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Systematics in Boron Hydride Reactivities. Acceptable Valence Structures and Rearrangement in Unimolecular and Bimolecular Nucleophilic and Electrophilic Reactions

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The topological approach previously used to determine allowed transition states for nucleophilic and electrophilic reactions in the boranes is revised so as to exclude *sty*(−1) valence structures on the basis of "awkward hybridization." A basis for the anticipation of framework rearrangement in the transition state and the selection of a reasonable framework geometry is suggested. Transition states which were previously excluded from consideration are discussed and typical intermediates presented.

Introduction

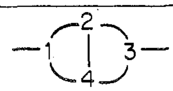
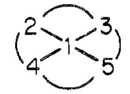
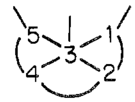
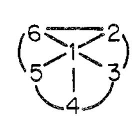
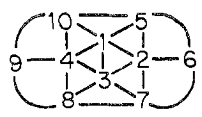
Because of our interest in systematic descriptions of the chemistry of boranes and heteroboranes[1] we have watched the development and application of topological approaches. The original formulation of the "topological" approach to boron hydride valence structures provided chemists with a scheme for describing the bonding in boron hydrides in terms of two- and three-center bonds.[2] Recently, there have been further discussions of topological descriptions of the boron hydrides;[3,4] the most drastic simplification of the approach was outlined by Epstein and Lipscomb,[5] who limited three-center BBB bonds to a single type, the closed BBB bond. Perhaps potentially more significant, however, is a recent effort to extend the latter revised topological approach to boron hydride reactivities, specifically, electrophilic and nucleophilic substitution in the boron hydrides B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$.[6] While this effort to delineate allowed reaction paths correlates with some observed reactivities, a close analysis of the method shows that the selectivity realized is rather arbitrary and depends on the "acceptability" of certain valence structures. In addition to acceptable valence structures, other aspects of reactivity which were not treated and/or essentially not allowed in the original approach, *i.e.*, framework rearrangement, electron-pair and vacant-orbital unimolecular transition states, and bimolecular transition states, are discussed below.

Acceptable Valence Structures

In the basic approach as previously presented,[6] four transition-state topologies per unique hydrogen (one each for SN1, SE1, SN2, and SE2) are tested to determine whether allowable valence structures are possible without intramolecular rearrangement. An "allowable" transition state then affords a *possible* reaction path. In the present case we followed a somewhat different procedure, which is however certainly equivalent in principle. Each unique hydrogen was not explicitly tested; rather, the *styx* notations[2,4] possible for each transition state were deduced from the equations of balance appropriate for each transition-state molecular formula.[7] Then the possible *styx* solutions were examined for allowed resonance structures.[5] If an allowed structure corresponded to a transition state in which no intramolecular rearrangement had occurred, the reaction was deemed as possible. This procedure confirmed all of the reactions noted in Table I of the previous paper[6] as *"allowed," if the styx solutions included x = −1 as a possibility.* A *sty*(−1) solution represents a valence structure in which one boron has no terminal hydrogen. However, for the transition states which arise from the molecules considered (B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, $B_{10}H_{14}$), we deem *sty*(−1) valence structures[8] as unacceptable because of the "awkward" hybridizations involved. These "awkward" valence structures arise when a boron hydride loses either H^+ or H^- and the electron pair or orbital, respectively, which results in "forced" into framework bonding. For instance, SE1 at the apical boron of B_6H_{10} gives a $B_6H_9^-$ intermediate with a 414−1 valence structure which appears to be reasonable in planar projection (Figure 1C) but which would impose an unreasonable hybridization on the apical boron. The pyramidal geometry of the actual B_6H_{10} molecule[9] would demand the projection of four bonds from the apical boron toward the pentagonal base of the framework, clearly a prohibited hybridization for a second-row element like boron. Since the latter "hybridization"

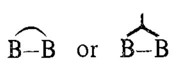
(1) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 11, 1974 (1972).
(2) For example, see W. N. Lipscomb, "Boron Hydrides," Benjamin, New York, N. Y., 1963, and references cited therein.
(3) R. B. King, *J. Amer. Chem. Soc.*, 94, 95 (1972).
(4) S. Liebowitz, I. R. Epstein, and D. J. Kleitman, *J. Amer. Chem. Soc.*, 96, 2704 (1974).
(5) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, 10, 1921 (1971).
(6) I. R. Epstein, *Inorg. Chem.*, 12, 709 (1973).
(7) It should be noted that those equations of balance presented in ref 5 are corrected in ref 6 but apply to a boron hydride of formula $(B_pH_{p+q})^l$, where l = charge; the conventions used in ref 2 and 4 and here are for $(B_pH_{p+q+c})^c$, where c = charge.
(8) Of course *sty*(−1) structures are acceptable when two frameworks are joined through a B–B bond or a shared face.
(9) F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, 28, 56 (1958).

Table I. Topologically Allowed Boron Hydride Substitution Reactions

Molecule	Allowed reactions[a]	Structure[b]
B_4H_{10}	SN1 at B1 (4101) SE1 at B1–B2 (3022)	
B_5H_9	*SE1 at B1 (404–1) SE2 at B1 (4201) *SN1 at B2 (421–1) SE1 at B2–B3 (3130) SN1 at B2–B3 (3300)	
B_5H_{11}	SE1 at B3 (3122) SE1 at B1–B2 (3122)[c] SE1 at B2–B4 (2213)	
B_6H_{10}	*SE1 at B1 (414–1) *SN1 at B1 (431–1) SE2 at B2 (4301) *SN1 at B3 (431–1) SE1 at B2–B3 (3230) SE1 at B3–B4 (3230)	
$B_{10}H_{14}$	*SE1 at B1 (454–1) *SN1 at B1 (471–1) *SE1 at B2 (454–1) *SE1 at B5 (454–1) *SN1 at B5 (471–1) *SN1 at B6 (471–1) SE1 at B5–B6 (3630)	

[a] The list includes all those reactions determined to be allowed by the approach of ref 6. However, those reactions preceded by an asterisk are deemed to be topologically disallowed by the present approach (see text). The *styx* notation of each transition state is listed in parentheses after the reaction site. A listing of two sites under one entry indicates substitution at the bridge position between the two borons. Refer to Figure 1 for a depiction of those transition states disallowed by the present approach. [b] n = a BH group at position n; n– = a BH_2 group at position n. Curved lines represent BHB bridges and straight lines represent topological connections in the sense of ref 5. [c] Allowed if the 4112 structure of B_5H_{11} is used to generate the transition state.

would certainly be more unusual than that necessary for two borons to be bonded simultaneously by a two-center and a three-center interaction



a situation which has expressly been termed as an unacceptable topological connection,[2] we conclude that *sty*(−1) valence structures must also be considered as unacceptable.[8] Application of this new constraint to the list of allowed reactions for B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$ gives the list shown in Table I. Those valence structures which were excluded in the process are illustrated in Figure 1. A comparison of the topologically allowed reactions found by the different methods shows that the exclusion of *sty*(−1) transition states drastically pares the list of allowed reactions. The most dramatic effect is evident for $B_{10}H_{14}$ where only one of the original list of seven paths remains allowed (SE1 at the bridge position). This result seriously compromises the usefulness of the approach in view of the rich reaction chemistry of $B_{10}H_{14}$ which has been established to proceed under both nucleophilic and electrophilic conditions to give substitution at a variety of positions.[2,10] The difficulties encountered for $B_{10}H_{14}$ are symptomatic of an oversimplified approach[6] which (1) treats no cases where intramolecular rearrangement is possible (intramolecular rearrangement is a rather common, sometimes facile process in boranes[2,10]), (2)

(10) For example, see E. L. Muetterties, "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967, and references cited therein.

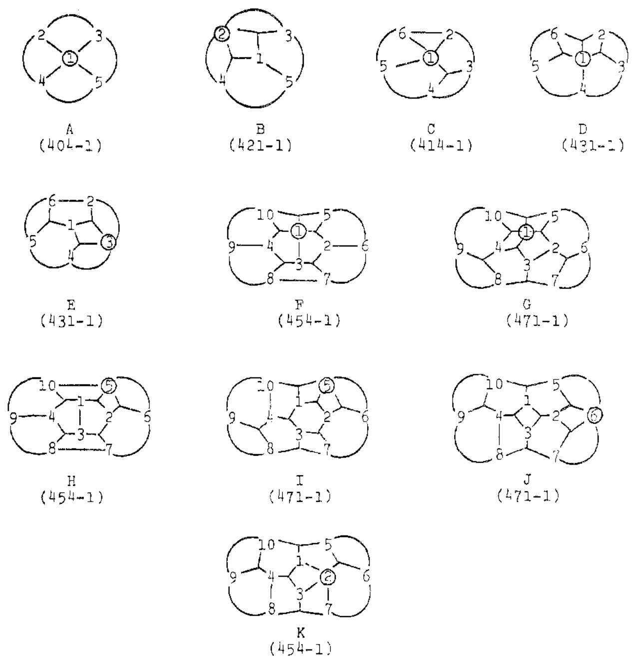


Figure 1. Awkward valence structures: n = BH group at position n; ⓝ = a boron without a hydrogen at position n; curved lines represent BHB bridges; straight lines represent B–B two center bonds; BBB closed three-center bonds are represented by a tripodal symbol ⅄ ; the *styx* number is listed under each structure.

treats no cases where an empty orbital or an electron pair is present in the transition state after dissociative loss of H^- or H^+, respectively (a pure topological approach provides no way of assessing how the solvent cage might stabilize such transition states), and (3) allows very few bimolecular transition states[6,11] [while not many definitive kinetic studies have been completed, a number are consistent with bimolecular paths for substitution of decaborane[12–14]].

The subsequent discussion, while not purported to be comprehensive, will attempt to introduce certain, perhaps viable, approaches to the three problem areas just mentioned.

Rearrangement

Recently, it was shown that a framework of n boron atoms varied from closo to nido to arachno as the electrons available for "framework bonding" correspondingly changed from $2n + 2$ to $2n + 4$ to $2n + 6$ in number.[1,15] In the context of the topological approach, the number of "framework electrons" is precisely the number used in the *styx* notation; *i.e.*, both approaches "factor out" bonds to exopolyhedral substituents. It follows that skeletal rearrangement would not be anticipated as long as the number of framework electrons remains unchanged as would be the case for both associative and dissociative electrophilic mechanisms since H^+ is the model electrophile. On the other hand, since H^- is the model nucleophile, associative and dissociative nucleophilic mechanisms would increase and decrease the framework electron count, respectively, in each case by two electrons. Thus, in nucleophilic mechanisms there is a reason to anticipate framework rearrangement. In order to propose a valence structure for nucleophilic transition states, it follows

(11) For SE2 at B1 in B_5H_9 and SE2 at B2 in B_6H_{10} topologically suitable transition states were generated.

(12) I. Dunstan and J. V. Griffiths, *J. Chem. Soc.*, 1344 (1962).

(13) S. Hermanek, J. Plesek, B. Stibr, and F. Hanousek, *Collect. Czech. Chem. Commun.*, 33, 2177 (1968).

(14) H. C. Beachell and D. E. Hoffman, *J. Amer. Chem. Soc.*, 84, 180 (1962).

(15) K. Wade, *Chem. Commun.*, 792 (1971).

that the proper framework classification, closo, nido, or arachno,[16] would first be determined from the framework electron count (*styx* number) and then tested to see which valence structures are topologically acceptable.[2,5] Although the approach would lead to the prediction of transition states, the path of atom movement could only be inferred in most cases, and the position of substitution would be difficult to predict *a priori*. In cases where an anticipated rearrangement would obviously be energetically unfavorable, the mechanism must be regarded as disallowed. The latter instance is illustrated by cases of a nido → closo conversion where the closo intermediate would require more than one bridge hydrogen, *e.g.*, *nido*-B_6H_{10} → *closo*-$B_6H_9^+ + H^-$. Closo molecules rarely have bridge hydrogens; the only well-substantiated case is B_5CH_7 where a four-center bridge hydrogen is found;[17] cationic polyhedral boranes are known only under forceful conditions ($B_6H_{11}^+$);[18,19] therefore, $B_6H_9^+$ does not appear eminently reasonable under typical reaction conditions. In contrast to the latter, dissociative nucleophilic conversions which provide more reasonable reaction paths can be inferred as the reverse of the SN2 processes discussed subsequently.

The literature is rather replete with examples of associative nucleophilic reactions for boranes and heteroboranes. Substitution or addition involving H^- is not found as commonly as with neutral lone-pair donors (L = ligand), but the theoretical treatments of each are similar in that L can be considered conveniently as H^-. Thus, nucleophilic attack on 4120 *nido*-B_5H_9 would probably favor a skeletal opening to give a 3122 *arachno*-$B_5H_{10}^-$ (B_5H_{11} skeleton). The latter pentaborane (10) anion is "isoelectronic" with $MeB_5H_8 \cdot NH_3$ which was recently investigated by Kodama;[20] an arachno structure was favored for such intermediates. Another $B_5H_{10}^-$ analog, $B_5H_9 \cdot PMe_3$, has been prepared by Shore and coworkers, who have also completed the X-ray structure for $B_5H_9 \cdot 2PMe_3$ which has an even more open framework[21] than B_5H_{11}. If $L = H^-$, $B_5H_9 \cdot 2PMe_3$ is equivalent to $B_5H_{11}^{2-}$ and represents the first well-characterized $2n + 8$ system, which might be termed hypho,[22] and suggests the existence of similar open skeletons based on other boranes especially as base-catalyzed reaction intermediates.[22] In some cases, cage opening ultimately results in cleavage into "symmetrical" and "unsymmetrical" fragments.[23]

Many more examples of framework opening attendant to nucleophilic attack are evident for the carboranes. Recent examples are

$$closo\text{-}B_4C_2H_6 \xrightarrow{L} nido\text{-}B_4C_2H_6 \cdot L$$ [24]

$$closo\text{-}B_9C_2H_{11} \xrightarrow{L} nido\text{-}B_9C_2H_{11} \cdot L$$ [25,26]

The facile opening of $B_9C_2H_{11}$ by donor molecules suggests a similar possibility for the isoelectronic ions $B_{10}CH_{11}^-$ and $B_{11}H_{11}^{2-}$. Since the nmr spectral evidence for the fluxional nature of $B_{11}H_{11}^{2-}$ and $B_{10}CH_{11}^-$ was obtained in donor solvents,[27,28] the fluxionality may be solvent induced and promoted by a rapid equilibrium, *i.e.*, *closo*-$B_{11}H_{11}^{2-}$ + L ⇌ *nido*-$(B_{11}H_{11} \cdot L)^{2-}$.[29,30]

The preceding discussion implies that closo, nido, and arachno boranes can be "opened" to their corresponding nido, arachno, and hypho[22] counterparts by nucleophilic attack of the appropriate electron-pair donor. (As a corollary, a hypho, arachno, or nido borane is related to its corresponding arachno, nido, or closo borane by a simple dissociative process.) The position of attack may be related to the relative charges of the various polyhedral sites and/or the localization of the LUMO.[2,25] In some cases attack and then dissociation can effect rearrangement, as exemplified by the base-catalyzed rearrangement of various pentaboranes,[20,31] so that any prediction of the ultimate disposition of substituents is in general difficult. By contrast, the ligand displacement studies completed on various *arachno*-$B_{10}H_{12}L_2$ species are consistent with a dissociative process involving a *nido*-$B_{10}H_{12}L$ intermediate[32] but do not indicate skeletal rearrangement so that perhaps a vacant-orbital transition state is present.

Although we have suggested a means for predicting skeletal rearrangement in borane and heteroborane reaction mechanisms, a discussion of H atom rearrangement was not included. For the present it is probably best handled in terms of the reasonable topological variants possible for a given molecule; *e.g.*, the 3311 form of B_6H_{10} (static form 4220) is probably an intermediate for the observed basal hydrogen tautomerism.[2]

Electron-Pair and Vacant-Orbital Unimolecular Transition States

Our regard of *sty*(−1) valence structures as unacceptable removed many SN1 and SE1 reactions from the allowed category in the topological discussion of reactivity.[6] Dissociation involving a B–H group gives rise to *sty*(−1) numbers, but this is not the case for a BH_2 group or a bridge hydrogen and the latter two moieties do give rise to topologically acceptable intermediates. For example, a BH_2 group in B_4H_{10} upon H^- dissociation can incorporate the vacant orbital into a 4101 valence structure (Table I), and as discussed elsewhere,[2,6] all bridge hydrogens give a two-center B–B bond upon loss of H^+. However, especially in the vapor state, it seems overly restrictive to require that a lone pair (SE1) or an empty orbital (SN1) be accommodated by a new

(16) R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971).
(17) G. L. McKown, B. P. Don, R. A. Beaudet, T. J. Vergamini, and L. H. Jones, *J. Chem. Soc., Chem. Commun.*, in press.
(18) H. D. Johnson, II, V. T. Brice, G. L. Brubaker, and S. G. Shore, *J. Amer. Chem. Soc.*, **94**, 6711 (1972).
(19) The topological consequences of four-center bridge hydrogens are discussed later in the text.
(20) G. Kodama, *J. Amer. Chem. Soc.*, **94**, 5907 (1972).
(21) S. G. Shore, *J. Amer. Chem. Soc.*, **96**, 3013 (1974).
(22) The prefix *hypho* is derived from the Greek for web and was suggested by R. E. Williams (private communication) for the $2n + 8$ series of boranes.
(23) R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959).
(24) B. Lockman and T. Onak, *J. Amer. Chem. Soc.*, **94**, 7923 (1972).
(25) V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, *J. Amer. Chem. Soc.*, **95**, 4560 (1973).
(26) D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 6002 (1969).
(27) E. I. Tolpin and W. N. Lipscomb., *J. Amer. Chem. Soc.*, **95**, 2384 (1973).
(28) R. J. Wiersema and M. F. Hawthorne, *Inorg. Chem.*, **12**, 785 (1973).
(29) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).
(30) Our EHMO calculations give the following symmetries for the molecular orbitals near the break between occupied and unoccupied levels: for $B_{11}H_{11}^{2-}(C_{2v})$, $(b_1)^2(a_2)^2(a_1)^0(b_1)^0(b_2)^0$; for $B_{11}H_{11}^{2-}(C_{5v})$, $(e_2)^4(e_1)^2(e_2)^0(e_2)^0(e_1)^0$ [B. Meneghelli and R. W. Rudolph, unpublished results]. Therefore the equilibrium might conceptually be viewed as a redox equilibrium $B_{11}H_{11}^{2-} + 2e^- \leftrightarrows B_{11}H_{11}^{4-}$. In the C_{2v} form, distortion of $B_{11}H_{11}^{2-}$ is not favored; however, for $B_{11}H_{11}^{4-}$ a B_1 motion is symmetry allowed[29] [HOMO × LUMO = $a_1 \times b_1$] and leads to the C_{5v} form. In C_{5v} $B_{11}H_{11}^{2-}$ does not have a closed shell and would be expected to distort *via* an E_2 motion to C_{2v}. The closed-shell C_{5v} $B_{11}H_{11}^{4-}$ also could deform *via* a symmetry-allowed E_2 motion with "oxidation" to C_{2v} $B_{11}H_{11}^{2-}$.
(31) T. P. Onak, *J. Amer. Chem. Soc.*, **83**, 2584 (1961).
(32) M. F. Hawthorne, R. L. Pilling, and R. C. Vasavada, *J. Amer. Chem. Soc.*, **89**, 1075 (1967).

valence structure in all transition states.[33] In the case of an empty orbital, weak donor solvents could stabilize the transition state by adduct formation. As a consequence the closo, nido, or arachno classification of the molecule would remain unchanged. The site of dissociation in some cases can be related to the molecular charge distribution (*vide supra*). Since cationic polyhedral boranes are not common, it is reasonable to propose H^- dissociation only in the case of an anionic borane or its isoelectronic analog.

Acid dissociation is certainly very common and sometimes facile for bridge hydrogens. This facility decreases in the case of a BH_2 group and again for a BH group.[2,10] The differences are such that SE1 mechanisms are expected mainly for bridge-hydrogen substitution reactions.

Bimolecular Transition States

As related in the section of this paper regarding rearrangement (*vide supra*), associative nucleophilic reactions are prevalent in borane chemistry. However, because the previous approach to reactivity[6] did not include a basis for choosing a borane skeleton after rearrangement, no SN2 reactions were found to be allowed for B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$. There is sufficient precedent to anticipate most closo, nido, and arachno structures[1,16] but very few hypho structures are well characterized; intuition must suffice until more are characterized.[22]

The presence of SE2 transition states in boranes may be adduced because of the correlation of negative charge density with the site of attachment for many substitutions effected under electrophilic conditions.[2,10] Clearly these observations are inconsistent with SE1 mechanisms where the opposite correlation would be expected.[34]

We note that the 4201 structure[5,6] of $B_5H_{10}^+$ may be prototypal of bimolecular electrophilic substitution at five-coordinate boron sites. The recently characterized protonated B-B bond[18] in $B_6H_{11}^+$ and the four-center bridge hydrogen[17] of B_5CH_7 probably model transition states in other cases. In a topological context, a four-center bridge hydrogen could result most simply from attack of H^+ on any triangular array of borons capable of being bonded by a closed three-center bond. Of course the H^+ attachment would favor faces of relatively high electron density which could be inferred from MO calculations[2,5] or perhaps merely by consideration of the coordination numbers of the borons to which the hydrogen is bridged. There appears to be substantial precedent for the placement of bridge hydrogens between boron atoms so that the lowest possible coordination number is obtained for each boron.[35] The conversion of a three-center bridge hydrogen to a four-center hydrogen requires the loss of an additional three-center BBB interaction and the formation of a B-B bond. The conversion of one hydrogen of a BH_2 group into a four-center bridge hydrogen results in the loss of two three-center BBB bonds and the formation of two B-B bonds. The equations of balance appropriate for the inclusion of four-center bridge hydrogens are

$$q + c = f + s + x$$

$$y = s - 2c - q/2 + 2f$$

$$t = p + c - s - 2f$$

Where the *styx* notation is expanded to an *fstyx* notation, f being the number of four-center bridge hydrogens in a boron hydride of formula $(B_pH_{p+q+c})^c$ where c = charge.

As exemplified by the prototypes B_5CH_7[17] and $(B_6H_{11}^+)$,[18] no major framework rearrangement is expected in SE2 transition states. The "extra" hydrogen in B_5CH_7 distorts one trigonal face of the closo octahedron but does not effect an opening to the pyramidal geometry of the nido family.[16] The available evidence favors nido frameworks for both B_6H_{10} and $B_6H_{11}^+$. In the same vein, the reactions of electrophiles with $B_{10}H_{10}^{2-}$ have been the subject of recent mechanistic studies which are consistent with a bimolecular intermediate, $B_{10}H_{11}^-$ being the prototype with H^+ as the electrophile.[36] It will be interesting to see if $B_{10}H_{11}^-$ retains the framework geometry of $B_{10}H_{10}^{2-}$.

Acknowledgments. It is a pleasure to acknowledge the partial support of this work by National Science Foundation Grants GP-41163X and GP-28619. We also wish to thank the referees and I. R. Epstein for helpful comments.

(33) L. C. Ardini and T. P. Fehlner, *Inorg. Chem.*, 12, 798 (1973), and references cited therein.

(34) W. N. Lipscomb, *J. Phys. Chem.*, 62, 381 (1958).

(35) R. E. Williams, paper presented at the Second International Meeting on Boron Chemistry, Leeds, England, March 1974.

(36) P. H. Wegner, D. M. Adams, F. J. Callabretta, L. T. Spada, and R. G. Unger, *J. Amer. Chem. Soc.*, 95, 7513 (1973).