polyhedral faces.[7,28] Molecular models indicate no similar stereochemical restrictions to structural change in either the $Fe(HB(pz)_3)_2$ or $[Fe((py)imH)_3]^{2+}$ species.

Acknowledgment. Support of this work by the National Science Foundation, the Robert A. Welch Foundation under Grant C-627, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. E.V.D. also thanks the Energy Research and Development Agency for a summer fellowship and travel grant (Grant T-179) to Brookhaven National Laboratory as administered under the auspices of the Associated Universities Program. We especially thank Drs. Mitchell Hoselton and Norman Sutin for the kind availability of and assistance with the laser *T*-jump apparatus and for many enlightening comments and rewarding discussions during the course of the work.

Registry No. $[Fe((py)imH)_3]^{2+}$, 65494-05-5; $[Fe((py)bimH)_3]^{2+}$, 58957-72-5; (py)imH, 18653-75-3; $[Fe((py)imH)_3](BPh_4)_2$, 65494-06-6; $[Fe((py)bimH)_3](BPh_4)_2$, 58957-75-8; $Fe((py)im)_3$, 65494-04-4.

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Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712

Ground States of Molecules. 46.[1] MNDO Study of Hydroboration of Alkenes and Alkynes

MICHAEL J. S. DEWAR* and M. L. McKEE

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MNDO calculations are reported for the reactions of borane with ethylene, propene, isobutene, vinyl chloride, vinyl fluoride, acetylene, and methylacetylene and of methylborane and dimethylborane with propene. The results are consistent with the available evidence and indicate that the orientation of addition to olefins is determined primarily by steric effects. Addition to vinyl chloride is predicted to take place with Markownikoff orientation but to vinyl fluoride with anti-Markownikoff orientation.

Introduction

In the 20 years since Brown and Rao[2] first reported addition of boranes to olefins, such hydroboration reactions have become of major importance in organic synthesis.[3-6] Olefins of all types react rapidly with BH_3, even if the double bond is highly hindered. If hindrance is low, the reaction proceeds further to a trialkylborane. If bulky substituents are present, the reaction may stop at the monoalkyl- or dialkylborane stage.

Hydroboration is usually carried out in ethereal solution, using an ether–borane complex as the source of BH_3. Tetrahydrofuran has been found especially suitable. Under these conditions addition to unsymmetrically substituted ethylenes leads to predominant anti-Markownikoff addition,[4-6] mono-*n*-alkyl derivatives giving tri-*n*-alkylboranes in which ca. 94% of the alkyl groups are attached to boron through C_1, the rest through C_2. This selectivity refers to an average over the three successive hydroborations leading to the final product. In more hindered cases, essentially 100% of one product can be obtained.

The role of the solvent is still uncertain. In ethers such as tetrahydrofuran, borane exists as a complex,[7] $R_2O \rightarrow BH_3$. This might react directly with the olefin, or it may first have to dissociate into its components. In the latter case, the dissociation may be reversible or rate determining. Pasto et al.[8] have concluded on the basis of kinetic studies that the eth-

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Table I. MNDO Forward and Reverse Activation Barriers of Hydroboration Reactions (kcal/mol)

	Markownikoff		Anti-Markownikoff		$\Delta(M_{fwd} - \text{anti-}M_{fwd})$, kcal/mol
Reacn	Fwd barrier	Rev barrier	Fwd barrier	Rev barrier	
$BH_3 + =$	7.6	4.6			
$BH_3 + =$	9.7	37.4	9.9	42.1	−0.2
$BH_3 + =$	11.0	32.1	11.8	37.1	−0.8
$BH_3 + =Cl$	11.6	48.2	12.0	50.7	−0.4
$BH_3 + =F$	10.6	37.1	9.3	44.5	1.3
$H_2BCH_3 + =$	9.1	43.2	8.9	46.4	0.2
$HB(CH_3)_2 + =$	21.8	50.3	16.5	50.2	5.3
$BH_3 + \equiv$	9.3	61.3			
$BH_3 + -\equiv$	7.6	51.4	7.4	54.8	0.2

er–borane complex reacts directly with the olefin with subsequent elimination of the ether.

Fehlner[9] has studied the kinetics of the hydroboration of ethylene by the flow reactor technique, using BH_3PF_3 as the source of borane. He concluded that the reaction of borane with ethylene proceeded with little or no activation energy barrier (2 ± 3 kcal/mol). The reverse reaction

$$H_2BC_2H_5 \rightarrow H_3B + C_2H_4 \qquad (1)$$

had an activation energy of 39.5 kcal/mol. An interesting point was that the latter reaction had a large positive entropy of activation, whereas that for the corresponding elimination of ethylene from triethylboron

$$(C_2H_5)_2BC_2H_5 \rightarrow (C_2H_5)_2BH + C_2H_4 \qquad (2)$$

was negative. This suggests that the transition states for the two reactions have different geometries, that for the latter being much more rigid.

Since MNDO[10] has been successfully parameterized for boron,[11] it seemed to us of interest to use it to study the mechanisms of these very important reactions. Here we report calculations for the addition of borane and its mono- and dimethyl derivatives to various olefins, acetylene, and methylacetylene.

Procedure

The MNDO method has been described in detail.[10] The calculations were carried out using the published parameters.[10–12] Geometries were optimized by the standard Davidon–Fletcher–Powell[13] method using internal coordinates. Reactions were followed by the usual reaction-coordinate method,[14] using the lengths of the forming BC and/or CH bonds as reaction coordinates. The transition states were refined by minimizing the scalar gradient of the energy and identified as saddle points by diagonalizing the Hessian (force constant) matrix, as suggested by McIver and Komornicki.[15] Lists of Cartesian coordinates for the reactants, products, and transition states are available as supplementary material (Table II).

Validity of MNDO

Since a referee has questioned the validity of MNDO in connections such as this and since this is the first paper reporting such calculations to be submitted to this journal, some brief comments seem in order.

Semiempirical procedures other than ours (EH, CNDO, INDO, etc.) have been parameterized to mimic the results of ab initio calculations and seem for the most part to give very poor estimates of molecular energies.[16] MINDO/3[25] and MNDO,[10] on the other hand, were parameterized to reproduce experimental geometries and heats of atomization and they do in fact reproduce the latter in a reasonably satisfactory manner, as has been shown by very detailed tests.[10,11,26] Attempts to parameterize MINDO/3 for boron proved unsuccessful but satisfactory parameters were obtained in MNDO.[11] As published tests indicate,[11] MNDO gives comparable results for boron compounds of all kinds, including the boron hydrides. While it does seem to underestimate somewhat the strengths of three-center bonds, the errors are small and indeed do not exhibit themselves by any detectable systematic error in the calculated heats of formation of compounds containing such bonds.

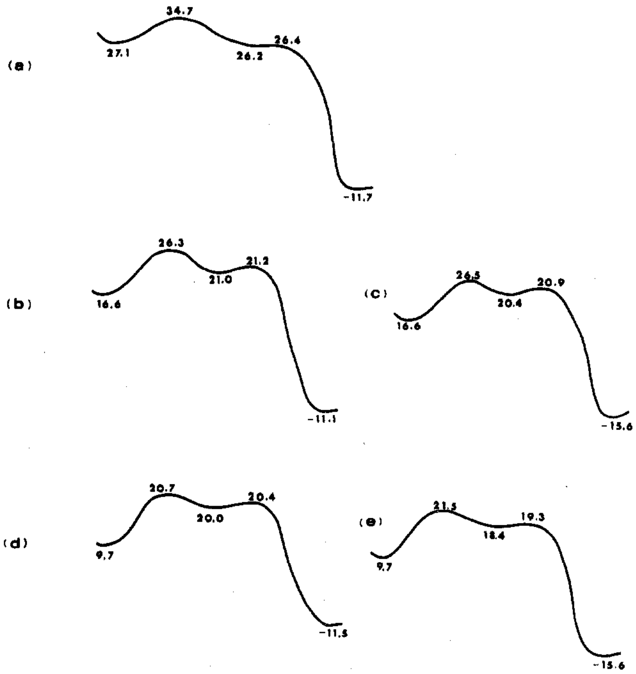


Figure 1. MERPs for hydroboration of (a) ethylene, (b, c) propene, and (d, e) isobutene by borane: (b, d) Markownikoff addition; (c, e) anti-Markownikoff addition.

Problems admittedly arise in applying any existing theoretical procedure to the study of reaction mechanisms because no such procedure can provide results that are accurate enough a priori and because there is very little experimental information available concerning the shapes of potential surfaces. The lack of such information was indeed the main incentive for our development of MINDO/3 and MNDO. MINDO/3 has, however, been used with success in the study of over 200 reactions, the results in all cases being consistent with experiment.[27,28] In particular, the average error in the calculated activation energies is no greater than that in the heats of atomization calculated for stable species. MNDO has been less thoroughly tested as yet but seems, as expected, to be equally satisfactory.

MINDO/3 and MNDO have also been shown to give satisfactory estimates of molecular vibration frequencies,[31,32] implying that they reproduce the curvatures of potential surfaces around the minima. Thermodynamic functions (entropies, specific heats) calculated from the MINDO/3 and MNDO vibration frequencies agree very well with experi-

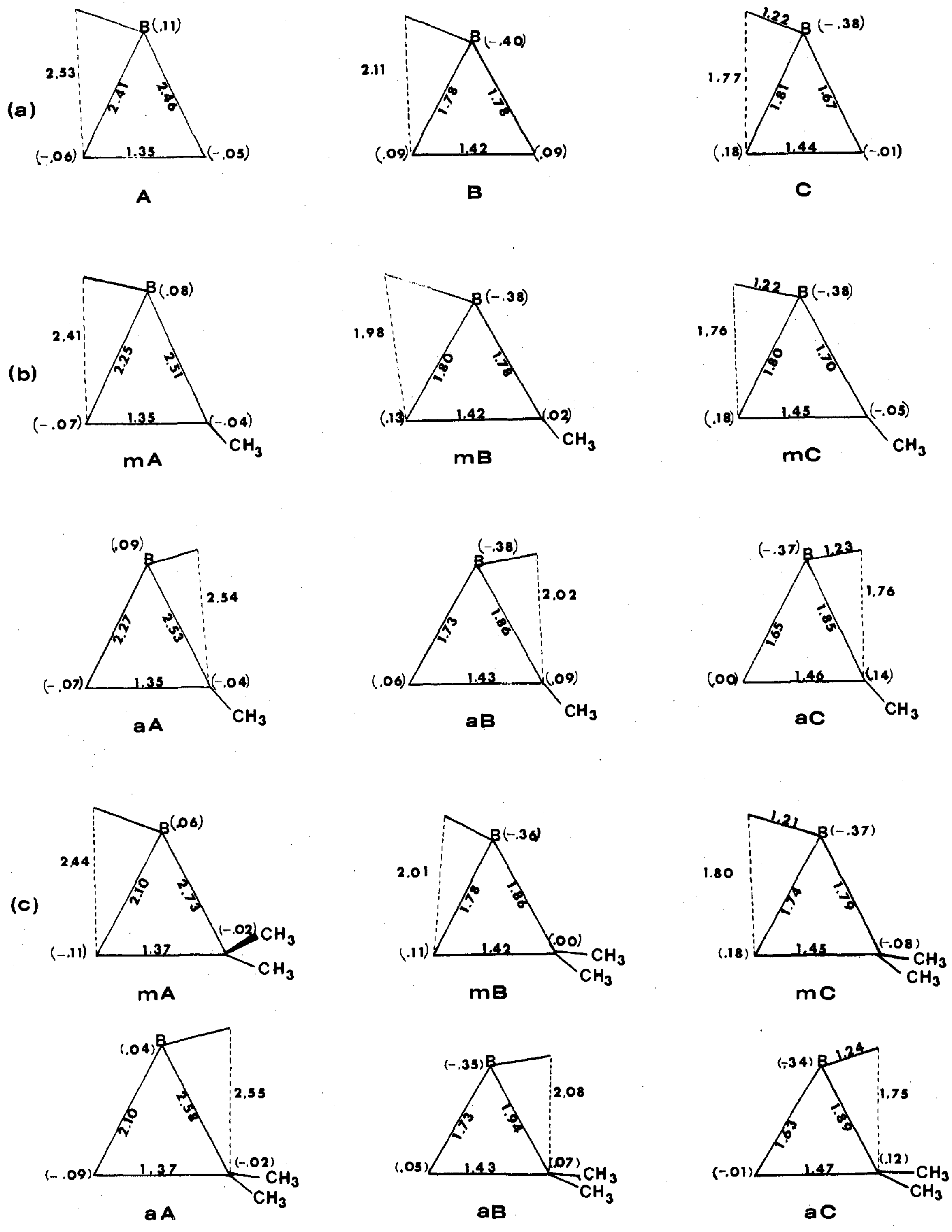


Figure 2. Geometries (formal charges) for π complexes B and for the transition states for formation of π complexes A and for conversion to products C, by Markownikoff, m, and anti-Markownikoff, a, addition: (a) borane addition to ethylene; (b) borane addition to propene; (c) borane addition to isobutene.

ment,[33] as do calculated isotopic frequency shifts.[34] A further check on the validity of our procedures has been provided by calculations of entropies of activation and kinetic isotope effects for a number of reactions,[27,30,35,36] the results in all cases agreeing with experiment to within the limits of experimental error.

Semiempirical methods have been distrusted in the past on the grounds that they are mere curve-fitting procedures, reliable only in the specific contexts where they have been parameterized and tested. This criticism does not, however, apply to MINDO/3 or MNDO, both of which have been shown to reproduce a very wide variety of properties unrelated to those used in the parameterization.[27] It seems clear that these procedures are providing real information concerning molecular structure and the basic ideas on which they rest have indeed been supported by a detailed analysis by Freed.[24]

There is therefore good reason to believe that our calculations of potential surfaces in general, and of transition states in particular, are realistic. Indeed, of the procedures applicable to molecules large enough to be of chemical interest, ours are the only ones that both have been thoroughly tested and have survived such tests.

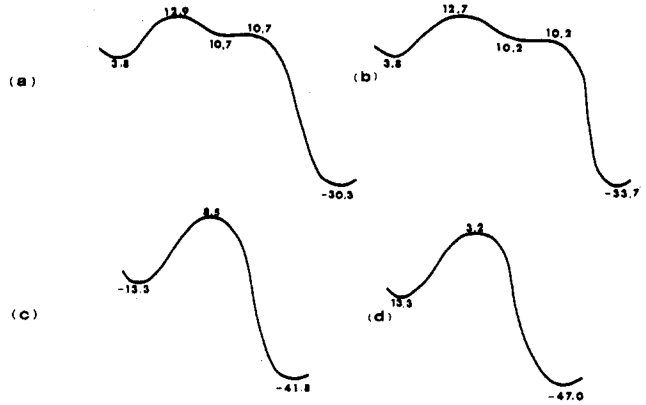


Figure 3. MNDO MERPs for hydroboration of propene by (a, b) methylborane and (c, d) dimethylborane: (a, c) Markownikoff addition; (b, d) anti-Markownikoff addition.

Results and Discussion

We first studied the addition of borane to ethylene, propene, and isobutene. The calculated minimum-energy reaction paths (MERPs) are indicated in Figure 1. In each case a loose adduct of π-complex-like type was formed as a marginally stable intermediate, this being the rate-determining step for the overall reaction. Rearrangement of the complex to the final product required little or no activation. In the case of propene, or isobutene, the complex existed in two isomeric forms, both apparently being local minima on the potential surface and leading to different products.

The overall activation energies for the forward and reverse reactions are shown in Table I. That for dissociation of ethylborane ($C_2H_5BH_2$) to ethylene and borane (46.4 kcal/mol) agrees reasonably well with experiment (39.5 kcal/mol).[37] The activation energy for the corresponding forward reaction has not been measured directly, the "experimental" value (2 ± 3 kcal/mol) being measured by an Arrhenius plot of relative mass spectral peak areas. In view of the uncertain correlation between these and molecular concentrations, the agreement with our calculated value (7.6 kcal/mol) also seems reasonable.

The activation energies and heats of reaction for formation of the intermediate π complexes show an unexpected increase in the order ethylene < propene < isobutene. Since methyl substituents lower the ionization potential of ethylene, the

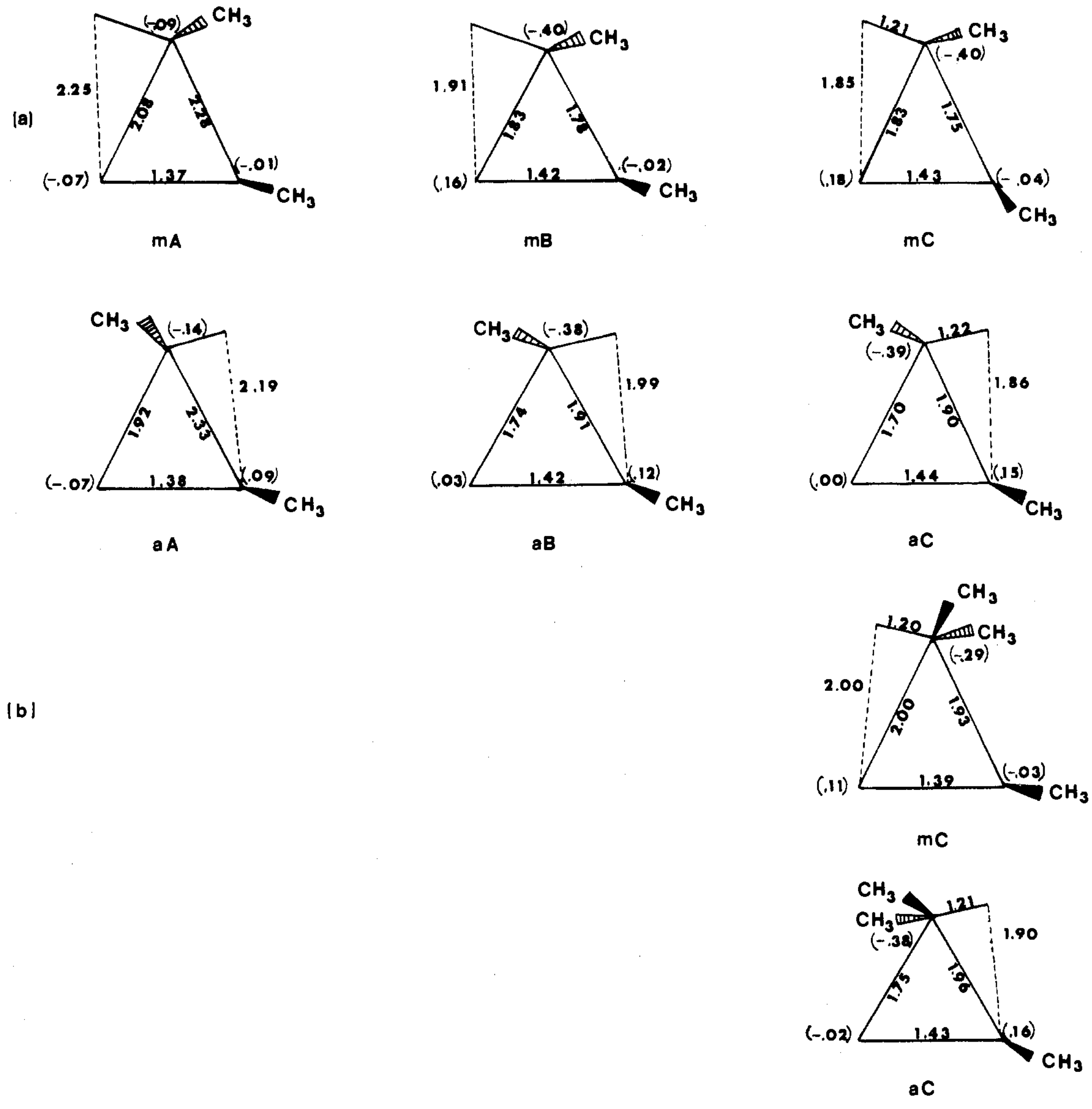


Figure 4. Geometries (formal charges) for π complexes B and for the transition states for formation of π complexes A and for conversion to products C by Markownikoff, m, and anti-Markownikoff, a, addition: (a) methylborane addition to propene; (b) dimethylborane addition to propene.

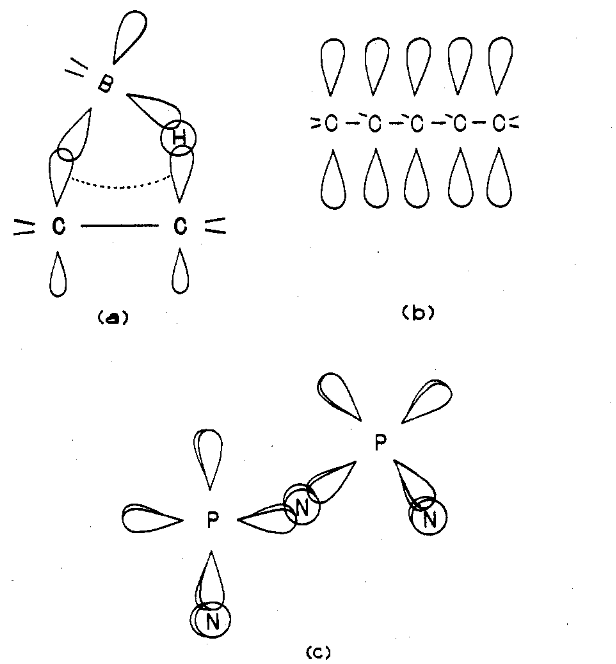


Figure 5. (a) Overlap of AOs in transition state for addition of BH_3 to ethylene. (b) The pentadienyl cation. (c) Overlap in PNP segment of phosphonitrilic chloride.

reverse order would have been expected. Evidently this electronic effect is outweighed by the steric repulsions between hydrogen atoms of the borane moiety and the methyl group(s), which are also indicated by the geometries of the π complexes (Figure 2). The mean BC bond distance increases in the order ethylene < propene < isobutene.

In the case of the π complexes from propene or isobutene, there are two distinct local minima on the potential surface, corresponding to species that give Markownikoff and anti-Markownikoff adducts, respectively (Figure 2). According to the π-complex theory,[38] the π electrons of the olefin should be polarized toward the unsubstituted carbon atoms, so the π complex leading to anti-Markownikoff addition should be the lower in energy. This is the case (Figure 2), the π complexes showing the same asymmetry as the isoelectronic π complexes formed by addition of CH_3^+ to olefins[39] ("corner-protonated cyclopropanes").

The energies of the transition states leading to the "Markownikoff" π complexes are, however, less than those of the corresponding "anti-Markownikoff" ones (Figure 2). This is also not unexpected, because the borane and the olefin are still almost planar in the transition state whereas in the π complex both are distorted from planarity. Examination of models shows that in this geometry, the steric repulsions in the transition states are greater for the "anti-Markownikoff" isomer. The reactant-like nature of the transition states is also indicated by the calculated distributions of formal charge (Figure 2).

Next we studied the additions of the monomethyl (CH_3BH_2) and dimethyl ($(CH_3)_2BH$) derivatives of borane to propene, as models of the second and third steps in the hydroboration of a terminal *n*-alkene by borane. The activation energies for the two modes of addition are shown in Table I and the MERPs in Figure 3.

The two modes of addition of CH_3BH_2 took place via very shallow (<0.05 kcal/mol) local minima on the potential surface, corresponding to π-complex-like intermediates. Their geometries, and those of the transition states leading to them, are indicated in Figure 4(a). Note the trans orientation of the methyl groups. Reactions involving a cis orientation are very much less favorable, a difference which can reasonably be attributed to steric repulsions between the two methyls.

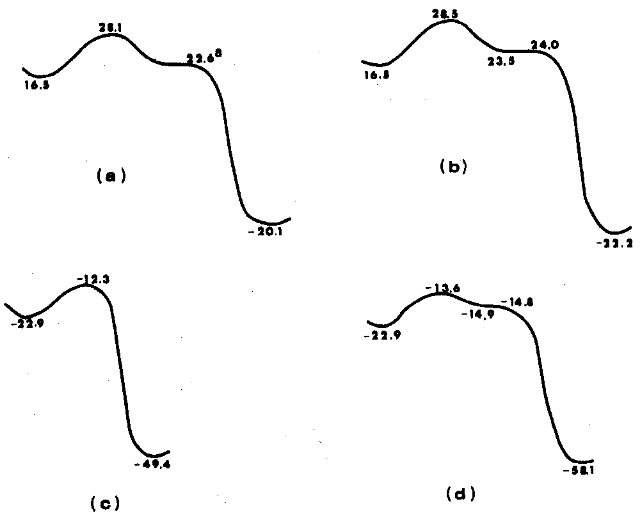


Figure 6. MNDO MERPs for hydroboration of (a, b) vinyl chloride and (c, d) vinyl fluoride by borane: (a, c) Markownikoff addition; (b, d) anti-Markownikoff addition. The local minimum for the π complex was too shallow to be located by our optimization procedure.

This conclusion is supported by the results for the additions of dimethylborane ($(CH_3)_2BH$) to propene, reactions in which a cis orientation of methyls cannot be avoided. Here no stable intermediates are formed and the activation energies are much higher than those for any of the other reactions so far discussed. The structures of the transition states (Figure 4(b)) are also quite different from those for the other reactions, corresponding indeed to a direct ($2\pi s + 2\sigma s$) cycloaddition of >BH to the olefin rather than to formation of a π-complex-like intermediate. This of course accounts very nicely for the observed[9] difference in entropy of activation between dissociation of ethylborane (eq 1) and of triethylborane (eq 2). The four-center transition state in the latter must be much more rigid than that leading to a loose intermediate complex.

In ethereal solution, the addition of borane to terminal olefins is highly regioselective, leading to ca. 94% of terminal addition of boron. Our calculations imply a much lower degree of selectivity in the gas phase, only the third step strongly favoring anti-Markownikoff addition. This predicted difference clearly could and should be tested. If it proves real, it will give strong support to the conclusion[8] that ether–borane adducts add to olefins directly, rather than by prior fission to borane. Indeed, the facility of hydroboration would be difficult to understand if the latter were the case since the activation energy would then be a sum of that for addition of borane and the energy required to dissociate the ether–borane complex.

It should be noted that the synchronous ($2\pi s + 2\sigma s$) cycloaddition of a borane to an olefin is *not* "forbidden". The extra (empty) 2p AO on boron leads to a situation entirely different from that in the analogous addition of an olefin to a C–X or N–X bond. As Figure 5 shows, the overlap of AOs in the transition state for addition of >BH can correspond to a structure isoconjugate with a linear pentadienyl cation (cf. Figure 5(a,b)) rather than cyclobutadiene, the boron using two different AOs to form bonds to the adjacent carbon and hydrogen atoms. A similar situation arises[40] in the phosphonitrilic chlorides where cyclic conjugation is avoided in a similar manner, the π bonds between each phosphorus atom and the two adjacent nitrogen atoms being formed by different d AOs of phosphorus (Figure 5(c)).

Figure 6 shows the MERPs calculated for Markownikoff and anti-Markownikoff addition of borane to vinyl chloride and vinyl fluoride. All the reactions take place via marginally stable intermediates of π-complex type except the anti-

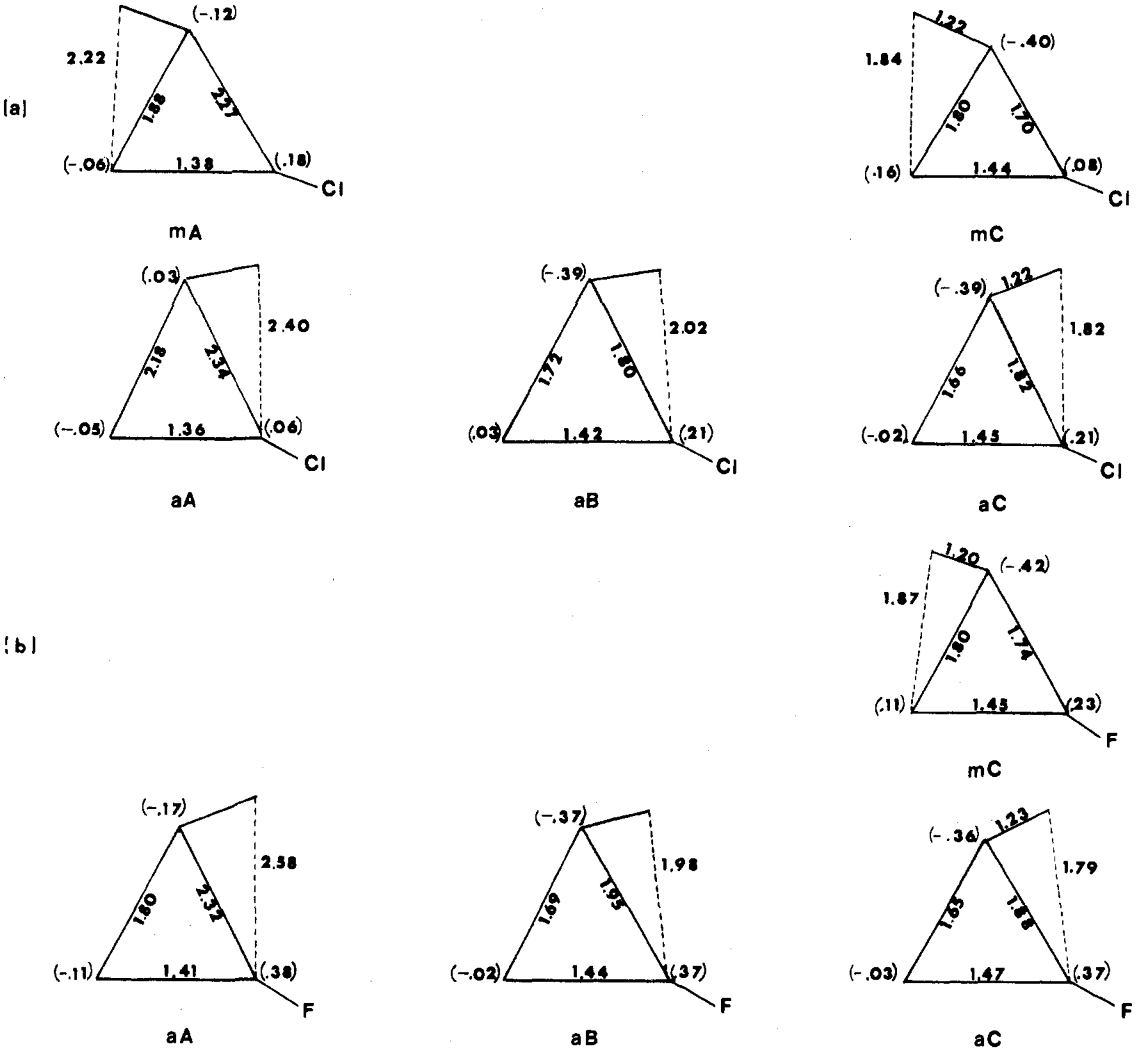


Figure 7. Geometries (formal charges) for π complexes B and for the transition states for formation of π complexes A and for conversion to products C by Markownikoff, m, and anti-Markownikoff, a, addition: (a) borane addition to vinyl chloride; (b) borane addition to vinyl fluoride.

Markownikoff addition to vinyl fluoride. The structures of the transition states and intermediates are shown in Figure 7. It will be seen that whereas vinyl fluoride undergoes anti-Markownikoff addition preferentially, like propene and isobutene, vinyl chloride is predicted to add in Markownikoff fashion

$$CH_2{=}CHCl + BH_3 \rightarrow CH_3{-}CHCl{-}BH_2 \qquad (3)$$

Since chlorine is a powerful $+I$ group with only weak $-E$ activity, one would expect the π electrons of the double bond in $CH_2{=}CHCl$ to be polarized, with a higher π density on the substituted carbon atom. The most stable form of the π-complex-like intermediate should then have the boron atom nearer this carbon, unless steric effects make this orientation unfavorable. Now chlorine is a smaller group than methyl and the CCl bond is much longer than the CC bond. The steric effects in the $BH_3{-}C_2H_3Cl$ complex should therefore be less than in propene. It is therefore not surprising that Markownikoff addition is favored. Fluorine, however, while also a powerful $+I$ group, also exerts strong $-E$ activity. Also while F is smaller than Cl, the CF bond is very short. The predicted anti-Markownikoff addition may then be due either to electromeric (conjugative) electron release by fluorine or to a greater repulsion between BH_3 and F.

While vinyl chloride itself does not seem to have been hydroborated, hydroboration of 2-chlorobutene-2 leads[41] initially to an adduct with boron adjacent to chlorine, in agreement with our predictions:

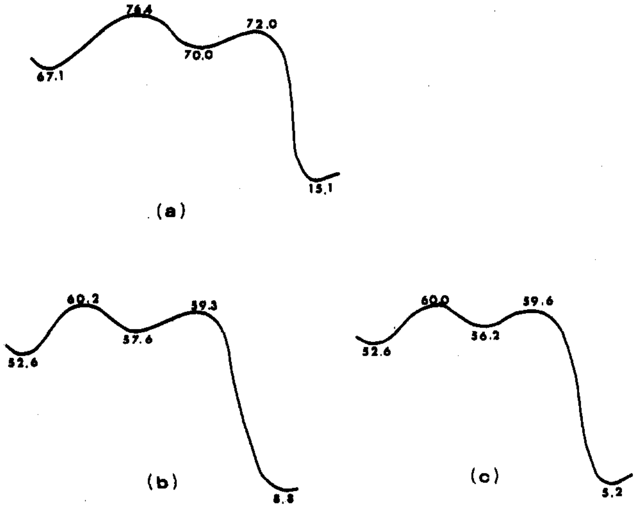


Figure 8. MNDO MERPs for hydroboration of acetylene and methylacetylene by borane: (a) borane addition to acetylene; (b) Markownikoff addition of borane to methylacetylene; (c) anti-Markownikoff addition of borane to methylacetylene.

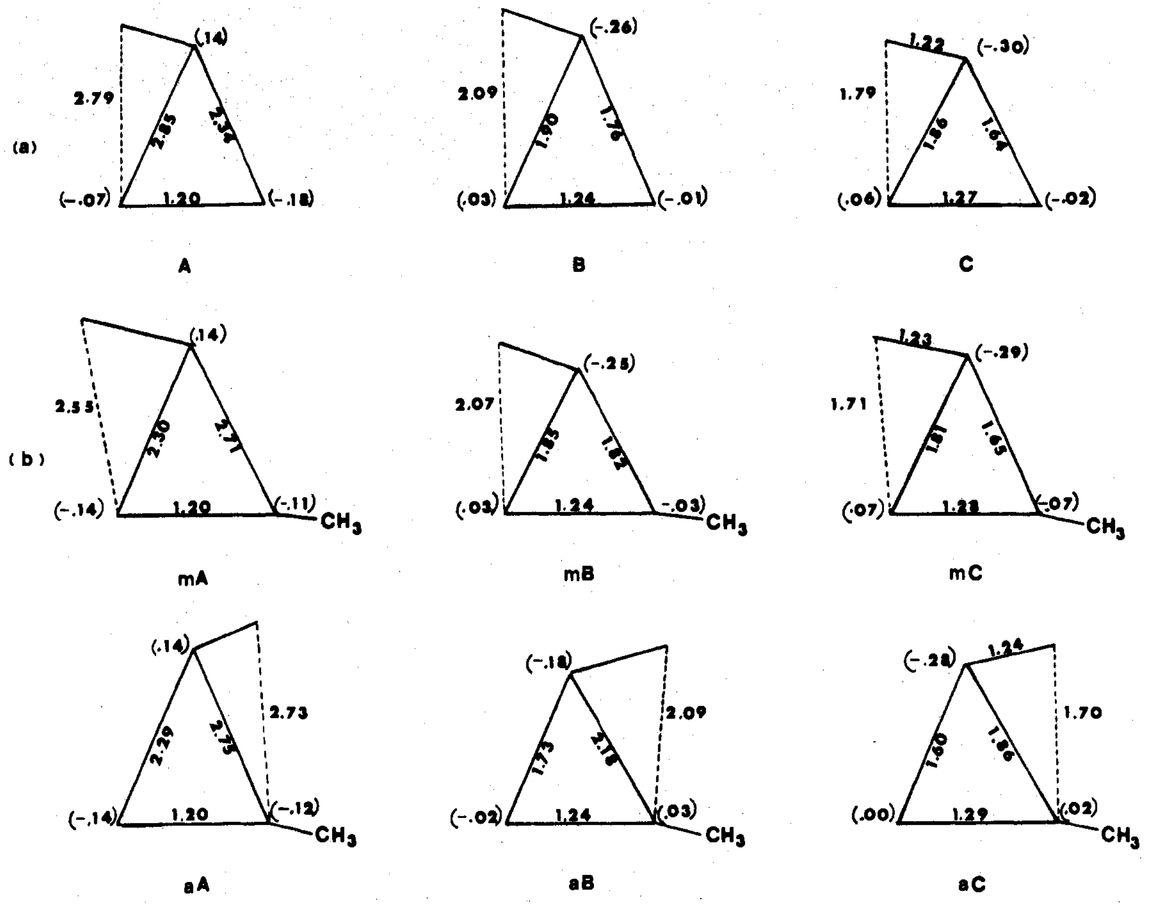
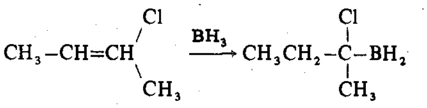


Figure 9. Geometries (formal charges) for π complexes B and transition states for formation of π complexes A and for conversion to products C by Markownikoff, m, and anti-Markownikoff, a, addition: (a) borane addition to acetylene; (b) borane addition to methylacetylene.



$$CH_3{-}CH{=}CH(Cl)(CH_3) \xrightarrow{BH_3} CH_3CH_2{-}C(Cl)(CH_3){-}BH_2 \qquad (4)$$

Hydroboration of vinyl fluoride has been carried out only under rather drastic conditions,[42] which led to secondary rearrangements to ethylboron fluorides, Et_nBF_{3-n}.

The last two reactions studied were the additions of BH_3 to acetylene and methylacetylene. Both reactions are predicted to take place via intermediate π complexes which are much more stable than those in the olefin additions. Indeed, if our calculations are correct, it might be possible to isolate the BH_3–C_2H_2 complex in matrices at low temperatures. This difference is presumably due to the smaller steric effects in the case of acetylene. Note in this connection our prediction that methylacetylene should react faster than acetylene whereas propene should react more slowly than ethylene. Alkylacetylenes react faster with BH_3 in ethereal solution than do the corresponding olefins. However, as we have already pointed out, it is not legitimate to compare reactions in the gas phase with ones in solution.

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Registry No. Borane, 13283-31-3; ethylene, 74-85-1; propene, 115-07-1; isobutene, 115-11-7; vinyl chloride, 75-01-4; vinyl fluoride, 75-02-5; acetylene, 74-86-2; methylacetylene, 74-99-7; methylborane, 12538-96-4; dimethylborane, 7216-97-9.

Supplementary Material Available: Table II listing Cartesian coordinates for reactants, products, and transition states (31 pages). Ordering information is given on any current masthead page.

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tested. Both, however, were parameterized to mimic the results of single-configuration ab initio SCF methods. Detailed studies by Schaeffer[22] and Goddard[23] have shown that such procedures do not give satisfactory results for potential surfaces, due to their neglect of election correlation. In MINDO/3 and MNDO electron correlation is tacitly taken into account by modification of the repulsion integrals, as originally suggested by Pariser and Parr.[26]

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Notes

Contribution from the Department of Chemistry,
University of Notre Dame, Notre Dame, Indiana 46556

Single-Crystal Electron Paramagnetic Resonance of Binuclear Mo(V) Complexes. μ-Oxo-bis(oxotetraphenylporphinatomolybdenum(V))

Robert G. Hayes* and W. Robert Scheidt

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The chemistry of molybdenum(V) complexes is dominated by the formation of strong Mo–O bonds. Binuclear Mo(V) species typically contain either a single oxo bridge or two oxo bridges and terminal MO=O groups although other species are known. The species containing a single oxo bridge are diamagnetic and the terminal Mo=O groups are cis to the linear Mo–O–Mo bridge.[1] However, the binuclear oxomolybdenum(V) porphyrins,[2,3] with molecular formula $O_3Mo_2(por)_2$,[4] have a nearly linear[5] O=Mo—O—Mo=O group and are paramagnetic. The paramagnetism marks the porphyrin derivatives as unique among well-characterized binuclear Mo(V) complexes. An interaction between the unpaired electrons on the two molybdenum atoms, which almost surely have the ground state $(4d_{xy})^1$,[1,6] would be expected. We have studied the EPR of a single crystal of $O_3Mo_2(TPP)_2$ in order to measure this interaction as well as the other magnetic parameters accessible to measurement.

Results and Discussion

The crystal structure of $O_3Mo_2(TPP)_2$ involves a four-molecule unit cell,[5] with the molecules so distributed that they are magnetically equivalent. Thus, one should see only one species in the EPR spectrum. We performed rotations about three orthogonal axes defined for convenience in the external morphology of the crystal. At each orientation, the spectrum consisted of a pair of lines which we interpreted as the spectrum of one triplet species with a zero-field splitting. We, therefore, set out to fit the spectrum to a spin Hamiltonian

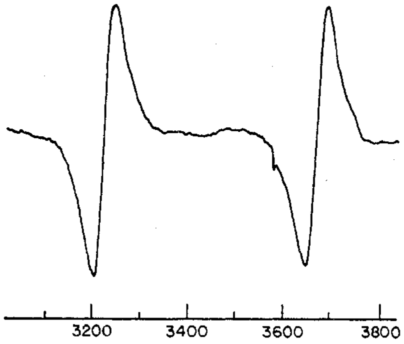

Figure 1. EPR spectrum observed at room temperature from a single crystal of $(MoTPP)_2O_3$.

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D[S_z^2 - {}^1/_3 S(S+1)]$$

In this equation $S = 1$, the z axis lies along the Mo–Mo direction, x and y are chosen arbitrarily in the plane perpendicular to z, and $g_{\parallel}$, $g_{\perp}$, and D have their conventional meanings. In our rotations about each axis (covering 180°) we found two local maxima in the splitting and one minimum which was essentially zero. One of the maxima was the same size in all three rotations; the other varied. We interpreted the equal maxima as representing the orientation in the plane of the rotation at which the magnetic field is perpendicular to the line connecting the two molybdenum atoms. There is, of course, one such position in all three planes of rotation. The maxima which differed in each rotation were interpreted as representing the position in the plane of rotation at which the magnetic field lay nearest to the Mo–Mo line. The angle between the magnetic field and the Mo–Mo direction differs in each plane, so the maxima differ. These assumptions allowed us to calculate D, the zero-field splitting parameter, and

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