Polyhedral Metallocarborane Chemistry. Thermal Rearrangements of Bimetallic Cobaltacarboranes

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Abstract: The chemical relationship of metallocarboranes containing two transition metal vertices to other polyhedral boron species was experimentally investigated by examining the thermal polyhedral rearrangements of representative examples of 10-, 11-, and 12-vertex bimetallic cobaltcarboranes, $(C_5H_5)_2Co_2C_2B_nH_{n+2}$. Rearrangements involving migration of cobalt as well as boron and carbon atoms in the polyhedral surface were observed. Several new bi- and trimetallic species were synthesized in the course of these studies and improved preparative routes to known metallocarboranes were discovered. Similarities in the polyhedral chemistry of the series $(C_5H_5)_2Co_2C_2B_{n-2}H_n$, $C_5H_5CoC_2B_{n-1}H_{n+1}$, and $C_2B_nH_{n+2}$ are discussed.

One of the earliest general reactions observed for closo polyhedral boranes, $B_{n+2}H_{n+2}{}^{2-}$, was thermal polyhedral rearrangement.[2] The isoelectronic carboranes, $CB_{n+1}H_{n+2}{}^-$ and $C_2B_nH_{n+2}$, were also found to undergo such reactions[3] and similar polyhedral rearrangements were observed in both icosahedral[4a] and nonicosahedral[4b] cobaltacarboranes, $C_5H_5CoC_2B_nH_{n+2}$. The recent development of several general metallocarborane syntheses, *viz.*, polyhedral expansion,[5,6] polyhedral contraction,[7,8] and thermal metal transfer,[9] has allowed the isolation of numerous bimetallic cobaltacarboranes of the general formula $(C_5H_5)_2Co_2C_2B_nH_{n+2}$. In efforts to further define the chemical consequences of substitution of transition metals in carborane polyhedra,[10,11] we investigated the polyhedral rearrangements of representative examples of 10-, 11-, and 12-vertex cobaltacarboranes containing two metal vertices. Some preliminary results have already been reported.[12]

Results and Discussion

Ten-Vertex Polyhedra: $(C_5H_5)_2Co_2C_2B_6H_8$. The green bimetallocarborane $2,6,1,10\text{-}(C_5H_5)_2Co_2C_2B_6H_8$[13] (I) (Figure 1) synthesized by the polyhedral expansion method,[5] was the first bimetallic species in which adjacent cobalt vertices were crystallographically confirmed.[15] Thermal rearrangement of I in hexadecane at reflux allowed the isolation of a red species II. The mass spectrum of II exhibited a cutoff at m/e 346 corresponding to the $^{11}B_6{}^{12}C_{12}{}^1H_{18}{}^{59}Co_2{}^+$ ion and high resolution mass spectrometry established that II was an isomer of I. The electronic spectrum and cyclic voltammetric data are reported in the Experimental Section. The ^1H nmr spectrum of II (Table I) contained a single broad carborane CH resonance and a single sharp signal for the cyclopentadienyl protons. Three doublets of relative area 2:2:2 were observed in the 80.5-MHz ^{11}B nmr spectrum (Table II). Assuming the carbon atoms do not migrate from their favored low coordinate positions[4b,5] 1 and 10 in I, the spectroscopic data uniquely define the structure of II as $2,7,1,10\text{-}(C_5H_5)_2Co_2C_2B_6H_8$ (Figure 1). This assignment is consistent with electronic spectral correlations for bimetallic cobaltacarboranes[12] with respect to the relative position of the cobalt vertices (*i.e.*, adjacent or nonadjacent) and agrees with empirical ^{11}B nmr correlations regarding low coordinate boron vertices adjacent to transition metals.[5,16]

The conversion of I to II, therefore, necessarily involves the movement of cobalt atoms since the cobalt–cobalt interaction is broken. While previous metallocarborane rearrangements could be explained by cobalt as well as boron and carbon atom migrations, this isomerization clearly demonstrates the mobility of the C_5H_5Co vertex in the polyhedral surface. This is not unexpected when the similarities of the C_5H_5Co and BH vertices with respect to skeletal bonding are considered.[10,11,17]

11-Vertex Polyhedra: $(C_5H_5)_2Co_2C_2B_7H_9$. Four isomers of $(C_5H_5)_2Co_2C_2B_7H_9$ were available for study, three formed by the polyhedral expansion technique[6] and the fourth isolated as a minor product from the large scale preparation of $C_5H_5CoC_2B_9H_{11}$.[8] This latter isomer III exhibited a mass spectrum cutoff at m/e 358 corresponding to the $^{11}B_7{}^{12}C_{12}{}^1H_{18}{}^{59}Co_2{}^+$ ion. A high resolution mass measurement (calcd, 358.080453; found, 358.0805 ± 0.0004) confirmed the $(C_5H_5)_2Co_2C_2B_7H_9$ formulation. Cyclic voltammetric data showed a reduction at -1.20 V and an oxidation at $+0.80$ V *vs.* SCE. The ^1H nmr spectrum of III (Table I) contained two carborane resonances and two signals for the cyclopentadienyl protons. Seven doublets of equal intensity were observed in the 80.5-MHz ^{11}B nmr spectrum (Table II). The downfield doublet at -86.0 ppm indicated a boron in a low coordinate position next to a high coordinate cobalt.[5,16] The greenish brown color and an absorption at 580 mμ in the uv indicated a cobalt–cobalt bond was possible.[12] Assuming an octadecahedral geometry, the spectral data allow a number of possible structural isomers for III. A likely structure for III is $1,6,2,4\text{-}(C_5H_5)_2Co_2C_2B_7H_9$ since this isomer contains adjacent carbon atoms, as they were initially in the starting complex.[8]

Thermal rearrangement of III was effected over a 20-hr period at reflux in heptane. The isomeric octadecahedral species obtained was the green $1,4,2,3\text{-}(C_5H_5)_2Co_2C_2B_7H_9$[6] (IV) (Figure 2). In the rearrangement, therefore, the migration of a high coordinate carbon atom in III to a preferred low coordinate position in IV had occurred. Thermal rearrangement of the isogeometric $1,2,4\text{-}C_5H_5CoC_2B_8H_{10}$ to the 1,2,3-isomer involves an identical carbon atom movement.[4]

Compound IV can also be obtained by the thermal rearrangement of the red-brown $1,8,2,3\text{-}(C_5H_5)_2Co_2C_2B_7H_9$[6] (V) (Figure 2) in heptane at reflux over a 4-hr period. In this isomerization two nonadjacent cobalt vertices in V move to adjacent positions in IV. Considering the possible polyhedral equivalence of the C_5H_5Co and BH vertices, this is not particularly unusual. However, the most stable ten-vertex bimetallocarborane, II, had nonadjacent cobalt atoms and one would expect a similar result for eleven-vertex polyhedra. Indeed this is the case (*vide infra*) for IV is simply an isolable intermediate in the isomerization of V to the most stable octadecahedral bimetallic complex

Table I. ¹H Nmr Spectra

Compound	Resonance τ (rel area)	Assignment
II	4.98 (5)	C_5H_5
	8.0 (1)	CH
III	5.04, 5.42	C_5H_5
	5.35, 4.32	CH
IV	4.50 (5), 4.75 (5)	C_5H_5
VI	4.67 (5), 5.10 (5)	C_5H_5
	6.3 (2)	CH
VII	5.25	C_5H_5
X	4.48 (5), 4.71 (5)	C_5H_5
	6.3 (1), 7.6 (1)	CH
XI	4.78 (5), 4.95 (5)	C_5H_5
XII	5.2	C_5H_5
XIII	5.0 (5), 5.35 (5)	C_5H_5
XIV	4.89 (5), 4.68 (5)	C_5H_5
	7.8 (2)	CH
XV	4.45	C_5H_5
XVI	4.46 (5), 4.98 (5)	C_5H_5

Table II. The 80.5 MHz ¹¹B Nmr Spectra

Compound	Solvent	Chemical shift[a]
II	$(CD_3)_2CO$	-30.5 (2), -4.6 (2), $+17.8$ (2)
III	CH_2Cl_2	-86.0 (1), -15.1 (1), -13.5 (1), -10.6 (1), -7.4 (1), -5.3 (1), $+19.8$ (1)
IV	$(CD_3)_2CO$	-15.1 (1), -6.4 (1), -2.8 (1), -1.2 (1), -0.4 (1), $+0.8$ (1), $+17.9$ (1)
VI	$(CD_3)_2CO$	-30.1 (2), -15.9 (2), $+4.1$ (2), $+21.2$ (1)
VII	CD_3CN	-27.4 (2), -19.0 (1), -5.0 (4)
X	CD_3CN	-14.1 (1), -9.4 (1), -4.2 (1), -0.6 (1), $+0.8$ (1), $+2.8$ (1), $+11.7$ (1), $+15.9$ (1)
XI	$CDCl_3$	-15.9 (2), -6.0 (1), -2.6 (1), $+3.0$ (1), $+5.4$ (1), $+8.1$ (1), $+20.1$ (1)
XII	CD_3CN	-14.0 (2), -6.0 (2), $+5.5$ (2), $+20.0$ (2)
XIII	CD_3CN	-20.6 (1), -1.7 (1), -7.6 (1), $+2.7$ (2), $+10.3$ (1), $+20.6$ (1), $+24.4$ (1)
XIV	$CDCl_3$	-15.0 (2), -10.3 (1), -2.2 (1), $+1.6$ (2), $+17.8$ (2)
XV	$(CD_3)_2CO$	-1.4 (4), $+6.4$ (4)
XVI	$(CD_3)_2CO$	-15.5 (1), -6.9 (1), $+0.6$ (1), $+5.0$ (1), $+5.8$ (1), $+9.9$ (1), $+17.1$ (1), $+20.5$ (1)

[a] Chemical shift, ppm from $BF_3 \cdot OEt_2$, (rel area).

Figure 1. The rearrangement of 2,6,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$ (I) to 2,7,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$ (II). (The enantiomeric 2,9,1,10-structure of I is pictured here.)
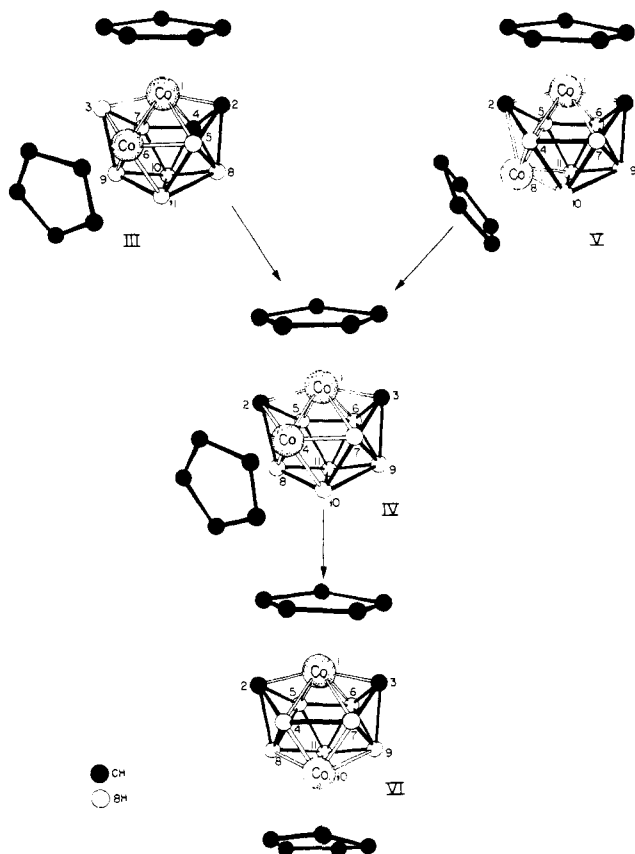

Figure 2. Rearrangements of octadecahedral bimetallocarboranes. The specific enantiomers shown have no mechanistic implications.

1,10,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$[6] (VI) (Figure 2) which has nonadjacent cobalt vertices.

The formation of VI from IV can be effected in undecane at reflux in 6.5 hr or in octane at reflux over a 68-hr period. Several additional interesting metallocarboranes were isolated in these IV to VI isomerizations. The main products of the undecane rearrangement of IV, in addition to VI, were two 12-vertex trimetallic species $(C_5H_5)_3Co_3C_2B_7H_9$, which were characterized by mass spectroscopy and ¹H and ¹¹B nmr spectra.[18] This result directly parallels the thermal metal transfer reaction[9] observed for the analogous 11-vertex monometallic 1,2,3-$C_5H_5CoC_2B_8H_{10}$ in which icosahedral products containing one additional transition metal vertex were formed from octadecahedral precursors.[19]

When IV was converted to VI in octane over a long time period, a new red-orange metallocarborane, VII, was obtained. The mass spectrum of VII contained a cutoff at m/e 358 corresponding to the $^{11}B_7{}^{12}C_{12}{}^{1}H_{19}{}^{59}Co_2{}^+$ ion and a high resolution mass spectrum confirmed this formulation. A single cyclopentadienyl signal was found in the ¹H nmr spectrum (Table I). The 80.5-MHz ¹¹B nmr spectrum (Table II) contained a highly symmetric 2:1:4 pattern of boron resonances. If VII has an octadecahedral geometry, six structures are consistent with the spectroscopic data. Assuming the carbon atoms are in the favored low coordinate positions 2 and 3, and assuming the cobalt vertices are nonadjacent since the compound is red-orange in color,[12] all but one structural possibility, 8,9,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ is eliminated.

This possible structure for VII is unusual since a IV to VII rearrangement would involve movement of a cobalt vertex out of the high coordinate position 1. Although this is consistent with the ¹¹B pattern and the equivalence of the CoC_5H_5 vertices, such a thermal migration is not in accord with empirical thermal rearrangement rules derived from

monometallocarborane isomerization studies.[4] A more likely explanation for the formation of VII is that initially IV undergoes a thermal metal transfer reaction to an icosahedral trimetallic $(C_5H_5)_3Co_3C_2B_7H_9$ which is unstable and decomposes to VII. This is reasonable in two respects: (1) stable trimetallic species were formed from IV under alternative conditions (vide supra) and (2) an example of the proposed decomposition, i.e., $(C_5H_5)_3Co_3C_2B_7H_9 \rightarrow (C_5H_5)_2Co_2C_2B_7H_9$, has been previously observed.[6] Furthermore, as expected,[4] VII is not the most stable isomer of the 11-vertex series and can be further rearranged to
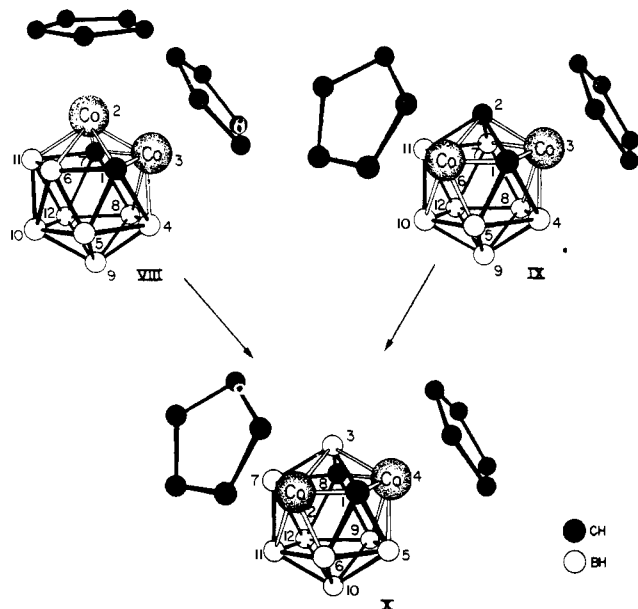
Figure 3. Rearrangement of 2,3,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (VIII) and 3,6,1,2-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (IX) to 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (X). (The enantiomeric 2,4,1,8-$(C_5H_5)_2Co_2C_2B_8H_{10}$ is pictured here for illustrative purposes.)

1,10,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (VI). Isolation of VII by using octane rather than undecane for the rearrangement of IV suggests that variation of experimental parameters in thermal rearrangement reactions may be as successful as the use of alternative reaction conditions in polyhedral expansion syntheses of unusual new metallocarboranes.[18,21]

The [11]B nmr spectrum of VII is noteworthy in that the resonance of area one attributed to the unique seven-coordinate boron atom in VII (position 1) is not found at highest field with respect to the other signals (Table II). Although few examples exist, the [11]B nmr resonance arising from a seven-coordinate boron atom generally is found at highest field in a given spectrum.[22] If VII is truly octadecahedral and has a static structure at room temperature, this would be the first example in which this correlation is not observed.

12-Vertex Polyhedra: $(C_5H_5)_2Co_2C_2B_8H_{10}$. Some ten isomers of $(C_5H_5)_2Co_2C_2B_8H_{10}$ formed by polyhedral expansion,[5,6,18] polyhedral contraction,[8] or thermal metal transfer[9] were available for rearrangement studies. Initially the thermal reactions of 2,3,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (VIII) and 3,6,1,2-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (IX) (Figure 3) were investigated. Both isomers were structurally well defined. An X-ray diffraction study of VIII, itself, had been conducted[23] while crystallographic studies of two derivatives of IX had been completed.[24,25] Conveniently, VIII and IX rearranged to the same product X, the reaction temperatures being 250 and 340°, respectively. Rearrangement of X was effected at 650° to form a series of products XI–XVI including some metallocarboranes synthesized by thermal metal transfer.[9] At 650°, IX rearranged directly to the same products, XI–XVI, as well as X.

Isomeric rearrangement was observed in all cases as the products X–XVI exhibited mass spectral cutoffs at m/e 370 corresponding to the [11]B_8[12]C_{12}[1]H_{20}[59]Co_2^+ ion. Elemental composition, verified by either chemical analysis or high resolution mass spectrometry, and spectral and voltammetric data are reported in the Experimental Section. The ^{1}H and [11]B nmr spectral parameters are given in Table I and II, respectively. In addition, these bimetallics were characterized by thin layer chromatography on silica gel, the order

of relative R_f values being XI $\gg$ XII > XIII $\gg$ XIV > XV > XVI $\gg$ X $\gg$ IX > VIII.

Structural assignments were made for the seven new bimetallic isomers, all of which were red, using both spectral and chemical data. There are 37 possible icosahedral isomers of formula $(C_5H_5)_2Co_2C_2B_8H_{10}$, not counting enantiomers. The boron atom environments found in these structures occur in six patterns: 1:1:1:1:1:1:1:1 (16 isomers), 2:2:1:1:1:1 (2 isomers), 2:2:2:1:1 (8 isomers), 2:2:2:2 (4 isomers), 2:4:2 (6 isomers), and 4:4 (1 isomer). The [11]B nmr spectrum of X indicated that it was one of the 16 isomers containing eight unique boron atoms. The eight isomers in this class with adjacent carbon vertices can be eliminated as structural possibilities for X since thermal formation of such structures from VIII which has nonadjacent carbon atoms is unlikely.[4b] Four additional candidates for the structure of X can be discarded since they have adjacent cobalt vertices which is inconsistent with the observed electronic spectrum and red color.[12] Of the four remaining structural possibilities for X, the structure 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ is most simply related to VIII and IX. The 2,4,1,7-isomer is generated from VIII by a single cobalt atom migration and from IX by a single carbon atom migration and hence is most likely for X (Figure 3).

Three other isomers of $(C_5H_5)_2Co_2C_2B_8H_{10}$ containing eight distinct boron environments were obtained. The area 2 resonances found in the [11]B nmr spectra of isomers XI and XIII are necessarily due to coincidental overlap since a 2:1:1:1:1:1:1 pattern is precluded by the symmetry of the system. Therefore, XI, XIII, and XVI all have eight unique boron vertices. Since the above arguments regarding adjacent carbon and adjacent cobalt vertices apply to XI, XIII, and XVI (as well as all the isomers formed from X), these three isomers form, with X, the complete set of icosahedral bimetallics with eight unique boron vertices, nonadjacent cobalt vertices, and nonadjacent carbon atoms. Consequently, XI, XIII, and XVI have the structures 4,10,1,7-, 4,12,1,7-, and 2,5,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$. The structure 4,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ is proposed for XI since it has the greatest heteroatom separation and might be expected to be most nonpolar and to have the largest R_f value, as observed. The structures for XIII and XVI can be differentiated and hence assigned, using the fact that XVI is a product of the thermal metal transfer reaction of 1,2,3-$C_5H_5CoC_2B_8H_{10}$ while XIII is not. The structure 2,5,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ is likely for XVI since it is closely related to the major thermal metal transfer product, X, and contains a carbon–cobalt–carbon relationship identical with that of 1,2,3-$C_5H_5CoC_2B_8H_{10}$. The remaining structure 4,12,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ is proposed for XIII since it does not have the above mentioned relationships and is not a thermal metal transfer reaction product.

The 4:4 pattern of [11]B nmr resonances specifies the structure of XV as 2,9,1,12-$(C_5H_5)_2Co_2C_2B_8H_{10}$, leaving the structures of XII and XIV to be assigned. Two isomers containing nonadjacent cobalt vertices, nonadjacent carbon vertices, and boron environments in a 2:2:2:2 pattern are possible for XII: 4,11,1,7- and 2,8,1,12-$(C_5H_5)_2$-$Co_2C_2B_8H_{10}$. The latter structure is slightly favored for XII since its formation from X requires less atomic movement. A 2:2:2:1:1 pattern of boron atoms is possible in four isomers of $(C_5H_5)_2Co_2C_2B_8H_{10}$ containing neither adjacent cobalt nor adjacent carbon atoms. Of these four structural possibilities for XIV, the isomer 2,10,1,7-$(C_5H_5)_2$-$Co_2C_2B_8H_{10}$ is most likely since it is closely related to X and also has the carbon–cobalt–carbon arrangement found in other thermal metal transfer reaction products.

Rearrangement studies of individual isomers could con-

ceivably provide further structural evidence, but, at temperatures high enough for significant conversion, nearly all the isomers are thermally accessible, obviating meaningful results. At 650°, for example, X, XII, XIII, XIV, XV, and XIV are formed from XI. Obviously not all of the above structures can be unambiguously assigned based on the available data and crystallographic studies are in progress. Nonetheless, these rearrangements are consistent with the results obtained for icosahedral monometallic compounds—a wide variety of isomers being obtained, and interconversions of the isomers being observed.[4a] The VIII → X rearrangement is, of course, another example of polyhedral cobalt atom movement. It might also be noted that these rearrangements constitute, with the thermal metal transfer reaction, complementary synthetic routes to icosahedral bimetallocarboranes.

Conclusion

Considerations[17] of structural and electronic similarities in polyhedral boranes and transition metal clusters suggested that the skeletal bonding contributions of certain transition metal moieties, e.g., C_5H_5Co, and the BH vertex were much the same in polyhedral systems. On this premise it was predicted[10] that the polyhedral chemistry of metallocarboranes containing C_5H_5Co vertices might parallel that of the carboranes. While exceptions are to be expected, and the various polyhedral reactions may differ in mechanistic detail from one class to another, the use of such a comparative basis provides a viable framework against which to view the whole of metallocarborane chemistry.

The polyhedral chemistry of the monocobaltacarboranes, $C_5H_5CoC_2B_nH_{n+2}$, which has been elaborated up to this point has shown, as predicted, many similarities to the chemistry of the carboranes, $C_2B_nH_{n+2}$, the general chemical behavior of polyhedral expansion,[5,6] polyhedral contraction,[3,7] and polyhedral rearrangement[3,4b] being applicable to both classes. In addition, the overall reaction in the recently reported thermal metal transfer synthesis[9] of polycobaltacarboranes has a direct analog in polyhedral borane chemistry.[2] In this, the first chemical investigation of bimetallic metallocarboranes, we find not only more examples of parallel polyhedral chemistry but also chemical behavior which could only be observed because of the two transition metal vertices.

Most striking is the demonstration of the mobility of the C_5H_5Co vertex in the polyhedral surface as evident in the I → II, V → IV, IV → VI, and VIII → X isomerizations. Incorporation of a second transition metal vertex in 11-vertex metallocarboranes does not modify the gross polyhedral chemistry, the III → IV rearrangement being a replication of a monometallic interconversion involving identical carbon atom positions, and the isolation of trimetallic species at higher temperatures being an analog of the thermal metal transfer reaction for the octadecahedral monometallocarborane. Similarities in the rearrangements of icosahedral mono- and bimetallic species were found as well. The general rules derived for monometallic rearrangements[4] appear valid in bimetallic systems, although here the isolation of isomers of intermediate stability, e.g., 1,4,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (IV), is possible and simply emphasizes the mobility of the C_5H_5Co vertex. Inclusion of an additional transition metal vertex in a metallocarborane, therefore, does not significantly alter the polyhedral chemistry explored to date and, in fact, effectively provides an additional vertex label which should be of considerable importance in future mechanistic studies. Examination of the other general polyhedral reactions of bimetallocarboranes should result in the synthesis of additional trimetallic species and effectively engender a continuing investigation of the consequences of successive substitution of transition metal vertices for boron vertices in carborane polyhedra.

Experimental Section

Physical Measurements. The 60-MHz proton nmr spectra were measured using a Varian A-60D. The 250-MHz ^{1}H and 80.5-MHz [11]B nmr spectra were measured using an instrument designed and built by Professor F. A. L. Anet and his coworkers. Electrochemical data were obtained from an instrument built by Dr. R. J. Wiersema based upon a design of Lawless and Hawley.[26] Ultraviolet-visible spectra were measured using either a Beckman DB or a Cary 14 spectrophotometer. Infrared spectra were determined using a Perkin-Elmer 137 sodium chloride spectrophotometer. Mass spectra were obtained using an Associated Electrical Industries MS-9 spectrometer.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Materials. Column chromatography was carried out using silica gel powder, 60–200 mesh, obtained from J. T. Baker Chemical Co. or 70–230 mesh, obtained from E. Merck Reagents. ChromAr Sheet 1000 was purchased from Mallinckrodt Chemical Co. for preparative thick layer chromatography. Thin layer chromatography was done on Silufol UV 254 obtained from Tar Residuals, Inc.

Spectroquality acetonitrile, heptane, and hexadecane were obtained from Matheson Coleman and Bell. Octane and n-undecane were obtained from Aldrich Chemical Co. Berl saddles (stoneware) were purchased from VWR Scientific. Washed and ignited sand were purchased from Mallinckrodt Chemical Works. Hexane, methylene chloride, and acetone were reagent grade.

Thermal Rearrangement of 2,6,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$ (I). A 50-ml three-neck flask equipped with a thermometer, reflux condenser, and stirring bar was charged with 10 mg (0.03 mmol) of 2,6,1,10-$(C_5H_5)_2Co_2B_6H_8$ (I) and 10 ml of degassed hexadecane. The reaction mixture was heated at reflux for 4 hr and then cooled to room temperature. The hexadecane was separated from the products by using a dry column of silica gel eluting with hexane, then changing to methylene chloride to elute the products off the column. The product solution was concentrated and purified by thick layer chromatography using hexane as an eluent. The major product, a red band, was further purified by a second dry column chromatographic separation in hexane followed by sublimation, giving pure 2,7,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$ (II): high resolution mass measurement, calcd 346.063042, found 346.0634 ± 0.0007; uv-visible spectrum, λ_{max} (relative absorption) (CH_3CN), 520 (1), 420 (5), 305 (50), 240 (45) nm. A reduction was observed at −1.50 V and an oxidation at +1.37 V.

Thermal Rearrangement of 1,6,2,4-$(C_5H_5)_2Co_2C_2B_7H_9$ (III). A 50-ml three-neck flask equipped with a thermometer, reflux condenser, and stirring bar was charged with 18 mg (0.05 mmol) of 1,6,2,4-$(C_5H_5)_2Co_2C_2B_7H_9$ (III) and 10 ml of degassed heptane. The reaction mixture was heated at reflux for 20 hr and cooled to room temperature. The solvent was removed on a rotary evaporator and the residue purified by thick layer chromatography using a hexane-methylene chloride eluent. Two major products were identified.

(a) 1,4,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (IV). The yield of this green-brown isomer was ca. 50%. Anal. Calcd for $(C_5H_5)_2Co_2C_2B_7H_9$: B, 21.21; C, 40.39; H, 5.37; Co, 33.03. Found: B, 21.34; C, 40.12; H, 5.45; Co, 32.63. Uv-visible spectrum, λ_{max}, nm (log ϵ) (CH_3CN), 250 (4.59), 280 (4.48), 360 (3.86), 516 (2.89), 640 sh (2.68); ir (cm^{-1}) Nujol, 2880 vs, 2480 s, 1470 m, 1420 m, 1370 s, 1120 w, 1080 m, 1060 m, 1040 w, 1010m, 930 m, 910 w, 880 w, 860 m, 840 s, 830 w, 810 m, 775 w, 725 w, 710 w, 700 m. A reduction was observed at −0.87 V and an oxidation at +0.87 V.

(b) 1,10,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (VI). The yield of this red-orange isomer was ca. 25%: high resolution mass measurement calcd 358.0805, found 358.0809 ± 0.0004; uv-visible spectrum λ_{max}, nm (log ϵ) (CH_3CN), 242 (4.44), 292 (4.30), 320 (4.19), 464 (3.30); ir (cm^{-1}) Nujol, 2900 vs, 2490 s, 1460 vs, 1420 m, 1375 s, 1340 w, 1260 m, 1120 m, 1090 m, 1060 w, 1030 m, 950 w, 940 m, 890 w, 840 m, 805 m, 750 m, 725 w. A reduction was observed at −1.17 V and an oxidation at +1.06 V.

Thermal Rearrangement of 1,4,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (IV). A three-neck 100-ml flask equipped with a thermometer, reflux condenser, and stirring bar was charged with 80 mg (0.22 mmol) of

1,4,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (IV) and 70 ml of degassed octane. A stream of nitrogen was passed through the solution for an additional 25 min and the reaction mixture was heated at 125° for 68 hr. After cooling to room temperature, the solution was filtered. The precipitate was dissolved in methylene chloride. Fifteen milliliters of silica gel was added to the solution and the solvent was removed on a rotary evaporator. The solids were then mounted on a column of silica gel (400 ml dry volume) in hexane initially eluting with the filtrate obtained above. Further elution of the column with hexane and gradually enriching with dichloromethane gave four fractions.

(a) 2,1,10-$(C_5H_5)CoC_2B_7H_9$. Formed only in trace amounts.

(b) 8,9,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (VII). The yield of this orange isomer was 10 mg (0.027 mmol, 12.5%): high resolution mass measurement calcd 358.0805, found 358.08017 ± 0.0007; ir (cm^{-1}) Nujol, 2900 vs, 2500 s, 1470 m, 1410 w, 1375 w, 1115 m, 1045 w, 1015 w, 900 m, 870 w, 830 s, 795 m. A reduction was observed at −1.41 V and an oxidation at +1.23 V.

(c) 1,10,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (VI). The yield of this brown isomer was 10 mg (0.027 mmol, 12.5%).

(d) 1,4,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (IV). The dark green-brown starting material recovered was 36 mg (0.10 mmol, 46%).

Thermal Rearrangement of 1,8,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (V). A three-neck 100-ml flask equipped with a thermometer, reflux condenser, and stirring bar was charged with 120 mg (0.33 mmol) of 1,8,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (V) and 70 ml of degassed heptane. A stream of nitrogen was passed through the solution for an additional 25 min and the reaction mixture was heated at 95° for 4.5 hr. After cooling to room temperature, the precipitate was dissolved by the addition of methylene chloride. Fifteen milliliters of silica gel was added to the solution and the solvent was removed on a rotary evaporator. The solids were then mounted on a column of silica gel (300 ml dry volume) in hexane. Elution of the column with hexane and gradually enriching with methylene chloride gave one major fraction. The yield of the dark green-brown 1,4,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (IV) was 105 mg (0.29 mmol, 88%).

Thermal Rearrangement of 8,9,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (VII). A three-neck 100-ml flask equipped with a thermometer, reflux condenser, and stirring bar was charged with 10 mg (0.03 mmol) of 8,9,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (VII) and 30 ml of degassed octane and the reaction mixture was heated at reflux for 160 hr. The progress of the reaction was followed by tlc. Tlc showed two products. The major product of the reaction was 1,10,2,3-$(C_5H_5)_2Co_2C_2B_7H_9$ (VI). The minor product of this reaction was one of two trimetallic species $(C_5H_5)_3Co_3C_2B_7H_9$ previously synthesized by the heating of IV in undecane.[18]

Thermal Rearrangement of 2,3,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (VIII). A 7-mm thick-walled tube was charged with 70 mg (0.99 mmol) of 2,3,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (VIII). A high vacuum was applied and the tube was sealed. The glass tube was then placed in an oven and heated at 250° for 84 hr. After cooling to room temperature, the tube was opened and the solid dissolved in methylene chloride. The blood red liquid was filtered, concentrated, and purified by thick layer chromatography using a methylene chloride-hexane (1:1 by volume) eluent. The only major product was characterized as the red 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (X), 39 mg (0.55 mmol, 55%).

Anal. Calcd for $(C_5H_5)_2Co_2C_2B_8H_{10}$: B, 23.46; C, 39.10; H, 5.47; Co, 31.97. Found: B, 22.42; C, 39.40; H, 5.56; Co, 31.54. Uv-visible spectrum λ_{max}, nm (log ϵ) (CH$_3$CN), 252 (4.25), 288 (4.60), 4.14 (3.19), 470 sh (3.0); ir (cm^{-1}) Nujol, 2900 vs, 2500 vs, 1460 vs, 1410 m, 1370 s, 1115 w, 1100 w, 1080 m, 1060 m, 1015 s, 1005 w, 995 m, 970 m, 930 m, 910 w, 890 w, 870 w, 855 w, 840 m, 830 vs, 780 w, 760 w, 730 w, 725 w. A reduction was observed at −1.23 V and an oxidation of +1.41 V.

Thermal Rearrangement of 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (X). 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (X) (304 mg, 0.824 mmol) was placed in the bottom of a quartz hot tube. The tube was then packed with ceramic saddles and a sublimer maintained at −78° was attached. A high vacuum was applied and the hot tube was heated to 650°. The solid was then sublimed up the hot tube by heating with a silicone oil bath at 240°. Twenty milliliters of silica gel was added to the sublimate, which was dissolved in methylene chloride. The solvent was removed on a rotary evaporator, and the solids were mounted on a column of silica gel (600 ml dry volume)

in hexane. The column was eluted with hexane gradually enriching with methylene chloride giving seven fractions.

(a) 4,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XI). The yield of this orange isomer was 75 mg (0.206 mmol, 25%): high resolution mass spectrometry calcd 370.097305, found 370.0978 ± 0.0007; ir (cm^{-1}) Nujol, 2900 vs, 2500 s, 1475 s, 1410 m, 1365 m, 1130 w, 1070 w, 1040 m, 1010 m, 990 m, 960 m, 930 m, 890 m, 855 m, 835 s, 725 w, 700 w. A reduction was observed at −1.65 V and an oxidation at +1.40 V.

(b) 2,8,1,12-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XII). The yield of this red-orange isomer was 61 mg (0.165 mmol, 20%): high resolution mass measurement calcd 370.097305, found 370.0976 ± 0.0007; ir (cm^{-1}) Nujol, 2900 vs, 2510 s, 1715 w, 1470 s, 1415 w, 1380 m, 1270 m, 1120 w, 1090 w, 1040 w, 1015 w, 960 w, 870 s, 830 m, 805 w. A reduction was observed at −1.43 V and an oxidation at +1.45 V.

(c) 4,12,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XIII). The yield of this orange isomer was 15 mg (0.041 mmol, 5%): high resolution mass measurement calcd 370.097305, found 370.0974 ± 0.0007; ir (cm^{-1}) Nujol, 2900 m, 2500 w, 1450 w, 1400 m, 1350 m, 1113 w, 1090 w, 1030 w, 0 w, 950 w, 920 w, 830 m, 740 w. A reduction was observed at −1.50 V and an oxidation at +1.3 V.

(d) 2,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XIV). The yield of this red isomer was 38 mg (0.103 mmol, 12.5%). Anal. Calcd for $(C_5H_5)_2Co_2C_2B_8H_{10}$: B, 23.46, C, 39.10, H, 5.47; Co, 31.97. Found: B, 22.54; C, 37.55; H, 5.33; Co, 30.63. Uv-visible spectrum λ_{max}, nm (log ϵ) (CH$_3$CN), 244 sh (0.42), 276 (0.86), 430 (0.565), 520 (0.225); ir (cm^{-1}) Nujol, 2900 vs, 2551 s, 1408 s, 1101 m, 1017 w, 1008 w, 992 s, 962 m, 943 m, 898 m, 858 m, 843 w, 818 s, 734 w. A reduction was observed at −1.23 V and an oxidation at +1.37 V.

(e) 2,9,1,12-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XV). This red purplish isomer was formed in trace amounts: high resolution mass measurement calcd 370.097305, found 370.0978 + 0.0007; ir (cm^{-1}) Nujol; 2900 vs, 2500 s, 1450 s, 1410 w, 1370 m, 1100 m, 1060 w, 990 s, 960 m, 940 w, 900 m, 860 m, 825 s, 735 m. A reduction was observed at −1.35 V and an oxidation at +1.40 V.

(f) 2,5,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XVI). The yield of this orange isomer was 7 mg (0.019 mmol, 2.3%): high resolution mass measurement calcd 370.097305, found 370.0978 ± 0.0007; ir (cm^{-1}) Nujol, 2900 vs, 2500 s, 1450 s, 1400 w, 1360 m, 1250 w, 1090 m, 1050 w, 1025 w, 930 w, 910 w, 860 w, 825 s, 725 m. A reduction was observed at −1.43 V and an oxidation at +1.40 V.

(g) 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (X). The recovered starting material was 13 mg (0.035 mmol, 4.2%).

Thermal Rearrangement of 4,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XI). 4,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XI) (100 mg, 0.27 mmol) was placed in the bottom of a quartz hot tube. The tube was then packed with ceramic saddles and sublimer maintained at −78° was attached. A high vacuum was applied and the hot tube was heated to 650°. The solid was then sublimed up the hot tube by heating up to 200° with a silicone oil bath. The sublimate, dissolved in methylene chloride, was concentrated and purified by thick layer chromatography. Using three elutions in a hexane-methylene chloride (20:1 by volume) solution, seven bands were identifed as orange 4,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XI) (67 mg, 0.18 mmol, 67%), orange 2,8,1,12-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XII) (6.5 mg, 0.017 mmol, 6.5%), orange 4,12,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XIII) (1 mg, 0.0027 mmol, 1%), red 2,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XIV) (4 mg, 0.011 mmol, 4%), purplish 2,9,1,12-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XV) (trace), orange 2,5,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XVI) (trace), and orange 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (X) (trace).

Thermal Rearrangements of 3,6,1,2-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (IX). In an argon atmosphere 1 g (2.71 mmol) of 3,6,1,2-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (IX) was heated to 350–380° for 3 hr (Wood's-metal bath). After cooling to room temperature the residue was extracted with acetone and stripped onto 10 ml of silica gel. The solids were mounted onto a column of silica gel (300 ml dry volume) in hexane. Benzene eluted two main intense red bands, which were separated, evaporated to dryness, and recrystallized from benzene-hexane solution yielding red 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (X) (0.4 g, 1.08 mmol, 40%) and red 2,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XIV) (0.09 g, 0.264 mmol, 9%).

Higher Temperature Thermal Rearrangement of 3,6,1,2-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (IX). 3,6,1,2-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (IX) (0.98

g,.0.264 mmol) was placed in the bottom of a quartz hot tube. The tube was packed with ceramic saddles and sublimer maintained at −78° was attached. A high vacuum was applied and the hot tube was heated to 650°. The solid was then sublimed up the hot tube by heating with a silicone oil bath between 250 and 290°. Thirty milliliters of silica gel was added to the sublimate which was dissolved in methylene chloride. The solvent was removed on a rotary evaporator, and the solids were mounted on a column of silica gel (600 ml dry volume) in hexane. The column was then eluted with hexane gradually enriched with methylene chloride giving eight fractions identified as orange 4,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XI) (105 mg, 0.029 mmol, 11%), orange 2,8,1,12-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XII) (90 mg, 0.0238 mmol, 9%), 4,12,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XIII) (10 mg, 0.0026 mmol, 1.0%), red 2,10,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XIV) (28 mg, 0.093 mmol, 3%), purplish 2,9,1,12-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XV) (10 mg, 0.0026 mmol, 1%), orange 2,5,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (XVI) (9 mg, 0.0024 mmol, 0.9%), orange 2,4,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (X) (15 mg, 396 mmol, 1.5%), and red 3,6,1,2-$(C_5H_5)_2Co_2C_2B_8H_{10}$ (IX) (70 mg, 0.0185 mmol, 7%).

References and Notes

(1) Institute of Inorganic Synthesis, Řez near Prague, Czechoslovakia, U.S. National Academy of Sciences Exchange Student.
(2) E. L. Muetterties and A. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, and references therein.
(3) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970, and references therein.
(4) (a) M. K. Kaloustion, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 6679 (1972); (b) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 3085 (1974).
(5) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95**, 4565 (1973).
(6) W. J. Evans and M. F. Hawthorne, *Inorg. Chem.*, **13**, 869 (1974).
(7) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 8391 (1972).
(8) C. J. Jones and M. F. Hawthorne, *Inorg. Chem.*, **12**, 608 (1973).
(9) W. J. Evans and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **96**, 301 (1974).
(10) C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 543 (1973).
(11) K. P. Callahan, W. J. Evans, and M. F. Hawthorne, *Ann. N. Y. Acad. Sci.*, in press.
(12) W. J. Evans, D. J. Jones, B. Štíbr, and M. F. Hawthorne, *J. Organometal. Chem.*, **60**, C27 (1973).
(13) Numbers preceding formulas refer in order to the positions of the heteroatoms (carbon and cobalt) listed in the formulas following IUPAC precedents;[14] *e.g.*, see Figure 1.
(14) R. M. Adams, *Pure Appl. Chem.*, **30**, 683 (1972).
(15) E. L. Hoel, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1388 (1974).
(16) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, **95**, 2830 (1973).
(17) K. Wade, *J. Chem. Soc., Chem. Commun.*, 792 (1971).
(18) W. J. Evans, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1973.
(19) The scope of this thermal metal transfer reaction appears to be quite broad, for not only is it applicable to bimetallic as well as monometallic octadecahedral systems but it is also synthetically viable when polyhedral precursors other than the octadecahedron are employed.[20]
(20) W. J. Evans and M. F. Hawthorne, to be submitted for publication.
(21) G. Eurard, J. A. Ricci, Jr., I. Bernal, W. J. Evans, D. F. Dustin, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, submitted for publication.
(22) R. E. Williams, *Progr. Boron Chem.*, **2**, 37 (1970).
(23) K. P. Callahan, C. E. Strouse, A. L. Sims and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1393 (1974).
(24) D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 2080 (1969).
(25) M. R. Churchill, A. H. Reis, Jr., J. N. Francis, M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 4993 (1970).
(26) J. D. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969).

Interaction of Catechol and Catechol Derivatives with Dioxovanadium(V). I. Kinetics of Complex Formation in Acidic Media[1]

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Abstract: The kinetics of complexation of dioxovanadium(V) by catechol and a series of catechol derivatives have been studied at $25.0 \pm 0.5°$ and ionic strength 1.0 M (ClO_4^-) in acidic media (0.2–1.0 M $HClO_4$). Upon mixing acidic solutions of vanadium(V) and catechol (or catechol derivatives) a highly colored complex is formed which subsequently disappears due to oxidation of the ligand. Rate constants for complex formation (k_f) and dissociation (k_r) have been determined by stopped flow. The rate constants show no detectable [H^+] dependence; it is therefore concluded that $HOVO^{2+}$ is not important, and the reactive species are VO_2^+ and fully protonated ligand. Both k_f and k_r are sensitive to the nature of the complexing ligand. For catechol, pyrogallol, 1,2,4-benzenetriol, L-dopa, and epinephrine, the respective k_f values are 1.84×10^4, 4.36×10^4, 9.91×10^4, 1.12×10^4, and 1.70×10^4 M^{-1} sec^{-1} and for k_r 41.9, 8.39, 10.8, 55.2, and 66.6 sec^{-1}. The values of k_f represent lower limits on the substitution rate constants. For example, with catechol, the vanadium(V) water exchange rate constant, k_0, is $k_0 \geq 6 \times 10^4$ sec^{-1}. This value is greater than k_0 for V(IV) and is explained by electrostatic effects on the bonding to the remaining water molecules; namely, the additional oxide ligand compensates for the higher charge on the central metal atom. The order in k_f and K, the complex stability constant, is the same, and may also be explained by an electrostatic effect. Substitution rate constants of V(V) in media of pH 0–9 lie within the narrow range 1 to 10×10^4 M^{-1} sec^{-1} due probably to rate controlling loss of coordinated aquo ligands.

Complexes of metal-containing oxo ions and organic ligands have long been employed in quantitative chemical analysis. However, interest in kinetics studies of complexation of d^0 ions such as those of Mo(VI), W(VI), Cr(VI), and V(V) is a late development. The lack of experimentation was due to the complex equilibria of these metal-containing ions, in which changes in coordination number, polymerization, and extensive hydrolysis occur as conditions are varied. Furthermore, complex formation frequently occurs so rapidly that fast reaction techniques are required. A