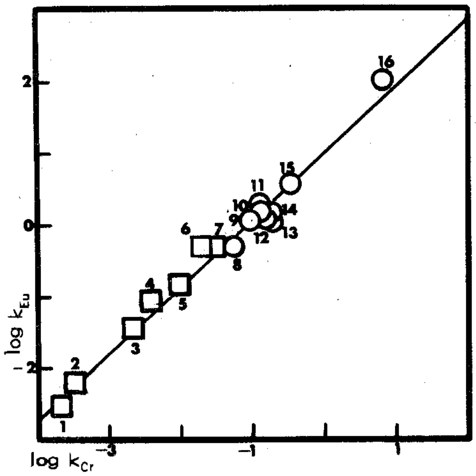

Figure 1. log–log plot comparing the specific rates for reductions of various cobalt(III) complexes by Cr^{2+} and Eu^{2+} (25 °C, $\mu = 1.0$). Squares designate complexes reacting via outer-sphere paths, whereas circles represent carboxylato complexes, for which reductions are mainly inner sphere.[7a,10] Individual oxidants are (1) $Co(NH_3)_6^{3+}$, (2) Ro(imidazole)$^{3+}$, (3) Ro(pyrazole)$^{3+}$, (4) Ro(pyridine)$^{3+}$, (5) Ro(dimethylformamide)$^{3+}$, (6) Ro(acetonitrile)$^{3+}$, (7) Ro(*N*,*N*-dimethylnicotinamide)$^{3+}$, (8) Ro(diphenylacetato)$^{2+}$, (9) Ro(*N*-methyl-2-pyridinecarboxylato)$^{3+}$, (10) Ro(3-pyridinecarboxylato)$^{2+}$, (11) Ro(difluoroacetato)$^{2+}$, (12) Ro(propionato)$^{2+}$, (13) Ro(cyclopropanecarboxylato)$^{2+}$, (14) Ro(acetoxyacetato)$^{2+}$, (15) Ro(furoato)$^{2+}$, and (16) Ro(lactato)$^{2+}$ (Ro = "roseo" = $(NH_3)_5Co^{III}$). The least-squares line shown corresponds to the equation log k_{Eu} = 0.93 log k_{Cr} + 0.97.

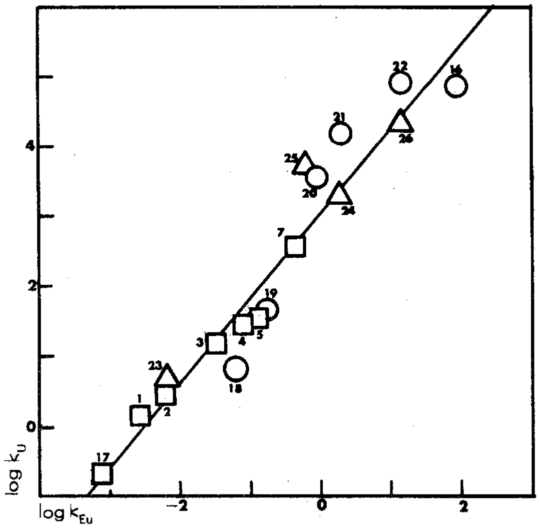

Figure 2. log–log plot comparing specific rates for reductions by U^{3+} (25 °C, $\mu = 0.20$) and Eu^{2+} (25 °C, $\mu = 1.0$). Squares designate Co(III) complexes reacting via outer-sphere paths, circles (carboxylato)cobalt(III) complexes, and triangles cobalt-free heterocyclic species. Individual points 1–5, 7, and 16 refer to oxidants listed in Figure 1. Other oxidants are (17) $Co(en)_3^{3+}$, (18) Ro(triethylacetato)$^{2+}$, (19) Ro(trimethylacetato)$^{2+}$, (20) Ro(cyclopentanecarboxylato)$^{2+}$, (21) Ro(acetato)$^{2+}$ (limiting rate at low acidity), (22) Ro(formato)$^{2+}$, (23) 3-pyridinecarboxamide (conjugate acid), (24) 4-pyridinecarboxamide (conjugate acid), (25) methyl viologen, (26) 4-pyridinecarboxylic acid (conjugate acid) (Ro = "roseo" = $(NH_3)_5Co^{III}$). The least-squares line shown corresponds to the equation log k_U = 1.23 log k_{Cr} + 3.05.

patterns overlap, and relative rates have become noninformative as to mechanism.

The warning here does not apply to comparisons in which the structure of one of the reductants requires that it react via an outer-sphere path (e.g., $Ru(NH_3)_6^{2+}$). Moreover, uncertainty may be diminished by showing not only that observed ratios correspond to outer-sphere values but also that they differ substantially from ratios found for bona fide inner-sphere series in the appropriate reactivity range. Because of the vagaries to which inner-sphere systems are subject, however, arguments of the latter type must be considered indicative rather than conclusive.

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(1) (a) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963); (b) *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).
(2) Opinion is divided as to the importance of nonadiabatic effects in electron transfer. Although evidence pointing to nonadiabaticity has been reported in isolated instances,[3] it is generally indicative rather than conclusive, and some workers lean toward the view that such effects do not contribute significantly to ordinary redox reactions.[4] Note also that Chou and co-workers[3c] have pointed out that certain aspects of the Marcus picture (including that under present discussion) may apply to nonadiabatic systems.
(3) (a) D. S. Matteson and R. A. Bailey, *J. Am. Chem. Soc.*, **91**, 1975 (1969); (b) M.-S. Chan, Ph.D. Thesis, Washington University, St. Louis, 1974; (c) M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 5615 (1977); (d) R. B. Fulton and T. W. Newton, *J. Chem. Phys.*, **74**, 1661 (1970).
(4) H. Taube *Adv. Chem. Ser.*, No. **162** 136 (1977).
(5) The mirror relationship, pertaining to oxidation of a series of reductants by pairs of oxidants, likewise holds. The arguments presented here can be applied to that situation also. A second limitation stipulated by Marcus pertains to reaction series where the thermodynamic driving force is inordinately large. Although such highly exergonic systems have been described,[6] they involve photochemically excited states. The limitation does not appear to be important for thermal reactions in aqueous media.
(6) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **99**, 241 (1977).
(7) See, for example, (a) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2647 (1974); (b) E. B. Fleischer and S. K. Cheung, *J. Am. Chem. Soc.*, **98**, 8381 (1976); (c) E. S. Gould, N. A. Johnson, and R. B. Morland, *Inorg. Chem.*, **15**, 1929 (1976).
(8) Among authors who appear to have used the criterion of relative rates, either directly or by implication, in inclusory form are the following: (a) K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1832 (1972); (b) M. Hery and K. Wieghardt, *Inorg. Chem.*, **17**, 1130 (1978); (c) J. P. Birk and S. G. Kozub, *ibid.*, **17**, 1186 (1978); (d) J. C. Thomas, J. W. Reed, and E. S. Gould, *ibid.*, **14**, 1696 (1975). Note that in each of these cases, additional evidence supporting the assigned outer-sphere mechanism was presented.
(9) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2639 (1974).
(10) (a) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964); (b) R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965); (c) M. V. Olson and H. Taube, *Inorg. Chem.*, **9**, 2072 (1970).
(11) M. K. Loar, M. A. Sens, G. W. Loar, and E. S. Gould, *Inorg. Chem.*, **17**, 330 (1978).
(12) (a) Y.-T. Fanchiang, R. R. Carlson, P. K. Thamburaj, and E. S. Gould, *J. Am. Chem. Soc.*, **99**, 1073 (1977); (b) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **17**, 1827 (1978).
(13) M. K. Loar, Y.-T. Fanchiang, and E. S. Gould, *Inorg. Chem.*, **17**, 3689 (1978).
(14) Y.-T. Fanchiang, J. C. Thomas, J. C.-K. Heh, and E. S. Gould, *Inorg. Chem.*, **16**, 1942 (1977).
(15) The scatter of points about the regression line in Figure 2 is somewhat more severe (correlation coefficient 0.967) than that in the Cr(II)–Eu(II) plot of Figure 1 (0.993), reflecting, in part, the circumstance that only Co(III) oxidants are included in the latter.

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Severe Distortions of a Polyhedral Metallocarborane Structure

Sir:

The readiness with which large polyhedral systems undergo distortions and rearrangements to isomeric species allows them to seek localized bonding patterns which may be related to smaller geometrically related species. Of the five structures

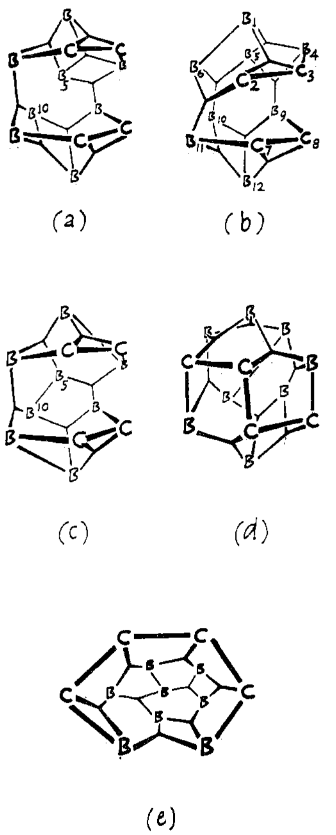

Figure 1. Hypothetical structure for $C_4B_8H_{12}$ (0860) opened up from the $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ analogue (b) in which the two $\eta^5\text{-}C_5H_5Co$ units are replaced by BH. The close relation of (a) to two $C_2B_4H_8$ valence structures leaves B(5) and B(10) unconnected, and hence (a) is expected to collapse to (b) or to take up an electron pair to give (c) as hypothetical $C_4B_8H_{12}^{2-}$ (0670). Structure (b) and hypothetical structures (a) and (c) are dominated[1] by $\eta\text{-}C_5H_5Co$ units (in place of BH) at positions 1 and 12, while the actual geometrical structure of $(CH_3C)_4B_8H_8$ (idealized as $C_4B_8H_{12}$) is shown in (d) in its dominant valence description. Here, in (d), a dominant localized structure is the zigzag C_4 group, while the single B–B bond is very delocalized. The valence structure of the nido-like form of $C_4B_8H_{12}$[3] (e) which is analogous to $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$[1b] is dominated by single bonds B–C–C–C–C–B around the open face, while there are alternative ways to place the remaining bonds.

established crystallographically for the 12-vertex, 28-electron system, I comment here on the severe distortion shown by one structure type[1] exemplified by $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ and $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6OC_2H_5$. This structure is idealized, for ease of discussion, as $(C_2B_4H_6)_2$, in order to exhibit the relationship of its framework bonds to those[2] in $C_2B_4H_8$ (4,5-dicarbahexaborane(8)).

First, open the structure to C_2 symmetry (Figure 1a). If we deploy the C=C double bonds each as a single and three-center bond, and the single bonds C(2)–B(6), C(3)–B(4), C(7)–B(11), and C(8)–B(9) as in $C_2B_4H_8$, and if we then require three framework bonds (omitting external BH or CH bonds) to each apex atom B(1) and B(12), there remain only two electron pairs for the equatorial region to bond B(4), B(5), and B(6) to B(9), B(10), and B(11) (Figure 1a). One way of placing these two equatorial bonds leaves B(5) and B(10) unconnected as shown in the open structure (Figure 1a). Any other placement of these two equatorial bonds would leave other pairs of boron atoms unconnected. Thus this molecular geometry could be stabilized by addition of two electrons to make a bond between B(5) and B(10) in the hypothetical ion $C_4B_8H_{12}^{2-}$ (Figure 1c).

The observed geometry for the analogue of neutral $C_4B_8H_{12}$ is therefore somewhat collapsed, so that C(2) is 2.02 Å from B_{11}. Hence, with few changes other than those associated with the conversion of a single C(2)–B(6) bond toward a three-center bond involving B(11), the framework bonding pattern of the two $C_2B_4H_6$ moieties is largely maintained. While there are other valence structures contributing to the resonance hybrids of these geometrical structures, the main features of the distortion of (a) to (b) and of the opening from the nearly icosahedral structure seem reasonable in terms of the bonding arrangement in $C_2B_4H_8$.

Relationships of these analogues (Figure 1a,b) to other known structures of $C_4B_8H_{12}$ or its analogues[3] are shown in Figure 1c–e the emphasis is on local dominant valence structures.

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A Comment on Ligand Designators

Sir:

I read with interest the recent article by Sloan and Busch[1] on proposed nomenclature for the "Designation of Coordination Sites for Ambidentate and Flexidentate Ligands". Especially pleasing was the apparent consistency of their proposed kappa (κ) notation with the enormously useful and simple *hapto* (η) notation introduced by Cotton[3]—allowing for minor changes in the *hapto* notation. However, in a following article, Leigh[2] proposed an alternative, ostensibly simpler system in which a single designator, Ω, could suffice for the η and κ designators. I fully appreciate the need for nomenclature with designators that are universal, simple, and unambiguous. However, it is the rare case that proposed systems can fully anticipate the problems that will be encountered in future structures, especially in the complex inorganic and organometallic area. I strongly urge that the Cotton *hapto* system be retained and remain unmodified. It is an elegant and widely used system. Just imagine the bewilderment of the chemistry student in the year 2052 as he reads "inorganic chemistry" articles in the 1960–2040 period if a succession of Greek letters were to parade by as designators.[4]

The *hapto* system as originally formulated[3] was free of electronic ambiguities. It was to be a topological designator that specified metal–ligand atom connexities subject to a precise[5] determination from crystallographic analysis and was to clearly avoid the ambiguities associated with "subjective judgements about bonding details".[3] It has succeeded well to date.