Reaction with $Na_2Cr_2O_7$. About 1 g of $Na_2Cr_2O_7 \cdot 2H_2O$ was dissolved in 10 ml of 0.10 *M* $Na_2B_{12}H_{12}$, and the reaction mixture stirred for 3 days at room temperature. Removal of the precipitated brown $Cr(OH)_2$ by filtration left a clear filtrate the tlc of which indicated the presence of $B_{12}H_{11}OH^{2-}$ in addition to the starting material, but no spots were seen corresponding to the positions occupied by $B_{24}H_{23}^{3-}$ or the $B_{24}H_{22}OH^{3-}$ species.[7,8] Addition of CsCl precipitated a mixture of $CsCl \cdot Cs_2B_{12}H_{12}$ and $CsCl \cdot Cs_2B_{12}H_{11}OH$. The ir spectra of precipitates obtained with either Cs^+ or Me_4N^+ showed no trace of the hydrogen-bridge band at 2270 cm^{-1} characteristic of the coupled ions.[7,8] The tlc and ir and uv spectra of salts precipitated by Cs^+ when dichromate was reduced by $B_{10}H_{10}^{2-}$ showed no evidence of $B_{20}H_{18}^{2-}$, $B_{20}H_{18}^{4-}$, or $B_{20}H_{17}OH^{4-}$. The ir spectra of Me_4N^+ salts reprecipitated from acidic solutions showed no evidence of $B_{20}H_{19}^{3-}$ or $B_{20}H_{18}OH^{3-}$ species.[9] The reduction of the dichromate proceeds much faster under reflux conditions.

Registry No. $B_{12}H_{12}^{2-}$, 12356-13-7; MnO_4^-, 14333-13-2.

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Behavior of Dieneiron Tricarbonyl Complexes in Strong Acid. Structures of the Protonated Species

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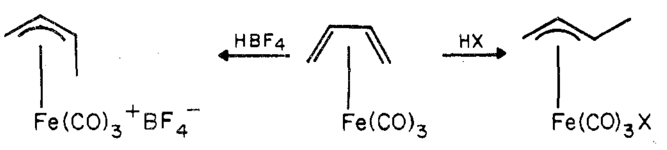
Received August 5, 1974 AIC40535F



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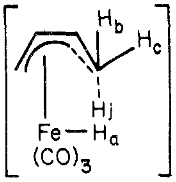

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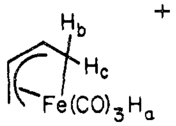


6

A wide range of behavior has been reported for diene–metal complexes in acidic media. In early work,[1,2] addition of acids such as HCl to dieneiron tricarbonyl complexes **1** was observed to give π-allyliron carbonyl halides **2**, while acids with poorly coordinating anions gave species formulated as the coordinatively unsaturated tricarbonyl species **3**. Gibson[3,4] later reported the isolation from acetic acid–HBF_4 of π-allyl tetracarbonyl species **4**, which resulted presumably from capture of CO by species **3**. We observed similar behavior[5,6] in trifluoroacetic acid (TFA) and have discussed some mechanistic aspects of the protonation reaction. In SO_2, Kaesz, *et al.*,[7] have reported that diprotonated species, formulated as having structure **5**, are formed from **3** with excess strong acid. This species shows rather curious behavior, in that proton H_j was suggested to exchange rapidly with excess acid, while protons H_a, H_b, and H_c undergo rapid (nmr time scale at −20°) intramolecular scrambling. Similar observations have been made by Lewis[8] on (π-cyclohexadiene)(π-cyclopentadienyl)rhodium(I) in TFA solutions. Brookhart[9] has recently suggested that species **5** is actually better written as a σ–π species, **6**, and that the initial compound (1 equiv of acid) in SO_2 is actually analogous to **2**, with the anion of the acid coordinated to iron. We wish to report experimental evidence that this hypothesis is in fact the case and that the species **6**, formed on treatment with excess HBF_4, is monoprotonated.

Experimental Section

General Data. All reactions involving organometallics were performed under an atmosphere of dry nitrogen, and nmr samples were likewise prepared under nitrogen. Silver trifluoroacetate[10] and η-allyliron tricarbonyl iodide[11] were prepared by known methods. Proton nmr spectra were obtained on a JEOL Model JNM-MH-100 spectrometer operating on external lock, at ambient temperature (∼31°). Conductivity measurements were performed using a Beckman Model RC-18A conductivity bridge at 31°. Solutions of anhydrous HBF_4 in TFA were made by the addition of a known quantity of 40% aqueous HBF_4 to a slight excess of trifluoroacetic anhydride, followed by dilution to the appropriate concentration with TFA.

(1-Phenyl-3-methylbutadiene)iron Tricarbonyl (7). 1-Phenyl-3-methylbutadiene[12] was prepared from benzalacetone by reaction with methylmagnesium bromide and dehydration. The complex was prepared by irradiation of a solution of 9.0 g (0.063 mol) of the diene and 7.84 g (0.040 mol) of iron pentacarbonyl in 75 ml of benzene contained in an annular photolysis well with a Hanovia 450-W medium-pressure mercury arc for 5 hr. The resulting solution was transferred out of the well with the aid of 25 ml of benzene and filtered, and the solvent and excess iron pentacarbonyl were removed by evaporation under reduced pressure. Distillation gave 9.82 g of yellow oil, bp 60–110° (0.005 mm), which crystallized on standing. Recrystallization from pentane, followed by sublimation (45°, 0.005 mm) gave 6.2 g (50%) of yellow crystalline material, mp 42–44°.

Anal. Calcd for $C_{14}H_{12}FeO_3$: C, 59.15; H, 4.26; Fe, 19.69. Found: C, 59.36; H, 4.44; Fe, 19.87.

(1-Phenyl-3,3-dimethylallyl)iron Tetracarbonyl Tetrafluoroborate (9). Carbon monoxide was bubbled into a solution of 5.68 g (20 mmol) of the above diene complex in 20 ml of TFA for 15 min. A solution of 20 mmol of HBF_4 in 25 ml of TFA was added, and the solution was allowed to stand a further 15 min under a vigorous stream of CO. The resulting solution was poured into 75 ml of ether, and the resulting yellow precipitate was filtered, washed with ether, and dried under a stream of nitrogen. It was then redissolved in a minimum volume of TFA and reprecipitated by the addition of ether. Filtration, followed by drying under vacuum for 8 hr at 50°, gave 6.3 g (78%) of yellow powder. Ir (CH_3NO_2): 2130 (s), 2080–2050 cm^{-1} (br, s) (ν_{CO}). Nmr (TFA): δ 2.00 (s, 3 H), 2.40 (s, 3 H), 5.52 (d, J = 13 Hz, 1 H), 6.45 (d, J = 13 Hz, 1 H), *ca.* 7.5 (m, 5 H).

Anal. Calcd for $C_{15}H_{13}FeO_4BF_4$: C, 45.05; H, 3.28; Fe, 13.96. Found: C, 44.76; H, 3.50; Fe, 13.83.

Allyliron Tetracarbonyl Tetrafluoroborate. Allyliron tricarbonyl iodide (1.54 g, 5 mmol) and $AgBF_4$ (1.17 g, 6 mmol) were dissolved in 10 ml of TFA. Carbon monoxide was bubbled rapidly through

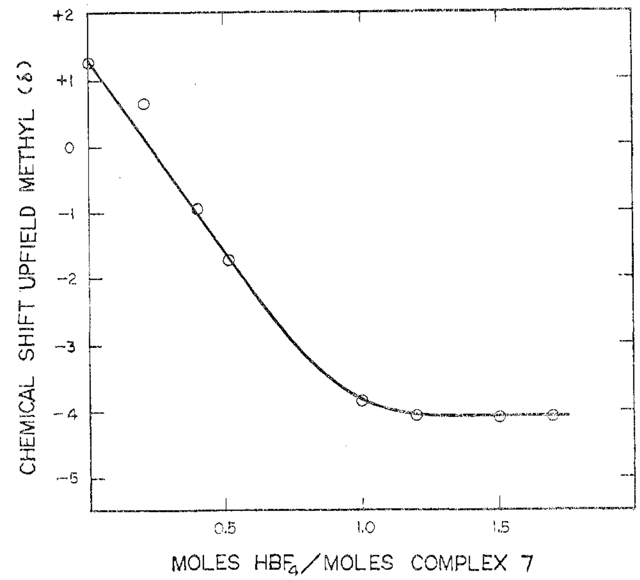


Figure 1. Titration of **7** with HBF_4 in TFA.

the resulting suspension for 15 min. Silver iodide was separated by filtration, and the filtrate added rapidly to ether. The off-white solid was separated by filtration and then reprecipitated as described for **9**. Drying *in vacuo* gave 1.18 g (80%) of light yellow solid. Ir (CH_3NO_2): 2150 (s), 2090–2075 cm^{-1} (br, s). Nmr (TFA): δ 3.30 (d, $J = 12$ Hz, 2 H), 4.30 (d, $J = 7$ Hz, 2 H), 5.90 (tt, $J = 7, 12$ Hz, 1 H).

Anal. Calcd for $C_7H_5O_4FeBF_4$: C, 28.43; H, 1.70; Fe, 18.88. Found: C, 28.53; H, 1.71; Fe, 19.04.

Allyliron Tricarbonyl Trifluoroacetate. Allyliron tricarbonyl iodide (1.54 g, 5 mmol) in 20 ml of TFA was allowed to react with 1.10 g (5 mmol) of silver trifluoroacetate. The reaction mixture was stirred for 5 min and then filtered. The solvent was removed under reduced pressure, and the residue was sublimed at 70° (0.25 mm). The sublimate, 0.922 g (62%), was a yellow solid, mp 60.5–61.0°. Ir ($CHCl_3$): 2105, 2020, 2060 cm^{-1} (ν_{MCO}); 1687 cm^{-1} (ν_{OCO}). Nmr (TFA): δ 2.70 (d, $J = 14$ Hz, 2 H), 4.73 (d, $J = 9$ Hz, 2 H), 5.40 (m, 1 H). Mass spectrum: *m/e* 238 ($m^+ - 2CO$), 210 ($m^+ - 3CO$), 181 ($m^+ - CF_3CO_2$).

Anal. Calcd for $C_8H_5O_5F_3Fe$: C, 32.69; H, 1.71; Fe, 19.00. Found: C, 32.92; H, 1.80; Fe, 18.75.

Nmr Studies of Diene Complexes in TFA–HBF_4 Mixtures. A weighed amount of the diene complex in an nmr tube under N_2 was dissolved in TFA containing a known concentration of HBF_4 and a small amount of TMS. An nmr was run as soon as possible (*ca.* 2 min) and every few minutes for about 30 min. The chemical shift of each signal was plotted as a function of time and extrapolated to zero time. The extrapolated values were then plotted as a function of the ratio of [HBF_4] to [diene complex]. This treatment was necessary because of the appreciable rate of decomposition of the initially formed species to form tetracarbonyl cations similar to **9**. Typical results are shown in Figure 1.

Results and Discussion

In our original work,[5] we observed complete protonation of diene complexes such as **7** in pure TFA. As described by Gibson,[3] the initially formed species **8** decomposes with a half-life of about 30 min (34°) to the tetracarbonyl species **9**. Addition of excess anhydrous HBF_4 to these solutions gave a species **10** whose nmr spectrum was analogous to that observed by Kaesz in SO_2 (Figure 2). Species **8** seemed to be ionic, because the conductivity of the solution was initially high and actually decreased slightly as the unambiguously ionic tetracarbonyl species **9** was formed. Furthermore, the *covalent* π-allyl trifluoroacetate **11**, a yellow, sublimable solid, showed

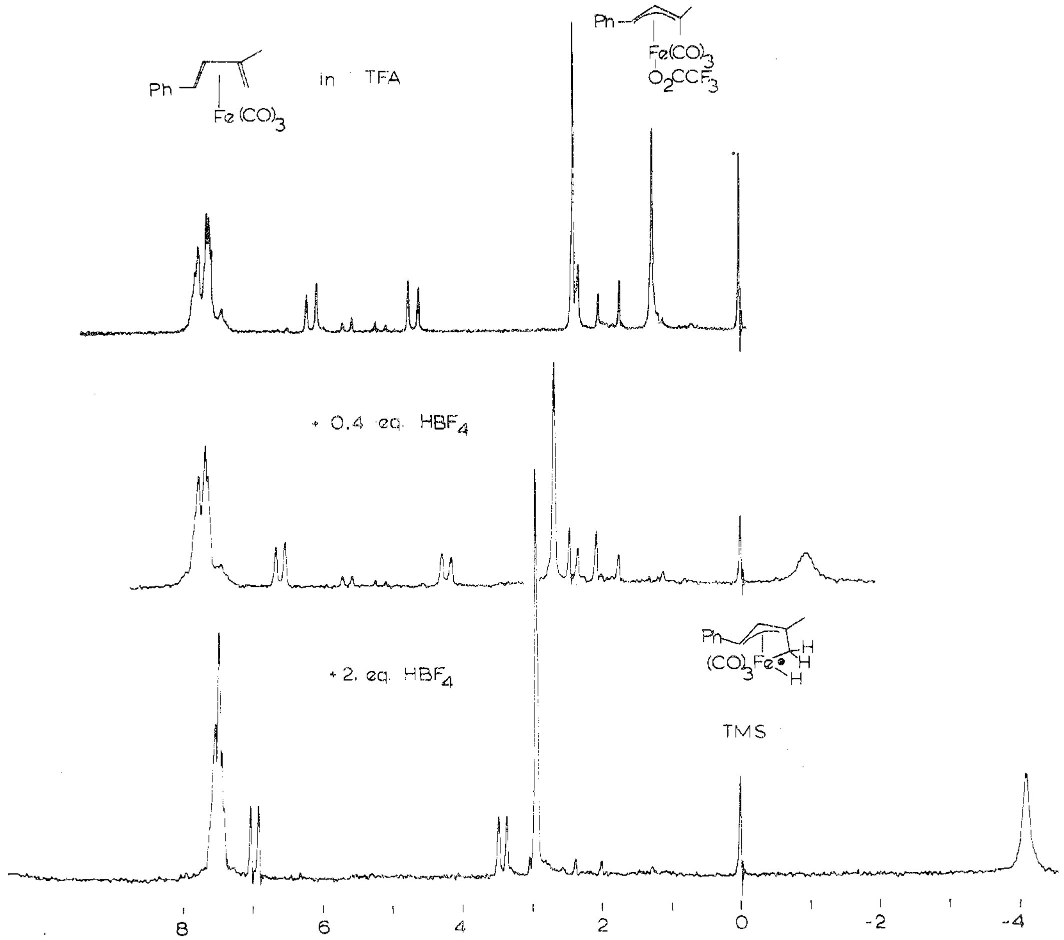
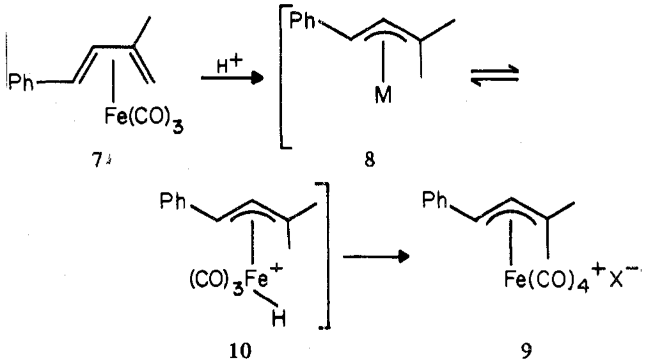
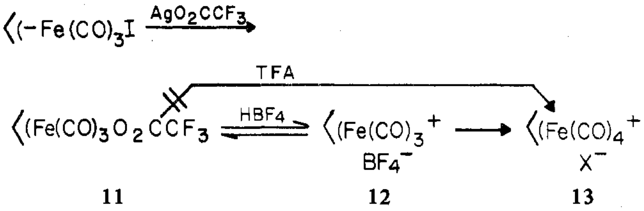


Figure 2. Nmr spectra of solutions of diene complex **7** in TFA containing varying quantities of HBF_4.



essentially no conducting properties in TFA and did not give rise to the corresponding tetracarbonyl. Also, on treatment with excess HBF_4 in TFA, **11** gave rise to a new species, presumably **12**, which *did* decompose to **13** (Figure 3). These observations are consistent with the formulation of **8** as the tricarbonyl cation (*i.e.*, M = $Fe(CO)_3^+$) and **10** as a diprotonated species.



However, as shown in Figure 2, the positions of the peaks of the species present in TFA solution are sensitive functions of the amount of HBF_4 added. In fact, the positions of the peaks of **8** change smoothly with the amount of HBF_4 added until about 1 (1.05) equiv, at which point the spectrum is that of **10**, and no further change occurs. This observation indicates that **8** and **10** are in rapid equilibrium and that only 1 equiv of strong acid is necessary to transform **8** into **10**. *This fact is uniquely interpretable in terms of a monoprotonated structure for* **10** *and therefore a (principally) covalent structure for* **8**. Thus, if **8** is ionic, the first equivalent of HBF_4 must neutralize the free trifluoroacetate ion and would not affect the structure of **8** until this neutralization is complete. Therefore ≥2 equiv of HBF_4 would be necessary to transform **8** to **10**. If, on the contrary, **8** is principally covalent (*i.e.*, M = $Fe(CO)_3O_2CCF_3$), then neutralization of trifluoroacetate effectively removes a ligand and thus results in the observed change in the nmr spectrum.

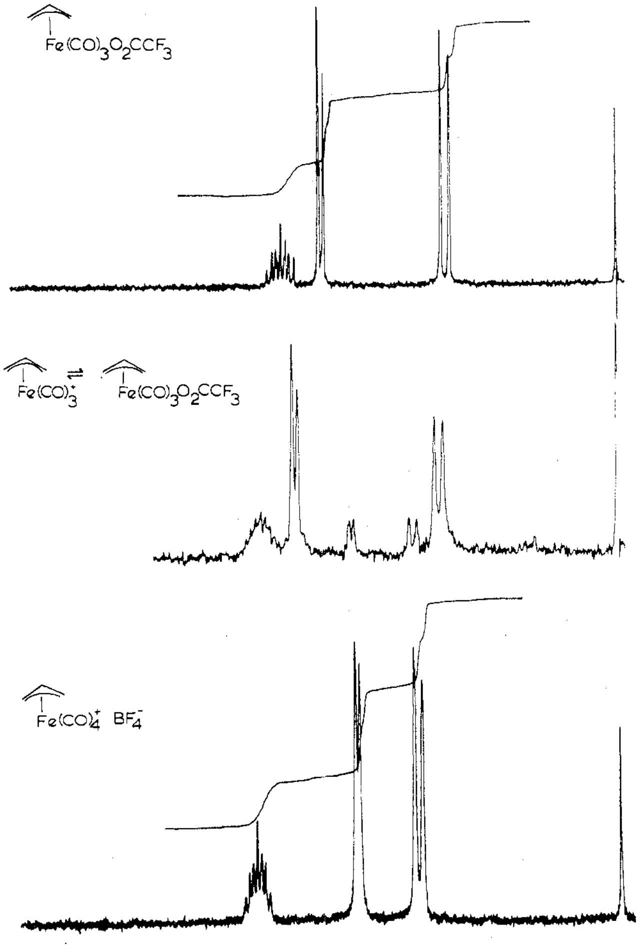
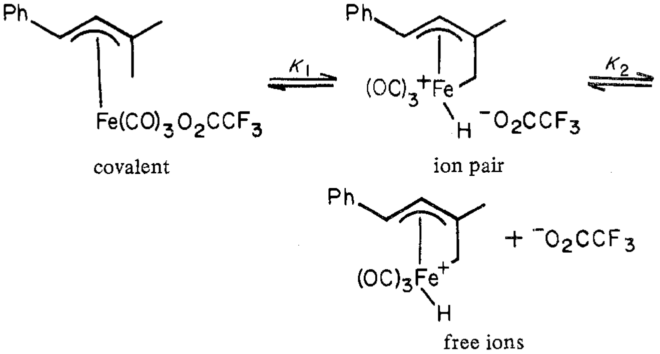


Figure 3. Nmr spectra of (from the top) **11**, a mixture in rapid equilibrium of **11** and **12**, and **13** ($X^- = BF_4^-$).

The high conductivity of solutions containing **8** remains to be explained. At a total concentration of 0.01 M, the specific conductance, K_{sp}, of a solution of **8** in TFA is about 70 × 10^{-6} ohm^{-1} cm^{-1}. For comparison, for $Bu_4N^+O_2CCF_3^-$ $K_{sp} = 200 \times 10^{-6}$ ohm^{-1} cm^{-1}, for $Et_2NH^+O_2CCF_3^-$ $K_{sp} = 109 \times 10^{-6}$ ohm^{-1} cm^{-1}, and for $Na^+O_2CCF_3^-$ $K_{sp} = 7.5 \times 10^{-6}$ ohm^{-1} cm^{-1}, all at 0.01 M. Due to the low dielectric constant of TFA ($\epsilon = 8.55$ (20°))[13] ion pairing will be important even for large ions. Thus, solutions of **7** in TFA will contain at least three different species: neutral covalent material, ion pairs, and free ions, all of which are postulated to be in rapid equilibrium.



covalent

ion pair

free ions

The degree of dissociation, γ, of the ion pairs increases by mass action at lower total ion concentration. The effect of the first equilibrium will be to reduce the effective total ion concentration; γ for those ions which do exist will be much larger than for a totally ionic material at the same total concentration. Since the conductivity depends principally on the free ion concentration, the solution will be qualitatively a much better conductor than expected. On a more quantitative basis, K_2 can be estimated[14] to be on the order of 10^{-4}; since no appreciable shift (±10 Hz) of the anti methyl peak of **8** is observed on dilution in the concentration range of 1.2–0.02 M,[15] $K_1 \leq 5 \times 10^{-2}$ (corresponding to about 2% ionization at nmr concentrations (~0.5 M)). Under these constraints, the ratio of specific conductivities of solutions of **8** and a salt of similar conducting properties is calculated to be between 3 and 4, depending on the choice of the equivalent conductance at infinite dilution,[16,17] comparable to the observed ratio of *ca.* 3 between **8** and $Bu_4N^+O_2CCF_3^-$ at 0.01 M. Considering the approximations involved, this agreement is regarded as satisfactory.

Consistent with this picture is the increased covalent character of the simple π-allyl species and the decreased basicity of cyclohexadieneiron tricarbonyl (**14**). Ionization of the π-allyl **11** must either give a true tricarbonyl or a solvent-coordinated species, both of which must be substantially higher in energy than the σ–π structure. The relatively rigid cyclic ligand of **14** may render difficult the geometric changes implied by the σ–π structure. At the same time, the steric hindrance of the ring may prevent trifluoroacetate ion coordination. We have observed that 1 equiv of HBF_4 will in fact give a protonated $C_6H_8Fe(CO)_3H^+$ of a structure analogous to **6**.

Acknowledgment. We thank the Research Corp., the NSF (Grant GP16358), and the Graduate School of the University of Wisconsin for support of this research and Professor Maurice Brookhart for valuable discussions.

Registry No. **7**, 34779-31-2; **9**, 53011-19-1; **13**, 43140-17-6; **11**, 42991-92-4; $Fe(CO)_5$, 13463-40-6; allyliron tricarbonyl iodide, 12189-10-5.

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(15) Assuming values for the equilibrium constants, the concentrations of covalent, ion-paired, and free ionic species may be estimated. Then, assuming rapid equilibria, the chemical shift of the anti methyl may be calculated from the expression $\delta_{obsd} = \delta_{covalent}(1 - \Gamma) + \delta_{ion}\Gamma$, where Γ is the degree of dissociation into ions and ion pairs, $\delta_{ion} = 4.0$, and $\delta_{covalent}$ was calculated from δ_{obsd} at one concentration.

(16) The equivalent conductance $\Lambda = \gamma(\Lambda° - (6.08\Lambda° + 188)\sqrt{C}) = 1000K_{sp}/C$, where γ is the degree of dissociation of ion pairs, C is the total ion concentration, and K_{sp} is the required specific conductance.[17]

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Correspondence

Slipped Sandwich Structures in Metal Carborane Systems

AIC40333J

Sir:

Bis complexes of the 1,2- and 1,7-dicarbollide ligands ($C_2B_9H_{11}^{2-}$) have some structural characteristics similar to bis-cyclopentadienide complexes. For metals of d^5, d^6, and d^7 electronic configuration, both ligands form complexes with the metal bound symmetrically to each of the two five-membered faces.[1,2] However, for metals with a d^8 and d^9 electronic configuration, the dicarbollide ligands form complexes with the metal bound asymmetrically to the five-membered face (in the case of the 1,2 ligand favoring the three boron atoms) while the cyclopentadienide ligand still forms symmetrical complexes. The dicarbollide complexes of this structure[3-6] have been called "slipped" and two interpretations of the bonding in these complexes have been proposed.[4,6] It was not, however, clear why slippage occurs in the dicarbollide case but does not occur in the cyclopentadienide case. Since the dicarbollide complexes involve a fusion of two icosahedra through the metal (the metal is not merely sandwiched between the ligands but is an integral part of each cage), we believe that an explanation of the slippage can be obtained from the known chemistry of icosahedral systems.

All the isomers of the closo icosahedral $C_2B_{10}H_{12}$ carborane system (1,2; 1,7; 1,12) undergo reduction followed by protonation to produce *nido*-$C_2B_{10}H_{13}^-$ ions.[7] In the case of the 1,2 isomer, reduction apparently initially occurs at the most electropositive triangular face of the icosahedral system C(1), C(2), B(3) since these atoms have no direct bonding interaction in the product ((13)-9,11-$B_{10}C_2H_{13}^-$). This result is compatible with other chemistry of $C_2B_{10}H_{12}$ such as nucleophilic attack which excises the B(3)–H unit. Evidence is not definitive whether cage opening occurs simply by a reductive process or whether it requires reduction followed by protonation.[8] Evidence is clear, however, that the $C_2B_{10}H_{12}^{2-}$ ion is very much favored over the radical ion $C_2B_{10}H_{12}^-$. The radical ion has not been observed spectrally nor have any products clearly derivable from it as opposed to $C_2B_{10}H_{12}^{2-}$ been observed.

In bis-dicarbollide complexes both fused icosahedra contain the 26 core electrons required for a closed-shell configuration. The situation for the metal can be examined utilizing a molecular orbital description by Gray of bonding in ferrocene.[9] An energy level diagram based on this description is reproduced in Figure 1. Six electrons can be accommodated, essentially on the metal, in the nonbonding or slightly bonding $1e_{2g}$ and $2a_{1g}$ orbitals. For electronic configurations greater than d^6, electrons go into the $2e_{1g}$ orbitals which are the antibonding orbitals related to the bonding $1e_{1g}$ orbitals. It should be emphasized that in the dicarbollide system the $1e_{1g}$ orbitals are not only bonding with regard to ligand–metal interactions but, since they contain core electrons, are also bonding with regard to maintaining the icosahedral system. Consequently the $2e_{1g}$ orbitals are antibonding not only with regard to metal–ligand interaction but also with regard to maintaining icosahedral geometry. In d^8 and d^9 bis-dicarbollide systems, two and three electrons would be present, respectively, in the $2e_{1g}$ orbitals. We suggest occupation of these orbitals accomplishes the same result as occupation of analogous orbitals in *closo*-$C_2B_{10}H_{12}$ systems, *e.g.*, loss of icosahedral geometry leading ultimately to a cage-opened nido structure. In the d^8 and d^9 cyclopentadienide systems apparently the occupancy of the antibonding orbitals does not affect the pentagonal pyramidal structure. However, complexes with configurations greater than d^6 are certainly more reactive toward reagents which remove the aromaticity of the cyclopentadienide ring and thus affect the overall structure.[2]

Finally, the distortion observed in the dicarbollide metal systems may give some insight into the reduction of the $C_2B_{10}H_{12}$ system. It has recently been suggested that solid-state evidence can be used to get information concerning a reaction pathway.[10] Consider the d^7 (one electron–two icosahedra), d^8 (two electrons–two icosahedra), and d^9 (three electrons–two icosahedra) complexes. Slippage (cage opening) is very small (or nonexistent) in the d^7 case but very large in the d^9 case.[3] The intermediate d^8 system has distinct slippage,