

# Substituent Effects in Hydroboration: Reaction Pathways for the Markownikoff and Anti-Markownikoff Addition of Borane to Propylene and Cyanoethylene

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**Abstract:** The method of the partial retention of diatomic differential overlap (PRDDO), coupled with the application of linear synchronous transits (LSTs) and orthogonal optimizations, is employed to construct reaction pathways for both the Markownikoff and anti-Markownikoff addition of borane to propylene and to cyanoethylene. Calculations at the 4-31G level including Møller-Plesset correlation corrections to third order on structures which had been optimized by using PRDDO reveal that the anti-Markownikoff addition to propylene and the Markownikoff addition to cyanoethylene are preferred by 1.1 and 1.6 kcal/mol, respectively. The regioselectivity of the hydroboration reaction is shown to arise from electronic effects induced by electron-donating or electron-withdrawing substituents in these situations, where steric effects are negligible. A description of the reaction in terms of the localized molecular orbitals is also presented.

Following the discovery of the hydroboration of organic carbonyl groups by Burg in 1934,<sup>1</sup> the hydroboration of unsaturated organic compounds has become a remarkably versatile route for the laboratory synthesis of organoboranes and their oxidation products, largely through the work of Brown.<sup>2-4</sup> In addition, the reaction between modified alkenes and modified boranes is a probe of the stereospecificity and regioselectivity of both the alkene and borane reactants.<sup>2-6</sup> Detailed mechanistic studies have, however, been limited by the rapidity of most hydroboration reactions, the complexity of the kinetics,<sup>7</sup> and the uncertain role of the borane-complexed solvent.

Much of the synthetic utility of hydroboration arises because the borane adds preferentially to one of the carbon atoms of the double bond of an alkene. Alkyl substituents on an olefinic double bond yield predominantly anti-Markownikoff (AM) addition of the borane to the  $\beta$ -carbon atom.<sup>8</sup> In alkylethylenes some 93-94% of boron addition occurs at the terminal carbon atom. In the 1,1-dialkylethylenes and trialkylethylenes these preferences for the AM product are at the 98-99% level, while in *trans*-2-pentene only 51% of the C2-bonded organoborane occurs. Both steric and electronic factors are involved in these selectivities, but these examples indicate a major role for electronic effects in the preferred pathway.

In spite of steric disadvantages, Markownikoff (M) addition is known to occur when electron-withdrawing, or partially positive, substituents exist on the olefin. For example, the boron atom adds to the secondary carbon atom with 74% selectivity in 1,1,1-trifluoropropene,<sup>9</sup> and the M product is observed at the 87-92% selectivity level in 1-(trimethylsilyl)cyclopentene and 1-(trimethylsilyl)cyclohexene under kinetic conditions.<sup>10</sup> Prior to further reaction, predominantly M addition has also been observed in (dimethylchlorosilyl)-, (methylchlorosilyl)-, and (trichloromethylsilyl)ethylenes<sup>11</sup> and in vinyl halides (60-95% level).<sup>12</sup>

When ester groups<sup>13,14</sup> or halides<sup>13,15</sup> are present on the aromatic ring of styrene<sup>16</sup> or when separated from the double bond by a methylene group, they enhance significantly the amount of M addition. While steric factors are also present here, the dominance of electronic effects is clearly evident.

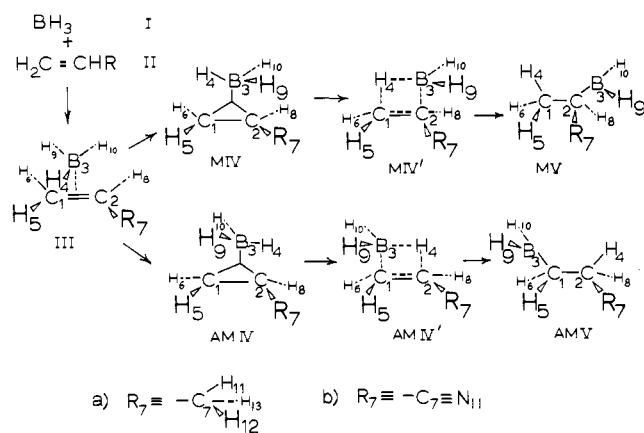
In the earliest qualitative description of the addition of BH<sub>3</sub> to an ethylenic double bond, Hurd<sup>17</sup> forms a B-C2 bond followed by transfer of H<sup>-</sup> to C1 to yield the organoborane product. A four-center transition state in a concerted mechanism was proposed<sup>8</sup> to account for cis addition, the rapidity of the reaction, and the AM addition to unsaturated hydrocarbons. In this proposal and in Hurd's description, positive charge develops at the carbon which receives the incipient hydride and the AM addition results from the stabilization of this intermediate by alkyl or aryl substituents. The initial presence of a vacant 2p atomic orbital on boron removes this process from the usual rules for ( $\pi_2s + \sigma_2s$ ) electrocyclic reactions.<sup>18</sup> An alternative proposal is a  $\pi$ -complexed intermediate,<sup>19</sup> symmetry allowed,<sup>20</sup> in which the same predictions of electronic effects occur as in the four-center transition state. However, steric effects appear to favor either the  $\pi$ -complex<sup>19</sup> or some type of transition state between these two extremes.

Prior to our theoretical work, described below, the only computational results for substituent effects on the hydroboration of substituted ethylenes have been obtained in a study by Dewar and McKee using the MNDO method.<sup>21</sup> For several alkylated or halogenated olefins they find, proceeding forward and backward from the  $\pi$ -complexes, only small barriers for the decomposition of the complex but substantial activation energies leading from reactants to the  $\pi$ -complexes. For the alkylated olefins they predict<sup>21</sup> that AM  $\pi$ -complexes are more stable than M  $\pi$ -complexes, but the larger activation barrier for AM addition than for M addition leads to some selectivity for the M addition of BH<sub>3</sub> to alkenes, in disagreement with experimental results on regioselectivity. Moreover, the activation energy for the formation of this complex is in disagreement with the gas-phase value of  $2 \pm 3$ -kcal/mol value for the addition of BH<sub>3</sub> to ethylene.<sup>22</sup> The

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Scheme I



MNDO prediction of rate-limiting  $\pi$ -complex formation is also contradicted by comparisons of positional and intermolecular selectivity in substituted styrenes<sup>23</sup> and by large primary H-D, H-T, and <sup>10</sup>B-<sup>11</sup>B isotope effects for the reaction of BH<sub>3</sub> in solution with tetramethylethylene.<sup>18</sup> The kinetic evidence, including the favorable entropy of activation,<sup>18,22,24</sup> suggests preassociation to a loose  $\pi$ -complex followed by rate-limiting rearrangement to the organoborane.

Two more refined theoretical studies<sup>25,26</sup> of the reaction of BH<sub>3</sub> with ethylene have yielded no activation energy for the formation of the  $\pi$ -complex. Clark and Schleyer<sup>25</sup> use the reaction coordinate method at the STO-3G level to find structures along the pathway. Their relative energies reveal no overall activation barrier to the forward reaction and a small barrier to the conversion of the  $\pi$ -complex. At the 4-31G level these STO-3G geometries yield an overall exothermicity which agrees well with experiment. Sundberg, Graham, and Lipscomb<sup>26</sup> (SGL) use the PRDDO method<sup>27,28</sup> (partial retention of diatomic differential overlap) to determine the structures of reactants, products, and the  $\pi$ -complex and then find intermediate structures along the pathway by using the LST (linear synchronous transit) method.<sup>29,30</sup> The channel of minimum energy was approximated by orthogonal optimizations,<sup>29,30</sup> and the energies of key structures were found at the STO-6G and 4-31G levels. Finally, zero-order configuration interactions were introduced in a double- $\zeta$  basis set. No barrier for formation of the  $\pi$ -complex was found, and at most a small barrier to its decomposition occurred. The optimal pathway after optimization was independent of whether one constrains it to pass through a  $\pi$ -complex. A donation-back-donation mechanism for charge transfer in a highly polarized transition state is a reasonable description of the activated complex, which can be viewed equivalently as a distorted  $\pi$ -complex or a distorted four-center structure. The regioselectivity arises from the effect of groups attached to the ethylene in stabilizing or destabilizing the polarization of the carbon-carbon interactions according to the AM or M choice of addition.

Here, we study this proposal for regioselectivity by examining the reaction pathways for the hydroboration of propylene, in which CH<sub>3</sub> donates electrons, and cyanoethylene, in which CN withdraws electrons. Of course, we recognize the difficulty that the CN group itself may complicate any actual experiments, but we chose CN

Table I. Path Coordinates<sup>a</sup> of the Key Intervening Structures along the Hydroboration Path from III to V

structure	path coordinates <sup>b</sup>			
	propylene		cyanoethylene	
	M	AM	M	AM
IV	0.516	0.513	0.625	0.570
IV'	0.543	0.531	0.673	0.636
IV''			0.719	0.662

<sup>a</sup> See ref 27 and 28. <sup>b</sup> Defined relative to the assignment of path coordinates  $P = 0.0$  and  $P = 1.0$  to all of the structures III and V, respectively.

rather than a halogen in order to alleviate the limitations of the small basis sets used in this study. We also give a localized molecular orbital (LMO) description along the reaction coordinates.

### The Computational Study

In order to facilitate internal comparisons, we considered both the Markownikoff and anti-Markownikoff reaction pathways for the addition of BH<sub>3</sub> to propylene and to cyanoethylene. The key structures lying along the reaction paths are illustrated in Scheme I. Starting geometries for these molecules were constructed by substituting a methyl or nitrile group for a hydrogen atom in the coordinates of the corresponding structure (II-V) of the SGL study with ethylene.<sup>26</sup> A tetrahedral methyl group with C-H distances of 1.09 Å was assumed. Structure III was formulated with the BH<sub>3</sub> and olefin moieties held separated by 3 Å, rather than the 2 Å of the SGL work, in order to test for the existence of any barriers to  $\pi$ -complex formation. In the calculations, each molecule was then subjected to the cyclical optimization of all of the key internal bonding parameters, consistent with the preservation of the overall molecular geometry in the case of the intermediary structures IV and IV', using the PRDDO method.<sup>27,28</sup> In general, all parameters were optimized except for the noncritical hydrogen bond lengths and angles (those excluding H4), although the rotational conformation of the methyl group in the propylene case and some of the angles between the boron-bonded hydrogen atoms were optimized. The subsequent rotational isomerization of V from an eclipsed to a staggered conformation was not considered.

While the minimum potential energy pathway for a chemical reaction is not, in general, formed by the linear extrapolation between the reactant and product bonding parameters generated by the LST method,<sup>29,30</sup> a linear approximation should be sufficiently accurate over short segments along the curved path. It was hoped that, since the -CH<sub>3</sub> or -CN substituents provide only a modest perturbation to the overall reaction dynamics of the SGL study, the initially computed IV and IV' structures would persist as intermediary minima and maxima, respectively, along the paths connecting III to V. The path coordinates<sup>29,30</sup> of the various IV and IV' structures were computed on the basis of the assignment of  $P = 0.0$  and  $P = 1.0$  for the part coordinates of the III and V molecules, respectively, and are reported in Table I. LST pathways were then constructed by connecting III to M IV, M IV to M IV', and M IV' to M V and connecting III to AM IV, AM IV to AM IV', and AM IV' to AM V, as implied by Scheme I, for both the propylene and cyanoethylene reactions. An examination of the PRDDO energies of the intervening structures revealed that, while the M and AM propylene paths computed by the three LST segments represented a smooth extrapolation between the optimized structures III-V with no additional extrema, the nitrile paths revealed the existence of new path maxima lying between structures IV and IV'. Orthogonal optimization<sup>29,30</sup> of all of the key bonding parameters of the M and AM path maxima, followed by further LST extrapolations between the new structures and M or AM IV and the old M or AM IV', showed the new points to be the true cyanoethylene reaction transition states. They are labeled M and AM IV' in order to preserve the analogy with the propylene path. The old path maxima were found to be points lying within the minimum energy reaction channel

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Table II. Selected Bond Lengths<sup>a</sup> and Angles<sup>b</sup> for Key Structures along the Hydroboration Pathway of Propylene

	M					AM			
	I	II	III	IV	IV'	V	IV	IV'	V
R(C1-C2)		2.530	2.535	2.567	2.803	2.925	2.567	2.803	2.925
R(C1-B3)			5.809	3.624	3.517	4.786	3.612	3.206	2.911
R(C2-B3)			5.809	3.729	3.172	2.905	3.714	3.516	4.790
R(B3-H4)	2.274		2.265	2.268	2.501	4.804	2.283	2.417	4.804
R(C1-H4)			6.235	4.230	3.107	2.075	5.264	4.589	4.186
R(C2-H4)			6.235	5.460	4.623	4.189	4.149	3.100	2.074
R(C2-C7)		2.882	2.880	2.929	2.934	2.955	2.927	2.927	2.941
∠C1-C2-C7		124.5	124.7	120.1	121.2	109.5	119.7	121.5	109.5
∠C7-C2-H8		115.5	115.5	115.7	109.4	106.1	116.5	109.4	107.2

<sup>a</sup> Bond lengths in atomic units (au). <sup>b</sup> Bond angles in degrees.

Table III. Selected Bond Lengths<sup>a</sup> and Angles<sup>b</sup> for Key Structures along the Hydroboration Pathway of Cyanoethylene

	M							AM			
	I	II	III	IV	IV'	IV''	V	IV	IV'	IV''	V
R(C1-C2)		2.538	2.545	2.633	2.692	2.803	2.974	2.628	2.704	2.803	2.962
R(C1-B3)			5.810	3.656	3.578	3.707	4.928	3.630	3.258	3.203	3.010
R(C2-B3)			5.810	3.765	3.356	3.165	3.029	3.576	3.558	3.580	4.934
R(B3-H4)	2.274		2.268	2.287	2.421	2.640	4.923	2.289	2.409	2.483	4.939
R(C1-H4)			6.237	4.096	3.336	2.600	2.082	5.316	4.692	4.452	4.218
R(C2-H4)			6.237	5.419	4.756	4.187	4.242	4.078	3.334	2.918	2.074
R(C2-C7)		2.769	2.770	2.755	2.784	2.771	2.841	2.785	2.789	2.800	2.852
R(C7-N11)		2.229	2.227	2.246	2.244	2.242	2.240	2.232	2.231	2.251	2.246
∠C1-C2-C7		123.9	124.0	122.0	119.2	117.0	110.4	120.8	120.4	119.9	110.7
∠C7-C2-H8		116.1	116.0	114.5	113.3	111.5	106.0	113.9	114.0	114.1	109.3

<sup>a</sup> Bond lengths in atomic units (au). <sup>b</sup> Bond angles in degrees.

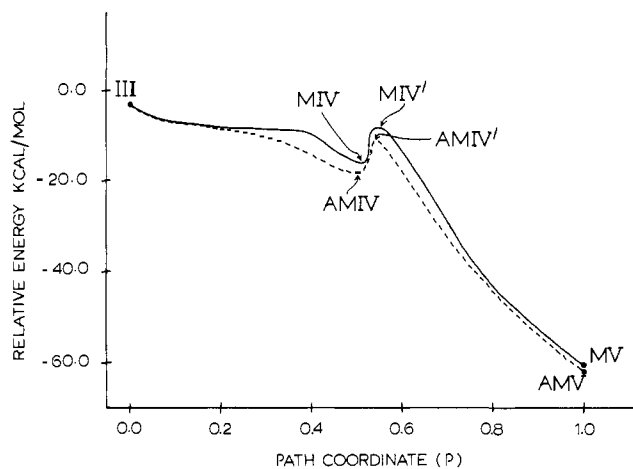


Figure 1. PRDDO potential curves for the Markownikoff (solid line) and anti-Markownikoff (dashed line) addition of borane to propylene.

connecting the transition states to products and are relabeled M and AM IV''. The final Markownikoff and anti-Markownikoff reaction pathways for the hydroboration of propylene and cyanoethylene are reproduced in Figure 1 and 2, respectively.

Mulliken atomic charges<sup>31</sup> and LMOs localized according to the Boys criterion<sup>32,33</sup> were generated for the key points along all of the reaction pathways on the basis of the PRDDO wave function. In order to assess more accurately the magnitudes of the energy differences between the key structures and to overcome some of the limitations inherent in minimum basis set methods, we carried out *ab initio* calculations employing the PRDDO-optimized geometries of the  $\pi$ -complexes IV and transition states IV' for all four reaction channels with the program GAUSSIAN 80,<sup>34</sup> using the extended 4-31G basis set.<sup>35</sup> In addition, the *ab initio*

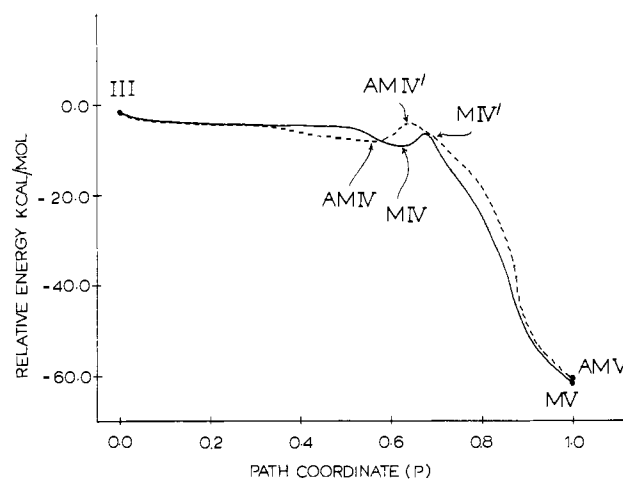


Figure 2. PRDDO potential curves for the Markownikoff (solid line) and anti-Markownikoff (dashed line) addition of borane to cyanoethylene.

SCF results were augmented by the estimation of electron correlation corrections using the Møller-Plesset perturbation theory carried to third-order (MP3).<sup>36,37</sup>

### Structural and Energetic Results

The optimized geometric parameters for the key molecules along the reaction paths for the addition of borane to propylene and to cyanoethylene are collected in Tables II and III, respectively. No substantial differences were found in the critical bond lengths (those involving C1, C2, B3, or H4) of the transition states relative to the structure IV' for the hydroboration of ethylene from the SGL study,<sup>26</sup> with the possible exception of the shorter C-H bonds in the case of propylene. The small variations observed are in accord with the experimental prediction, based on the kinetic activation parameters,<sup>22</sup> that the transition states along the hy-

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Table IV. PRDDO Relative Energies of Key Structures along the Hydroboration Pathway of Propylene and Cyanoethylene

structure	relative energy <sup>a</sup>	
	propylene <sup>c</sup>	cyanoethylene <sup>d</sup>
I + II	0.0	0.0
III	-3.3	-1.6
M IV	-16.2	-9.3
M IV'	-8.0	-6.9
M IV''		-16.2
M V	-61.1	-61.7
AM IV	-18.1	-8.4
AM IV'	-11.2	-3.9
AM IV''		-5.1
AM V	-62.0	-61.0

<sup>a</sup> Energies in kcal/mol relative to the sum of the total energies of I<sup>b</sup> and II. <sup>b</sup> Total energy of I is -26.340 94 au. <sup>c</sup> Total energy -116.869 16 au. <sup>d</sup> Total energy -169.370 67 au.

droboration paths should be of the loose type.

Comparisons between the final structures predicted for the M and AM reaction pathways in the two systems studied also reveal only minor structural differences. The largest discrepancies occur in the  $\pi$ -complex geometries, where the borane unit tends to be bound further from the olefin in the case of Markownikoff addition. Also, even though the boron atom of the M IV compounds will eventually be bonded to C2, the C1-B3 distances are shorter than the C2-B3 bond lengths for both M  $\pi$ -complexes. These effects are a result of the greater steric repulsions arising when addition occurs at the more highly substituted carbon site.

The geometries reported in Tables II and III for the IV' structures are all consistent with the interpretation that the transition state is a distortion from the  $\pi$ -complex rather than a classical four-centered form. The differences between the distances from the boron atom to the two olefin carbons are all within 0.4 au. Furthermore, even the shorter of the carbon-hydrogen distances in the  $\pi$ -complexes are significantly longer than the B3-B4 bond lengths and are within the range of the C-B distances. The fact that the transition states for the cyanoethylene reactions are found to be between IV and the structures corresponding to the ethylene path local maxima (IV'') suggests that the transition state should be structurally closer to the  $\pi$ -complexes for the hydroboration of cyanoethylene than for propylene. This hypothesis is borne out by a comparison of the key bond lengths listed in Tables II and III, especially the olefin carbon-carbon distances. The path coordinates of the intermediates, shown in Table I, do not indicate that IV' is structurally closer to IV for the cyanoethylene reaction, but this may be largely an artifact of the choice of definition of the path coordinate.<sup>29,30</sup> This definition tends to ascribe a disproportionately large weight to the short bond lengths<sup>38</sup> and can be highly sensitive to changes of the internal coordinates not central to the reaction transformation. As shown below, these conclusions are corroborated by a comparison of the different energetics of the two addition reactions.

The PRDDO energies, relative to the sum of the energies of I and II, for the principal molecules along the hydroboration pathways for propylene and cyanoethylene are collected in Table IV. The reaction energies for the production of M or AM V from both of the olefins lie between -61 and -62 kcal/mol. These results are considerably more exothermic than the experimental value of -33 kcal/mol<sup>18</sup> but are in line with the PRDDO energy profile computed for the hydroboration of ethylene. The discrepancy between the theoretical and experimental estimates of the heat of reaction has been shown to arise primarily from the inadequacies of a minimum basis set.<sup>26</sup> By analogy to the SGL investigation, it is expected that, while the absolute magnitudes of the energy differences may be of limited accuracy, the qualitative features of the reaction profiles should be valid.

One unequivocal prediction made by the PRDDO reaction pathways is the absence of any internal barrier to the formation

Table V. 4-31G and 4-31G/MP3 Total Energies of the  $\pi$ -Complex and Transition-State Structures

structure <sup>b</sup>	total energies <sup>a</sup>			
	propylene		cyanoethylene	
	4-31G	4-31G/MP3	4-31G	4-31G/MP3
M IV	-143.234 82	-143.620 42	-195.830 44	-196.309 44
M IV'	-143.213 71	-143.605 81	-195.827 60	-196.307 80
AM IV	-143.237 65	-143.623 35	-195.828 41	-196.307 52
AM IV'	-143.219 68	-143.610 45	-195.820 08	-196.303 31

<sup>a</sup> Total energies in atomic units (au). <sup>b</sup> Structures were optimized at the PRDDO level.

Table VI. PRDDO, 4-31G, and 4-31G/MP3 Energy Differences among the  $\pi$ -Complex and Transition-State Structures

energy difference <sup>a</sup>	propylene			cyanoethylene		
	PRDDO	4-31G	4-31G/MP3	PRDDO	4-31G	4-31G/MP3
M IV' - M IV	8.2	13.2	9.2	2.4	1.8	1.0
AM IV' - AM IV	6.9	11.3	8.1	4.4	5.2	2.6
M IV - AM IV	1.9	1.8	1.8	-0.9	-1.3	-1.2
M IV' - AM IV'	3.2	3.7	2.9	-2.9	-4.7	-2.8
$\Delta E_{act}^b$	1.2	2.0	1.1	-2.0	-3.4	-1.6

<sup>a</sup> Energy differences in kcal/mol. <sup>b</sup> The difference in the internal activation energies (IV' - IV) between the M and AM paths.

of the  $\pi$ -complexes from reactants. No such energy barrier was found in the SGL work,<sup>26</sup> but in that study the reacting moieties were constructed with a 2.0 Å separation in structure III; Dewar and McKee predict that the path maximum for  $\pi$ -complex formation occurs at a greater olefin-borane separation for these compounds. However, even when III was constructed at a 3.0 Å separation, the initial energies of the propylene or cyanoethylene III structures are several kilocalories per mole more stable than the sum of the energies of I and II, and the LST extrapolations between the III and IV geometries, illustrated in Figures 1 and 2, yield intervening structures that decrease monotonically in energy.

In order to overcome some of the quantitative limitations of a minimum basis set method, we performed 4-31G calculations augmented by MP3 correlation corrections on the PRDDO-optimized structures for the  $\pi$ -complexes and transition states for both reactant systems. The 4-31G and 4-31G/MP3 total energies are reported in Table V, and Table VI lists the important energy differences among these structures at the PRDDO, 4-31G, and 4-31G/MP3 levels. These computational methods are seen to produce results that are generally in close agreement. As might be expected, the explicit inclusion of electron correlation reduces slightly the energy differences between the IV' and IV molecules along all four pathways. This is due to the greater multicenter bonding character of the transition states vs. the  $\pi$ -complexes. However, since both structures possess three-center bonds (see below), the changes in relative energies are small. The findings also bear out the conjecture made on the basis of the optimized geometries that the transition states for the hydroboration of cyanoethylene are closer to the  $\pi$ -complexes than are the corresponding points along the propylene reaction coordinate. The smaller energy differences between the IV and IV' structures for the nitrile compounds reflect a decrease in the olefin  $\pi$ -electron density and hence in  $\pi$ -complex stability, caused by the presence of the electron-withdrawing group. This trend is also reflected in the lower carbon-carbon bond orders and overlap populations predicted for the nitrile as opposed to the methyl-substituted  $\pi$ -complexes.

All four reaction channels studied exhibit internal barriers to the conversion of the  $\pi$ -complex to products. The activation energies of 1.0 and 2.6 kcal/mol at the 4-31G/MP3 level encountered for the M and AM addition of BH<sub>3</sub> to cyanoethylene are within the range of the gas-phase experimental values. These energy differences are smaller than the propylene barriers due to the decreased stability of the cyanoethylene  $\pi$ -complex caused by the presence of an electron-withdrawing group on the olefin

and to the diminished steric repulsion likely encountered during the conversion of the nitrile as opposed to the methyl-substituted compound. The propylene 4-31G/MP3 activation barriers are larger than the  $2 \pm 3$  kcal/mol gas-phase values found for ethylene<sup>22</sup> but are in accord with the results of prior 4-31G calculations.<sup>26</sup> It should be noted that the gas-phase experiment was conducted in a fast flow reactor at low pressures, so that the exothermicity of the initial formation of the  $\pi$ -complex from III may be retained by the molecule long enough to allow for the facile reaction of an energetic IV to form product prior to any deactivating collisions. Thus, such an activation energy may be a result of the overall reaction dynamics more than any internal barriers below the energy of the starting materials. In solution, where collisional contacts are frequent, the energy released in the formation of IV is quickly removed, and the measured activation energy would be expected to parallel the theoretical results more closely. Thus, our results are in surprisingly good agreement with the solution activation energy of 9.2 kcal/mol for the hydroboration of tetramethylethylene,<sup>18</sup> even though the reactant borane in solution is complexed with the solvent.

The observed regioselectivity of the hydroboration reaction is reflected in the differences in the stability of the transition states and in the internal path barriers between the Markownikoff and anti-Markownikoff channels. Table VI shows that the AM transition state for the hydroboration of propylene is 2.9 kcal/mol more stable than the M IV' structure and that the activation energy for the AM addition pathway is 1.1 kcal/mol lower. This result agrees well with the approximately 1.5–1.6-kcal/mol activation differential expected from the 93–94% to 6–7% observed selectivity<sup>8</sup> favoring the hydroboration of monosubstituted terminal alkenes in the AM sense. It should be noted that these theoretical energy differences are not really true activation energies, as they omit zero-point energy variations and the effects of the enhanced reactivities of vibrational and rotational nonground-state molecules.

The 4-31G/MP3 energy differences between the M and AM transition-state structures and reaction barriers of 2.8 and 1.6 kcal/mol, respectively, for the addition of  $\text{BH}_3$  to cyanoethylene show a preference for the Markownikoff channel. While no experimental work on the hydroboration of unsaturated nitriles or closely related compounds per se have been reported, the bulk of experimental evidence strongly suggests that electron-withdrawing groups should direct addition to the olefin carbon  $\alpha$  to the substituent. The magnitude of the energy differential is slightly larger than for propylene and implies a regioselectivity roughly comparable to that reported in the experimental studies, although the quantities involved are small and the methods used cannot be expected to yield results of precise chemical accuracy. A cyano group is commonly believed to be a stronger electron-withdrawing functionality than a methyl group is an electron donor, so that a somewhat larger energy differential between M and AM addition in the nitrile case is not unreasonable. In addition, the conjugative interaction between the nitrile triple and carbon-carbon double bond may serve to shift an abnormally large amount of charge density away from C1 toward the C2–C7 bond, increasing the preference for the electrophilic borane to add at the more highly substituted carbon.

It should be noted that the selectivities implied by the energetic results of this study were derived without reference to the involvement of solvent molecules directly in the  $\pi$ -complexes or transition states. While strong experimental evidence exists in support of the presence of a borane-complexed solvent molecule in the intermediary structures for reactions in tetrahydrofuran solvent,<sup>18</sup> we do not concur with Dewar and McKee's claim<sup>21</sup> that the presence of a solvent molecule is necessary to account for the observed regioselectivity of hydroboration.

#### Electronic Control of the Hydroboration Path

Since the direction and magnitude of the regioselectivity of the hydroboration reaction appears to depend upon the electronic character of the olefin substituent, this control should be manifest in a differing variation of atomic charges over the course of the reaction in the presence of electron-donating or electron-with-

Table VII. Methyl and Nitrile Group Charges and C1–C2 Charge Separations for the Key Structures along the Hydroboration Pathway of Propylene and Cyanoethylene

structure	group charge <sup>a, b</sup>		C1–C2 charge separation <sup>b, c</sup>	
	methyl	nitrile	methyl	nitrile
III	+0.025	–0.114	0.175	0.106
M IV	+0.079	–0.062	0.210	0.141
M IV'	+0.029	–0.099	0.073	0.033
M IV''		–0.131		0.055
M V	–0.006	–0.151	0.152	0.163
AM IV	+0.080	–0.071	0.204	0.114
AM IV'	+0.079	–0.063	0.277	0.257
AM IV''		–0.065		0.248
AM V	–0.006	–0.144	0.193	0.151

<sup>a</sup> Group charge is defined as the sum of the  $\text{CH}_3$  carbon and three hydrogen charges for the methyl and as the sum of the CN carbon and nitrogen charge for the nitrile group. <sup>b</sup> Charges in electrons. <sup>c</sup> The difference between the C2 and C1 atomic charges. Carbon C1 bears the greater negative charge.

drawing groups. The overall redistribution of charge, apart from substituent effects, which occurs in the reaction of  $\text{BH}_3$  with ethylene has already been analyzed in terms of a donation-back-donation mechanism for hydroboration<sup>26</sup> and will not be repeated here. Instead, we look for deviations from the basic donation-back-donation scheme that may be ascribed to the olefin substituents. However, it must be remembered that Mulliken charges are somewhat arbitrary and that any charge distribution determined by a minimum basis set calculation is not entirely accurate.<sup>39,40</sup>

There is an initial separation of charge between the olefin carbons of structure III of the propylene reaction, with more electron density placed on the unsubstituted C1 atom, as revealed in Table VII. This polarization of charge may be partially accounted for by a small donation from the methyl group into the  $\pi$  system that ends up principally on C1 but more likely arises simply from the tendency of charges to alternate along bonded networks. Thus, the presence of negative charge on the methyl carbon atom C7 (but not on the methyl group as a whole) tends to induce a more positive charge on the  $\alpha$ -carbon atom C2 and a more negative charge on the  $\beta$ -carbon atom C1. As the  $\pi$ -complexes are formed, a roughly equivalent donation of charge from the rest of the molecule to the boron atom occurs along both the M and AM reaction pathways. This donation is reflected in the increase in positive charge on the methyl group in forming IV from III, as shown in Table VII.

The significant differences between the M and AM addition paths occur in the formation of the appropriate transition states. For the AM channel, the polarization of charge along the C1–C2 axis increases; the extra charge on C1 comes from the olefin hydrogens and borane hydrogens as well as from C2. Although C7 does become slightly more negative, the donation from the methyl group as a whole remains constant. The polarization decreases, however, in the case of M addition, where atom C2 of the  $\pi$ -complex is populated, primarily through the shifting of charge away from the hydrogen atoms. The molecular dipole component along the C1–C2 bond now is directed with the negative terminus at C2, rather than at C1, and C2 acquires a substantial negative charge. As a result, the adjacent methyl group decreases its electron donation to the rest of the molecule (Table VII). The reactions then proceed to the organoborane products where all of the other atoms of the molecule are repopulated at the expense of B3. Thus, even though the transition-state AM IV' is more highly polarized, anti-Markownikoff addition is favored due to the ability of the methyl group to continue to donate electrons in the presence of an adjacent more positively charged

(39) Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 732.

(40) Graham, G. D.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 4572.

carbon atom, as opposed to the reduction in donor ability that accompanies the accumulation of negative charge on the  $\alpha$ -carbon.

In the reaction of cyanoethylene with borane, the initial charge separation between the olefin carbon atoms in III, with C1 more negative, is noticeably smaller than in the propylene III, again most likely due to inductive effects or to the conjugative interaction with the nitrile. As the  $\pi$ -complexes are formed, B3 is again populated at the expense of the other atoms, and the charge separation between the two carbons increases. As shown in Table VII, the cyano group releases to the  $\pi$ -complexes some of the electron population which it had withdrawn from III. The slightly greater magnitude of release occurring along the M path may account for the lower energy of the M vs. the AM IV structure, in spite of stereochemical effects.

As the transition state for the M reaction of cyanoethylene is formed, negative charge accumulates at C2 and the charge separation between C1 and C2 is reduced to only 0.033 electrons. The buildup of negative charge on C2 is stabilized by the electron-withdrawing activity of the nitrile group, which removes an increased amount of electron density from M IV' than it did from M IV. Conversely, along the AM reaction coordinate the polarization between C1 and C2 increases dramatically, with C2 becoming more positively charged in IV' than in IV. While the nitrile does release a small additional quantity of charge to this structure, Table VII reveals that the amount of charge donated is less than the additional charge withdrawn from M IV'. As was the case for propylene, the component of the dipole moment along the C1-C2 axis differs in direction between the M and AM transition states; the magnitude of the dipole in M IV', which has the negative pole toward C2, is larger. The depopulation of the boron atom and repopulation of the rest of the molecule, including the cyano group, marks the completion of the formation of the organoborane product. Overall, the M addition of  $\text{BH}_3$  to cyanoethylene is preferred due to the greater stabilization of the negatively charged adjacent olefin atom in M addition through the uptake of electronic charge by the nitrile as compared to the stabilization by the release of nitrile charge density to a more positively charged  $\alpha$  center along the AM channel.

It is interesting to note that for both of the unsaturated compounds studied, the preferred reaction pathway gives rise to the more highly polarized transition state, as measured by the total or the C1-C2 axis component of the molecular dipole moment. Thus, it is seen that substituents direct the regioselectivity of hydroboration not through a reduction of charge assumption but by the stabilization or destabilization of the charge separation arising during the course of the reaction. The preferences observed should be even more pronounced in the solution-phase reaction. Here, interactions with polar solvent molecules will provide additional stabilization for that reaction pathway which involves the larger polarization of electronic charge in the intermediary structures.

### The LMO Description of Hydroboration

In order to gain a clearer conception of the nature of the bonding that occurs in the intervening structures between the hydroboration reactants and products, we calculated localized molecular orbitals from the PRDDO wave function for the principal path structures. The overall bonding schemes determined for both the propylene and cyanoethylene reactions were essentially equivalent, and M and AM path LMO structures differed only in the direction of addition. The subtler differences in the reaction profiles of the two olefins and between the pathways for the M and AM addition of the borane are reflected only by variations in the electronic populations of the two- and three-center LMOs of corresponding structures.

The LMOs of the hydroboration  $\pi$ -complexes and transition states for both the M and AM reactions are drawn in Figure 3. It is seen that the creation of the  $\pi$ -complexes IV from III involves the formation of a three-center bond with high p orbital character between C1, C2, and B3. In the transition state, the portion of the three-center bond linking the carbon to which H4 is to be transferred is weakened and is compensated for by the conversion

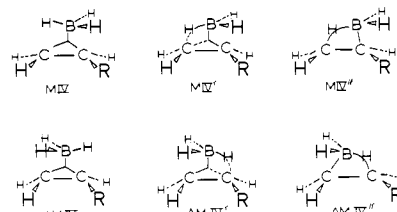


Figure 3. Localized molecular orbitals of the key structures along the hydroboration reaction pathway.

of a two-center B-H bond to a three-center bond involving this carbon atom. Although five "bonds" are formally drawn to the carbon undergoing hydrogen transfer, the populations of the two three-center bonds are far less than unity, as symbolized by the dashed lines of Figure 3. The transformation of IV' to the organoborane products is then facile, simply requiring the conversion of the three-center bonds to the appropriate two-center linkages. The LMO analysis indicates that hydroboration proceeds in a concerted manner; at no point is a bond to the hydrogen which is being transferred totally ruptured. This smooth conversion of a two- to three- to a two-center bond, reminiscent of numerous boron hydride rearrangements,<sup>41</sup> helps to explain the favorable activation parameters for this reaction. The overall portrait of hydroboration provided by the LMOs corresponds closely to the scheme proposed by Jones<sup>20</sup> to account for the apparent allowedness of the reaction.

Several small differences in the populations of the LMO bonds help to illuminate the effects of the olefin substituents. The two bent  $\tau$  bonds that, in the Boys formalism, represent the double bond in III have a larger electronic contribution from C1 in the case of methyl and C2 in the case of nitrile substitution, forming a basis for the observed preference for anti-Markownikoff and Markownikoff addition of  $\text{BH}_3$ , respectively. Differences also exist in the population of the three-center LMOs of the IV' molecules. For both the M and AM paths, the carbon atom undergoing the hydrogen transfer makes a smaller population contribution to the forming BHC bond and a greater contribution to the breaking CBC bond in the cyanoethylene reaction, in line with the notion that the transition state here occurs earlier along the reaction pathway than for addition to propylene. Further demonstration of this fact is provided by the LMOs for the IV'' structures, drawn in Figure 3, in which the CBC bond of IV' has already been converted to a two-center CB bond, even though the geometries of IV'' are in many ways very similar to those of the transition states for the propylene reaction.

### Conclusion

The findings of this study confirm the overall description of the course of the hydroboration reaction first proposed in the SGL paper on the addition of borane to ethylene. In all cases, a  $\pi$ -complex between the reactants is formed which subsequently deforms through an asymmetric four-center transition state to yield the organoborane product in a donation-back-donation mechanism. This description has also been borne out in a recent theoretical paper<sup>42</sup> subsequent to the SGL work. The only remaining discrepancy among the various theoretical methods applied to the hydroboration problem occurs in the location of the transition state energies above or below those of the sum of the reactants. However, any observed reaction barrier to hydroboration or reaction regioselectivity observed will, in most cases, arise from the internal barrier to the conversion of  $\pi$ -complex to transition state.

The predicted preference for Markownikoff addition to cyanoethylene underscores the importance of electronic effects in controlling the direction of hydroboration. We expect electronic control to predominate for the hydroboration of olefins with small substituents where steric effects are of minor importance. The nature of the directive effects is reflected in the variations in atomic

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and group charges over the course of the reaction, which depend on the electronic character of the olefin substituent.

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## Electrochemical Responses of Electrodes Coated with Redox Polymers. Evidence for Control of Charge-Transfer Rates across Polymeric Layers by Electron Exchange between Incorporated Redox Sites

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**Abstract:** Redox polymers prepared by the reaction of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  with poly(4-vinylpyridine) were used to coat pyrolytic graphite electrodes. The number of redox groups within the polymer was varied systematically while monitoring the resulting changes in the electrochemical responses of the electrode coatings. Coatings composed of the preformed redox polymer yielded responses close to that expected for an ideal nernstian reactant confined to the electrode surface, while coatings prepared by coordinating redox centers to PVP films that were already attached to the electrode gave less ideal responses. Effective diffusion coefficients for the transfer of charge through the polymer films were estimated. Decreasing the number of redox sites in the films caused no change in the rates of charge transfer at high concentrations of sites, but a drop in rate occurred when the number of redox sites was decreased sufficiently. The effect is believed to reflect the composition of the polymer-redox center mixture where electron transfer between adjacent pairs of redox centers begins to limit the rate of charge transfer through the polymer.

Previous studies of electrodes with polymeric coatings attached to their surfaces<sup>1,2</sup> have usually employed coating techniques that result in films with properties that are determined by the particular coating procedure. Consequently, systematic studies of the variations in electrochemical responses produced by changes in the physical characteristics and, especially, the chemical compositions of the deposited films have only rarely been reported.<sup>3</sup> In our own previous work on this topic various approaches were used to attach metal complexes to polymer coatings on electrode surfaces<sup>4</sup> but in every case the polymeric ligands were applied to the electrode surface before the metal complexes had been incorporated in the polymers because of difficulties in preparing solutions in which both the polymers and metal complexes were soluble. This obstacle has now been overcome by the combination of poly(4-vinylpyridine) (PVP) and  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$ . Both of these reactants are soluble over a reasonable range of mole ratios in a mixed methanol-water solvent (50 vol % of each). By taking advantage of the well-documented coordination chemistry of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  with heterocyclic nitrogen ligands such as pyridine,<sup>5</sup> it was possible to prepare homogeneous solutions containing

$\text{Fe}(\text{CN})_5^{3-}$  centers coordinated to pyridine groups in PVP at levels as high as one  $\text{Fe}(\text{CN})_5^{3-}$  complex for every third pyridine group (precipitates form at higher ratios). Films cast on graphite electrode surfaces by evaporation of aliquots of these solutions proved to be quite stable in perchlorate or trifluoroacetate supporting electrolytes where their electrochemical responses were examined. Of particular interest was a comparison of the behavior of films formed from the homogeneous solutions of polymer-metal complexes with that of similar films formed by coating electrodes with pure PVP followed by coordination of  $\text{Fe}(\text{CN})_5^{3-}$  to the films from aqueous solutions of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  in which the polymer is not soluble. The considerable differences that were encountered in the morphology of current-potential and current-time curves for these two types of films are described in this report. The effects of film thickness and composition on the apparent diffusion coefficients of the attached complexes and on the fraction of them that are electroactive are also discussed.

### Experimental Section

**Materials.** Poly(4-vinylpyridine) (PVP) (Borden Co.) was purified and its average molecular weight ( $7.4 \times 10^5$ ) was measured as described previously.<sup>4d</sup>  $\text{Na}_3\text{Fe}(\text{CN})_5\text{NH}_3 \cdot 3\text{H}_2\text{O}$  (Eastern Chem. Co., Hauppauge, N.Y.) was purified by repeated recrystallization from saturated ammonia.<sup>5b</sup> Solutions of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  were prepared by dissolving this salt in aqueous solutions under conditions where substitution of the  $\text{NH}_3$  group by  $\text{H}_2\text{O}$  proceeds rapidly.<sup>5</sup> Solutions of  $\text{Fe}(\text{CN})_5\text{py}^{3-}$  (py = pyridine) were prepared by mixing  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  and pyridine in situ.<sup>5b</sup> Solutions containing PVP to which various quantities of  $\text{Fe}(\text{CN})_5^{3-}$  groups were coordinated were prepared by mixing aqueous solutions of  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  and methanolic solutions of PVP having appropriate concentrations to produce a final mixture with the desired stoichiometric ratio of PVP to  $\text{Fe}(\text{CN})_5\text{OH}_2^{3-}$  in a 50/50 vol % methanol-water mixture. Neither PVP nor  $\text{Na}_3\text{Fe}(\text{CN})_5\text{OH}_2$  precipitated from the mixed solvent when both reagents were present although precipitates did form if either one was absent. The mixture was neutralized to pH 6-7 by

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