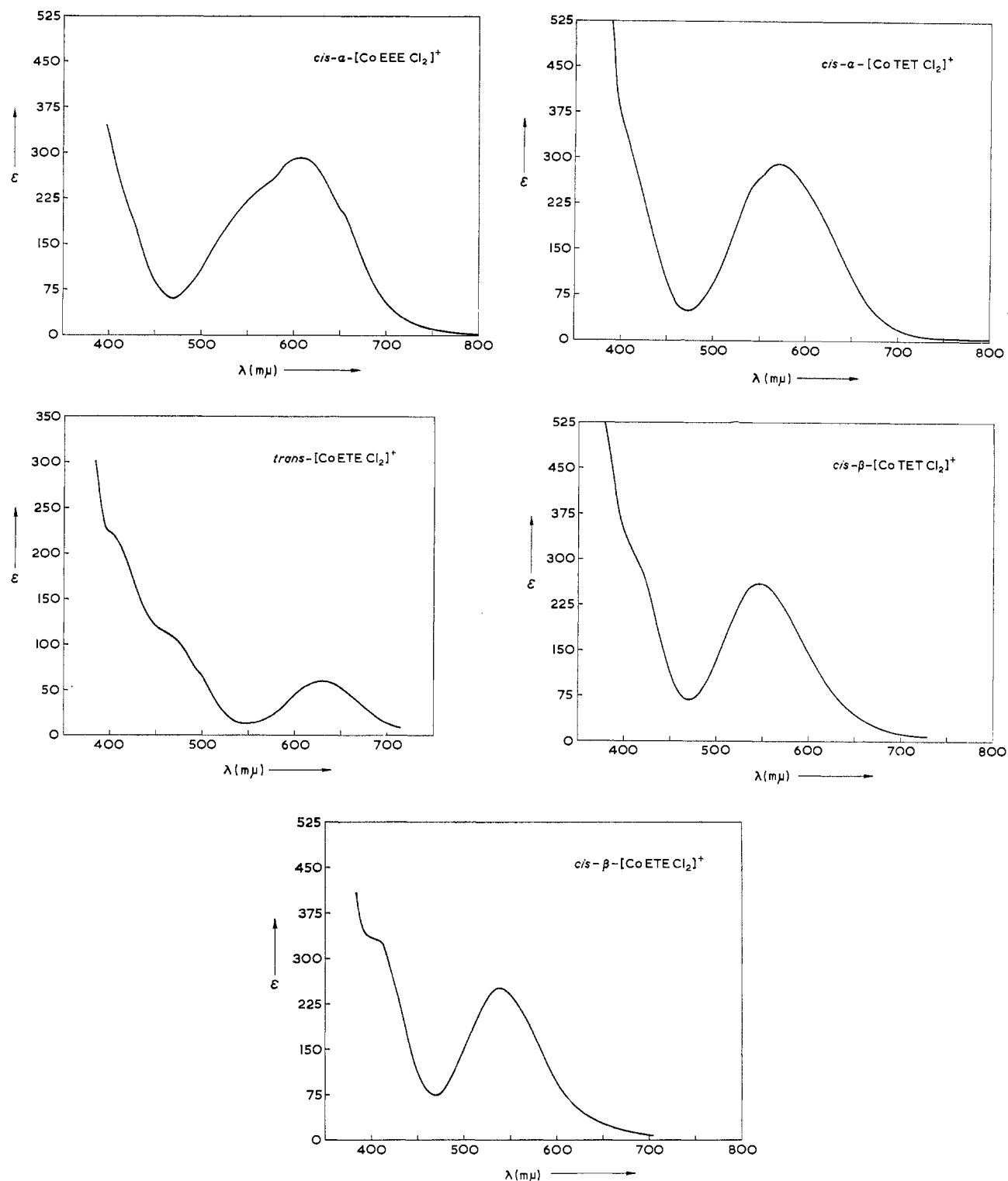
Figure 3.—The visible absorption spectra of the complexes *cis*-α-CoEEECl$_2$+, *trans*-CoETECl$_2$+, *cis*-β-CoETECl$_2$+, *cis*-α-CoTETCl$_2$+, and *cis*-β-CoTETCl$_2$+.

isomer and the least displaced component of the *trans* isomer.

Figure 3 shows the visible absorption spectra of the blue, red-violet, and green isomers of the various dichloro complexes formed by the three ligands. We assign the blue complexes to the *cis*-α configuration, the red-violet complexes to the *cis*-β configuration, and the green complexes to the *trans* configuration on the follow-

ing spectral evidence. The two blue complexes Co-EEECl$_2$+ and CoTETCl$_2$+ have almost the same visible spectra as the *cis*-α-CoPEPCl$_2$+ ion (PEP = 1,8-dimethyl-1,8-diamino-3,6-dithiaoctane) whose *cis*-α configuration has been established on the basis of nmr and circular dichroism data.[11] As can be seen (Figure 3)

(11)   B. Bosnich and A. T. Phillip, *J. Chem. Soc.*, in press.

TABLE II

Compound	Color	λ_{max},[a] mμ	ϵ[b] at λ_{max}	Λ_M[c]	τ(N–H)[d]
cis-α-[CoEEECl₂]ClO₄	Blue	607	290	100	4.3, 4.8
cis-α-[CoEEEBr₂]ClO₄	Green	620	394	120	4.5, 4.9
cis-α-[CoEEE(NO₂)₂]ClO₄	Yellow	457	525	111	4.2, 5.2
cis-α-[CoEEE(NCS)₂]ClO₄	Red-brown	527	870	89	3.9, 6.5 sh
cis-α-[CoEEE(N₃)₂]ClO₄	Brown-green	543	755	96	4.5, 5.2
cis-α-[CoEEEox]ClO₄	Red	518	223	81	4.4, 4.9
cis-α-[CoEEEbipy](ClO₄)₃	Brown	486	384	316	. . .
cis-β-[CoETECl₂]ClO₄	Red-violet	537	250	84	3.75, 4.1, 4.25, 6.15
trans-[CoETECl₂]ClO₄	Green	630	60	80	4.15
cis-α-[CoTETCl₂]ClO₄	Blue	570	290	84	. . .
cis-β-[CoTETCl₂]ClO₄	Red-violet	545	258	76	. . .

[a] λ_{max} refers to the maximum absorption of the first d–d transition ($^1A_{1g} \rightarrow {}^1T_{1g}$). The apparent disparity between the two blue forms and the two red-violet forms arises from differences in intensity of the components of the split manifold and is not due to the positions of the components (Figure 3). [b] ϵ refers to the extinction coefficient at maximum absorption. The spectra of the EEE complexes were taken in water and the others were taken in 2 M HCl. [c] Λ_M (cm² ohm⁻¹ mol⁻¹) is the molar conductance of 10^{-3} M solutions in water at 20°. [d] N–H proton nmr in deuterated DMSO; TMS reference.

the splitting of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band is poorly resolved in these complexes although it is evident in the Co-EEECl₂⁺ ion as two shoulders which occur at 645 and 550 mμ. The circular dichroism data[11] of the cis-α-CoPEPCl₂⁺ ion identify these two components at about 635 and 550 mμ, respectively. The lowest energy (two-component) transition of the green Co-ETECl₂⁺ ion occurs at 630 mμ while the higher energy component, which is poorly resolved, probably occurs at about 500 mμ (Figure 3). These observations are consistent with the predictions of Table I if we assign the blue isomers to the cis-α configuration and the green isomer to the *trans* geometry. The $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the red-violet complexes has a maximum absorption at about 535 mμ and shows evidence of splitting to lower energies. This is consistent with the expectations emanating from Table I and supports our assignment of the cis-β configuration for these red-violet complexes. Further support for these assignments is afforded by their nmr spectra in deuterated dimethyl sulfoxide.

The nmr of these complexes is complicated in the regions where the aliphatic protons absorb but the rather broad absorptions shown by the amino protons provide positive stereochemical information. The blue CoEEECl₂⁺ ion shows two signals of equal area at τ 4.3 and 4.8, the red-violet CoETECl₂⁺ ion shows four signals of equal area at τ 3.75, 4.1, 4.25, and 6.15, and the green CoETECl₂⁺ ion shows only one signal at τ 4.15. These observations are consistent with the assignments made on the basis of the visible absorption spectra because, of the four N–H protons in these complexes, two pairs are environmentally equivalent in the cis-α geometry, no two are equivalent in the cis-β geometry, and all are essentially equivalent in the *trans* geometry. The N–H proton signals shown by the blue and red-violet CoTETCl₂⁺ ions occur over about 3τ and do not show a simple pattern. It seems probable that these complex nmr patterns are due to the presence of a number of conformational isomers which are thermally accessible because of the greater flexibility of the terminal six-membered ring systems. The various complexes of the type CoEEEX₂⁺ (X⁻ = Br⁻, N₃⁻, NCS⁻, NO₂⁻, oxalate) all show two N–H proton signals

and, on this basis, are assigned the cis-α configuration. The relevant physical data for these and the CoEEE-bipy³⁺ ion are collected in Table II.

The present series of complexes is relatively stable in acid solutions at room temperature but the dihalogeno complexes are susceptible to very rapid base hydrolysis in alkaline solutions. Although in basic media the initial reaction is undoubtedly one of hydroxide substitution of the chloro ligands, there is a subsequent reaction which occurs and which leads to the precipitation of a brown material. We have not investigated this subsequent reaction in any detail but it appears that the process involves reaction between the coordinated ligand and hydroxide ions. Nearly all of these dithiadiamino complexes are very sensitive to hydroxide ions, and, in the case of the cis-α-CoEEEox⁺ ion, for example, the complex cannot be recrystallized from hot neutral water without considerable decomposition.

In order to make meaningful comparisons of the preferred isomeric forms adopted by any one ligand it is necessary to distinguish between two types of equilibria: (a) those which involve the movement of the chelate arms with respect to a fixed configuration of the sulfur atoms and (b) those which are established by circumstances where both the sulfur atoms and the chelate are allowed to move freely. This distinction is important because, as we have seen, the configurations of the sulfur atoms have a strong influence on the final stereochemical outcome. We have investigated the equilibria of the first kind by the following methods.

When a 2 M hydrochloric acid solution of the cis-α-[CoEEECl₂]ClO₄ complex is boiled for 5 hr, a small violet shift of the visible absorption spectrum occurs which is undoubtedly due to the production of a small standing concentration of the aquo species. The addition of perchloric acid to this solution eventually leads to the almost quantitative precipitation of the blue cis-α-[CoEEECl₂]ClO₄ starting complex. Prolonging boiling of dilute methanol solutions of the cis-α-[CoEEECl₂]ClO₄ complex eventually leads to decomposition but at all times the remaining complex is spectrophotometrically identical with the starting material. (Under these latter circumstances the cis-Co(trien)-

Cl_2^+ ion is converted to the *trans* isomer.[4]) These results are in accord with the prediction, based on conformational arguments, that the *cis-α* geometry is the most stable for the EEE ligand.

The equilibrium between the green and red-violet [CoETECl$_2$]ClO$_4$ complexes was measured spectrophotometrically at 80° in 2 M hydrochloric acid solutions. Starting with either the red-violet *cis-β*-[CoETECl$_2$]ClO$_4$ or the green *trans*-[CoETECl$_2$]ClO$_4$ complexes an essentially constant spectrum was obtained and in both cases corresponded to a mixture of about 60% *cis-β*-CoETECl$_2^+$ and 40% *trans*-CoETECl$_2^+$. These proportions, however, are only approximate because of the presence of a small concentration ($\sim$5%) of aquo species in the solution. The presence of these aquo species was inferred from the nature of the spectrophotometric changes during the reactions. Thus the initial spectrophotometric changes do not give isosbestic points although after about 1 hr the reaction settles down and the products are formed in essentially constant proportions. The absence of isosbestic points initially is due to a small blue shift in the spectrum caused by the coordination of the spectrochemically stronger aquo group. This initial blue shift is seen clearly in the early stages of the isomerization of the *cis-β*-CoETECl$_2^+$ species. Like most cobalt(III) isomerizations, it seems probable that the present systems isomerize mainly *via* the aquo species.

The equilibrium between the red-violet and blue [CoTETCl$_2$]ClO$_4$ complexes was measured at 40° in 2 M hydrochloric acid solution. The red-violet isomer slowly changed to the blue form and after about 6 hr an essentially constant spectrum was obtained. An analysis of the final spectrum indicated that more than 95% of the blue isomer was present at equilibrium. Under the same conditions the blue isomer showed only a slight blue shift in its spectrum which was undoubtedly due to a small standing concentration of the aquo species. We have been unable to detect any of the red-violet form in either of the equilibration experiments although a dilute perchloric acid solution of the blue isomer does precipitate the less soluble red-violet isomer on standing at room temperature for 1 month. As in the ETE systems the isomerization probably proceeds *via* the aquo species.

The simplest way of achieving the equilibria of the second kind without excessive decomposition is by an electron-transfer mechanism where scrambling can occur *via* a cobaltous intermediate. We have reported elsewhere[11] that the reaction between NO$_2^-$ ions and the *cis-α*-CoPEPCl$_2^+$ ion leads, by an electron-transfer process, to complete isomeric equilibration and we have used this fact in order to investigate the equilibria of the second kind in the complexes described here.

The *cis-α*-CoEEECl$_2^+$, *cis-β*-CoETECl$_2^+$, *trans*-CoETECl$_2^+$, *cis-β*-CoTETCl$_2^+$, and *cis-α*-CoTETCl$_2^+$ ions were treated with NO$_2^-$ ions to form the dinitro complexes. All of the substitutions are characterized by an induction period similar to that described for the *cis-α*-CoPEPCl$_2^+$ ion and in the case of each of the

CoETECl$_2^+$ and CoTETCl$_2^+$ isomeric pairs the spectrum of the solutions containing the dinitro products was the same for each pair irrespective of the starting isomer. These observations strongly suggest an electron-transfer substitution process which leads to ligand scrambling. When each of these dinitro complexes was converted back to the dichloro complexes, the CoEEE(NO$_2$)$_2^+$ species gave only *cis-α*-CoEEECl$_2^+$, CoETE(NO$_2$)$_2^+$ gave a mixture of 60% *cis-β*-CoETECl$_2^+$ and 40% *trans*-CoETECl$_2^+$, and CoTET(NO$_2$)$_2^+$ gave only *cis-α*-CoTETCl$_2^+$. The details of these interconversions are given in the Experimental Section. These results are not totally conclusive, however, since (a) the equilibrated species are the dinitro and not the dichloro complexes and (b) there may be some isomeric change during the dinitro to dichloro interconversions; but they do allow for the establishment of the equilibrium of the donor sulfur atom geometries. Furthermore, in the preparative reaction of the CoTETCl$_2^+$ ions, the decomposition of the dinitro species to form the dichloro complexes leads, under similar conditions, to the isolation of the less stable *cis-β*-CoTETCl$_2^+$ ion. This latter fact suggests that the dinitro to dichloro transformation does not initially lead to the establishment of the equilibria of the first kind and so the present results are probably meaningful in the sense that the formation of any unstable isomers would be detected if they occurred in concentrations greater than 10% of the reaction mixture.

Thus both types of equilibria lead to the same isomeric proportions and it would appear that the complexes isolated from the preparative reactions have their donor sulfur atoms in the most stable configurations.

3. Discussion

Our initial premise that ring sizes and ring conformations of these quadridentate ligands have an important influence on the final stereochemistries of their complexes has been substantiated by the results described here. However, these considerations alone are not sufficient in all cases to predict the preferred stereochemistry although they do suggest the stereochemistries which are likely to be unstable. Thus, we have found that the CoEEEX$_2^{n+}$ complexes all have the *cis-α* geometry as would be predicted from the conformational arguments given previously but not all the isomers allowed on conformational arguments are found to occur under equilibrium conditions for the CoETECl$_2^+$ and CoTETCl$_2^+$ complexes. We may rationalize the isomeric behavior of the CoETECl$_2^+$ complexes if we assume that the most stable configuration of the sulfur atoms in this complex is R,S. This, as we have seen (Figure 3), allows the ligand to take up the experimentally observed *cis-β* and *trans* geometries but not the *cis-α* geometry. The fact that the CoTETCl$_2^+$ complex can adopt the *cis-α* geometry establishes (Figure 2) that the sulfur atoms are R,R or S,S and thus the ligand should be able to adopt strainlessly all of the three possible isomers. The

factors which favor the almost exclusive presence of the cis-α-CoTETCl$_2$+ at equilibrium are not clear.

It is interesting to contrast the behavior of these ligands with their all-nitrogen analogs. Unlike the CoEEECl$_2$$^{n+}$ complexes, the stereochemistries adopted by the corresponding cobalt(III) derivatives of the ligand triethylenetetramine are dependent on the nature of the X ligands.[12] The trans-(R,S)-Co-2,3,2-tetCl$_2$+ ion (2,3,2-tet = 1,4,8,11-tetraazaundecane) is more stable than the corresponding cis-β isomer and is present almost exclusively at equilibrium[3] whereas the analogous CoETECl$_2$+ system gives a mixture which contains somewhat more of the cis-β than the trans isomer. Finally, whereas the cis-α-CoTETCl$_2$+ ion is the most stable isomer, the trans-dichloro isomer of the all-nitrogen analog is the most stable.[13] In general terms, therefore, it would appear that the sulfur ligands tend to prefer cis geometries, whereas the all-nitrogen analogs tend to favor the trans isomers. The reason for this general tendency is probably connected with the larger size of the sulfur atom. Scale molecular models suggest that increasing the size of the two inner donor atoms of quadridentate chelates will tend to favor cis configurations over the trans configurations.

4. Experimental Section

The ligands EEE, ETE, and TET were prepared by methods described elsewhere.[14]

Preparations. cis-α-[CoEEECl$_2$]ClO$_4$.—To a solution of EEE (16 g) in methanol (100 ml) was added a solution of cobalt chloride hexahydrate (21 g) in methanol (300 ml). A dark brown solution resulted and air was drawn through it for 3 hr, during which time the color intensified and some brown crystals separated. Hydrochloric acid (20 ml, 10 N) was added to the resulting mixture and after warming on a steam bath for 10 min a clear, deep blue solution was obtained. Most of the methanol was removed by distillation to give a residual volume of about 150 ml, and upon the addition of sodium perchlorate (10 g) in water (50 ml), deep blue crystals of the complex were obtained (10.5 g; 30%). These were collected and washed with a little water followed by acetone. They were recrystallized from hot 2 M hydrochloric acid by the addition of sodium perchlorate. After several hours the crystallization was complete. Anal. Calcd for C$_6$H$_{16}$N$_2$O$_4$S$_2$Cl$_3$Co: C, 17.6; H, 3.9; N, 6.9; S, 15.7. Found: C, 17.8; H, 4.1; N, 6.8; S, 15.9.

cis-α-[CoEEEBr$_2$]ClO$_4$.—Hydrobromic acid (2 ml; 48%) was added to a hot solution of cis-α-[CoEEECl$_2$]ClO$_4$ (0.68 g) in water (20 ml). The mixture was warmed on a steam bath for 10 min during which time the color changed from blue to green. After filtration, sodium perchlorate (2 g) in water (5 ml) was added and upon cooling deep green crystals were obtained. These were collected and washed with a little water followed by acetone. Anal. Calcd for C$_6$H$_{16}$N$_2$O$_4$S$_2$ClBr$_2$Co: C, 14.5; H, 3.2; N, 5.6; S, 12.9. Found: C, 14.6; H, 3.1; N, 5.8; S, 13.0.

cis-α-[CoEEE(N$_3$)$_2$]ClO$_4$.—A solution of sodium azide (0.165 g) in water (5 ml) was added to a hot solution of cis-α-[Co-EEECl$_2$]ClO$_4$ (0.52 g) in water (20 ml). Upon warming the resulting solution at 80° for 5 min a change from blue to deep green-brown occurred. Sodium perchlorate (2 g) in water (5 ml) was added to the hot filtered solution and on cooling deep green-brown, almost black crystals were obtained. These were col-lected and washed with a little cold water followed by methanol-ether (80% ether) and finally with ether (0.25 g; 47%). Anal. Calcd for C$_6$H$_{16}$N$_8$O$_4$S$_2$ClCo: C, 17.1; H, 3.8; N, 26.5; S, 15.2. Found: C, 17.5; H, 3.8; N, 26.7; S, 15.4.

cis-α-[CoEEE(NO$_2$)$_2$]ClO$_4$.—Sodium nitrite (0.15 g) in water (5 ml) was added to a hot solution of cis-α-[CoEEECl$_2$]ClO$_4$ (0.44 g) in water (15 ml) and the mixture was warmed on a steam bath for 5 min. Sodium perchlorate (1 g) in water (5 ml) was added to the resulting orange solution, and upon cooling, bright yellow crystals deposited. These were collected and washed with a little water followed by acetone (0.28 g; 60%). Anal. Calcd for C$_6$H$_{16}$N$_4$O$_8$S$_2$ClCo: C, 16.7; H, 3.7; N, 13.0; S, 14.9. Found: C, 16.9; H, 3.8; N, 12.9; S, 14.8.

cis-α-[CoEEE(NCS)$_2$]ClO$_4$.—Sodium thiocyanate (0.21 g) in water (5 ml) was added to a hot solution of cis-α-[CoEEECl$_2$]-ClO$_4$ (0.53 g) in water (20 ml). On warming the mixture at 80° for 5 min the color changed to deep red. The solution was filtered while hot and sodium perchlorate (2 g) in water (5 ml) was added. Upon cooling, the solution deposited dark reddish brown crystals which were collected and washed with a little iced water, then with acetone in ether (20% acetone), and finally with ether. Anal. Calcd for C$_8$H$_{16}$N$_4$O$_4$S$_4$ClCo: C, 21.2; H, 3.5; S, 28.2. Found: C, 21.3; H, 3.9; S, 28.1.

cis-α-[CoEEEbipy](ClO$_4$)$_3$.—2,2'-Bipyridyl (0.24 g) in methanol (5 ml) was added to a hot solution of cis-α-[CoEEECl$_2$]ClO$_4$ (0.64 g) in water (15 ml). The mixture was warmed at 50° just long enough to complete the change from blue to deep brown (ca. 1-2 min) and then without delay (disproportionation) the solution was filtered and quickly cooled in an ice bath. Sodium perchlorate (2 g) in water (5 ml) was added, and upon scratching the walls of the vessel, brown crystals were obtained (0.49 g; 45%). These were collected and washed with a little iced water, followed by acetone. Anal. Calcd for C$_{16}$H$_{24}$O$_{12}$S$_2$Cl$_3$Co: C, 27.7; H, 3.5; S, 9.2. Found: C, 28.2; H, 3.4; S, 9.4.

cis-α-[CoEEEox]ClO$_4$.—Lithium oxalate, prepared by dissolving lithium carbonate (0.11 g) and oxalic acid (0.135 g) in water (5 ml), was added to a hot solution of cis-α-[CoEEECl$_2$]-ClO$_4$ (0.61 g) in water (20 ml). The resulting bright red solution was acidified with concentrated perchloric acid (0.2 ml) and filtered while warm, and the complex was induced to crystallize by cooling to 0°. The red crystals were taken in water at 30°, filtered to remove some brown material, and cooled to 0°. Upon the addition of concentrated perchloric acid (0.5 ml), shiny bright red leaflets were obtained. These were collected and washed with a little iced water and finally with acetone. Anal. Calcd for C$_8$H$_{16}$N$_2$O$_8$S$_2$ClCo: C, 22.5; H, 3.8; S, 15.0. Found: C, 22.7; H, 4.2; S, 15.0

[CoETECl$_2$]ClO$_4$.—To an ice-cold solution of cobalt acetate tetrahydrate (2.5 g) in methanol (150 ml) was added sodium nitrite (1.4 g) in cold water (10 ml), and then, without delay, the ligand ETE (2.02 g) in hydrochloric acid (20 ml; 1 N) was added. The resulting brown solution was transferred to an ice bath and air was drawn through the solution for 2 hr during which time the color deepened and a brown solid deposited. Both the solid and solution were transferred into an evaporating dish and urea (1.2 g) was added. The mixture was heated on a steam bath and hydrochloric acid (5 ml; 10 N) was slowly added. Gas was evolved, the solid slowly dissolved, and the solution turned dark red. After 0.75 hr perchloric acid (1.2 ml; concentrated) was added to the now clear solution, which was then evaporated down under a stream of air for a further 0.25 hr during which time crystals began to appear. The whole mixture was cooled in an ice bath for 1 hr and the violet crystals (1.9 g) were collected and washed with acetone. A second crop was obtained by further evaporation and cooling (0.6 g). The product obtained by the above procedure consisted of a mixture of the green trans-[CoETECl$_2$]ClO$_4$ and red-violet cis-β-[CoETECl$_2$]ClO$_4$ complexes. These were separated as follows.

trans-[CoETECl$_2$]ClO$_4$.—The mixture of isomers (2.5 g) was taken up in boiling hydrochloric acid (30 ml; 5 M). The solution was filtered and allowed to cool to room temperature. After

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(13) B. Bosnich and M. L. Tucker, unpublished observations.

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3 hr the green needles of the *trans* complex were filtered off and washed with a little water and then with acetone (0.66 g). *Anal.* Calcd for $C_7H_{18}N_2O_4S_2Cl_3Co$: C, 19.9; H, 4.3; N, 6.6; Cl, 25.1. Found: C, 19.5; H, 4.3; N, 6.5; Cl, 24.9.

cis-β-[CoETECl₂]ClO₄.—After the addition of perchloric acid (1 ml; concentrated), the red-violet filtrate obtained after the separation of the *trans* isomer was allowed to stand in a refrigerator for 1 day. The red-violet needles thus obtained were washed with a little ice water and then with methanol (0.5 g). *Anal.* Calcd for $C_7H_{18}N_2O_4S_2Cl_3Co$: C, 19.9; H, 4.3; N, 6.6; Cl, 25.1. Found: C, 19.7; H, 4.3; N, 6.6; Cl, 25.2.

[CoTETCl₂]ClO₄.—The ligand TET (6.3 g) in methanol (30 ml) and hydrochloric acid (30 ml; 1 *N*) was added to an ice-cold solution of cobalt acetate tetrahydrate (7.5 g) in methanol (100 ml), followed by sodium nitrite (4.5 g) in water (10 ml). Air was passed through the solution for 2 hr during which time the initial bluish color faded and a brown solid precipitated. The resulting mixture was transferred to an evaporating dish on a steam bath and urea (3.6 g) in water (10 ml) was added. The solution was warmed and hydrochloric acid (30 ml; 10 *M*) was slowly added. The brown solid gradually dissolved with the evolution of gas to form, after about 0.5 hr of heating, a deep brown solution. After heating on the steam bath for a further 0.25 hr the solution became bluish. The clear solution was filtered and perchloric acid (6 ml; concentrated) was added. It was again heated on a steam bath under a current of air for 5 min whereupon deep purple crystals began to deposit. After cooling in an ice bath for 1 hr, these were collected and washed with a little iced water and then methanol. These crystals consisted of a mixture of the blue *cis-α-*[CoTETCl₂]ClO₄ and the red-violet *cis-β-*[CoTETCl₂]ClO₄ complexes. They were separated as follows.

cis-β-[CoTETCl₂]ClO₄.—The mixture of isomers (2.1 g) was taken up in boiling hydrochloric acid (35 ml; 5 *M*) and filtered. Red-violet needles were obtained after the filtrate was allowed to stand at room temperature for 3 hr. These were collected and washed with a little iced water followed by acetone. The filtrate remaining was brought to boiling and set aside overnight in a refrigerator. A second crop of red-violet crystals was obtained. These were filtered and washed as before (total yield 1.0 g). *Anal.* Calcd for $C_8H_{20}N_2O_4S_2Cl_3Co$: C, 22.0; H, 4.6; N, 6.4; Cl, 24.3. Found: C, 22.1; H, 4.7; N, 6.4; Cl, 24.4.

cis-α-[CoTETCl₂]ClO₄.—The filtrate remaining from the second crop of red-violet crystals was boiled for 5 min, and perchloric acid (1 ml; concentrated) was added. After allowing the now blue solution to stand in a refrigerator overnight, the resultant blue crystals were filtered and washed with a little iced water and then with acetone (0.4 g). *Anal.* Calcd for $C_8H_{20}N_2O_4S_2Cl_3Co$: C, 22.0; H, 4.6; N, 6.4; Cl, 24.3. Found: C, 21.6; H, 4.6; N, 6.4; Cl, 24.2.

All of these compounds were stored over calcium chloride.

Chemical Interconversions.—The following general method was used for converting the dichloro complexes to the dinitro derivatives and then back to the dichloro complexes. The dichloro complex (5×10^{-5} mol) and sodium nitrite (10^{-4} mol) were dissolved in water (25 ml) and were heated to 80°. The color changed within a few minutes to orange and the solution was heated for a further 5 min and cooled, and the visible spectrum was taken. (The rate of nitrite substitution is more than ten times as fast as aquation, which suggests that the former is Co(II) catalyzed.) The resulting solution (20 ml) was made up to 25 ml with concentrated hydrochloric acid and heated with urea (1.1×10^{-4} mol) at 80°. The color changed rapidly and the conversion was complete in 0.5 hr. (This time is insufficient for complete equilibration of the dichloro complexes and any isomers formed in greater than 10% yield would be detected.) The solutions were cooled and the dichloro products were analyzed spectrophotometrically.

Instruments.—The absorption spectra were measured using a Unicam SP 800 (recording) spectrophotometer and the nmr spectra were taken by means of a Varian HA-100 spectrometer.

Contribution from the Departments of Chemistry, University of North Carolina, Chapel Hill, North Carolina, and Stanford University, Stanford, California

Synthesis of σ-Bonded Allenyl Complexes of Iridium, Platinum, and Cobalt

By JAMES P. COLLMAN, JAMES N. CAWSE, and JUNG W. KANG

A series of complexes containing the novel σ-bonded allenyl ligand has been prepared from iridium(I), platinum(0), and cobalt(I) compounds. The complexes were formed by Sn2′ attack on substituted 3-halopropynes. Provisional structures have been assigned to these complexes on the basis of their infrared, Raman, and nmr spectra. Kinetic evidence is presented demonstrating the second-order nature of the reaction. The reductive cleavage of the metal–carbon bond in the cobalt complexes, yielding allenes and the regenerated cobalt(I) species, has been demonstrated.

Introduction

The central element in low-valent organo–transition metal complexes often possesses nonbonded d-electron pairs which can act as nucleophilic centers.[1] Alkylation of such a metal is a conceptual oxidation. Thus reactions between alkylating or acylating agents and low-valent transition metals can be included in the broad class of *oxidative-addition* processes.[2] In the course of studying oxidative additions of d⁸ complexes, we treated Vaska's[3] iridium(I) complex 1 with α-haloacetylenes and were surprised to find σ-bonded metalloallenes to be the major products of this reaction. Further investigation revealed that other transition metal centers which are susceptible to oxidative addition react with α-haloacetylenes in this way and that the σ-bonded metalloallenes are stable members of a hitherto little-known type of transition metal complex.

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