ordination. 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**.

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**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 $\Gamma$ is the degree of dissociation into ions and ion pairs, $\delta_{ion} = 4.0$, and $\delta_{covalent}$ was calculated from $\delta_{obsd}$ at one concentration.

(16) The equivalent conductance $\Lambda = \gamma(\Lambda° - (6.08\Lambda° + 188)\sqrt{C}) = 1000K_{sp}/C$, where $\gamma$ 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,

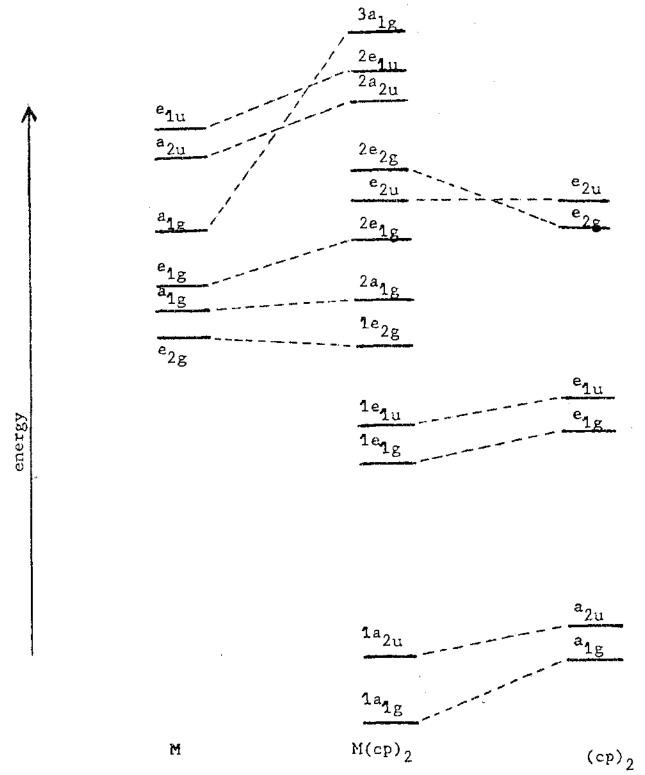

**Figure 1.** Relative energies of the molecular orbitals in metallocene complexes.[9]

but it is closer in structure to the $d^7$ than to $d^9$ case.[5] These data when considered with the apparent differences in stability between the $C_2B_{10}H_{12}$, $C_2B_{10}H_{12}^-$, and $C_2B_{10}H_{12}^{2-}$ systems may indicate that opening of the icosahedral system occurs simply upon addition of the second electron and may not require a proton.

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## Electron-Transfer Reactions with Unusual Activation Parameters. A Treatment of Reactions Accompanied by Large Entropy Decreases

AIC40369B

*Sir:*

The activation enthalpies for the oxidation of $Fe(H_2O)_6^{2+}$ by poly(pyridine)iron(III) and -ruthenium(III) complexes (reactions 1 and 2, for example) are small or slightly negative.[1-3] This has led to the suggestion[2,3] that these reactions occur by a "non-Marcus" path which includes at least one distinctive feature not considered in a current outer-sphere electron-transfer model.[4-8] We wish to point out that small or even negative activation enthalpies are in themselves not necessarily inconsistent with this model and indeed are predicted by it for the systems under consideration.

$$\mathrm{Fe(H_2O)_6{}^{2+} + Fe(bipy)_3{}^{3+} \rightarrow Fe(H_2O)_6{}^{3+} + Fe(bipy)_3{}^{2+}} \tag{1}$$

$$\mathrm{Fe(H_2O)_6{}^{2+} + Ru(bipy)_3{}^{3+} \rightarrow Fe(H_2O)_6{}^{3+} + Ru(bipy)_3{}^{2+}} \tag{2}$$

In terms of the model referred to above, the rate constant for an outer-sphere electron-transfer reaction is given by

$$k = pZe^{-\Delta G^*/RT} \tag{3}$$

where $p$ is the probability of electron transfer in the activated complex and $Z$, the collision frequency between two uncharged particles in solution, is taken to be $10^{11}$ $M^{-1}$ sec$^{-1}$. The following relations between the kinetic parameters for a cross reaction and the component self-exchange reactions can also be derived from this model[4-8]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \tag{4}$$

$$\log f_{12} = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \tag{5}$$

$$\Delta G_{12}{}^* = \frac{\Delta G_{11}{}^*}{2} + \frac{\Delta G_{22}{}^*}{2} + \frac{\Delta G_{12}{}^\circ}{2} + \frac{(\Delta G_{12}{}^\circ)^2}{8(\Delta G_{11}{}^* + \Delta G_{22}{}^*)} = \frac{\Delta G_{11}{}^*}{2} + \frac{\Delta G_{22}{}^*}{2} + \frac{\Delta G_{12}{}^\circ}{2}(1 + \alpha) \tag{6}$$

$$\alpha = \frac{\Delta G_{12}{}^\circ}{4(\Delta G_{11}{}^* + \Delta G_{22}{}^*)} \tag{7}$$

where $k_{12}$, $K_{12}$, $\Delta G_{12}{}^*$, and $\Delta G_{12}{}^\circ$ refer to the cross reaction and $k_{11}$, $k_{22}$, $\Delta G_{11}{}^*$, and $\Delta G_{22}{}^*$ refer to the exchange reactions.[5-10] Usually $\alpha$ is small; it is negative in reactions of negative $\Delta G_{12}{}^\circ$ and becomes increasingly so with decreasing $\Delta G_{12}{}^\circ$.

The value of $\Delta S_{12}{}^*$ can be obtained by differentiating eq 6 with respect to temperature $[\Delta S = -\partial(\Delta G)/\partial T]$

$$\Delta S_{12}{}^* = \left[\frac{\Delta S_{11}{}^*}{2} + \frac{\Delta S_{22}{}^*}{2}\right](1 - 4\alpha^2) + \frac{\Delta S_{12}{}^\circ}{2}(1 + 2\alpha) \tag{8}$$

The value of $\Delta H_{12}{}^*$ can similarly be obtained from eq 6 by using a Gibbs–Helmholtz equation $[\Delta H = \partial(\Delta G/T)/\partial(1/T)]$ for $\Delta H_{12}{}^*$, $\Delta H_{11}{}^*$, $\Delta H_{22}{}^*$, and $\Delta H_{12}{}^\circ$

$$\Delta H_{12}{}^* = \left[\frac{\Delta H_{11}{}^*}{2} + \frac{\Delta H_{22}{}^*}{2}\right](1 - 4\alpha^2) + \frac{\Delta H_{12}{}^\circ}{2}(1 + 2\alpha) \tag{9}$$

It is readily apparent from eq 9 that $\Delta H_{12}{}^*$ will decrease with decreasing $\Delta H_{12}{}^\circ$ and that $\Delta H_{12}{}^*$ will be small or even negative if $\Delta H_{12}{}^\circ$ is sufficiently negative.

The relationship between $\Delta G^*$, $\Delta H^*$, and $\Delta S^*$ and the usual experimentally derived quantities $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ is

$$\begin{aligned} \Delta G^‡ &= \Delta G^* - RT \ln (hZ/kT) \\ \Delta S^‡ &= \Delta S^* + R \ln (hZ/kT) - {}^1\!/_2 R \\ \Delta H^‡ &= \Delta H^* - {}^1\!/_2 RT \end{aligned} \tag{10}$$