1564 *J. Am. Chem. Soc.* **2001,** *123,* 1564−1568

Correlation of Relative Rates of $PdCl_2$ Oxidation of Functionalized Acyclic Alkenes versus Alkene Ionization Potentials, HOMOs, and LUMOs

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Received June 19, 2000

Abstract: Investigations of the title reaction, carried out by plotting logs of the relative reaction rates vs IPs, vs HOMOs, and vs LUMOs, reveal multiple nearly parallel lines of correlation with small negative slopes in each. Overall, the natural grouping into monosubstituted and disubstituted alkenes gives better correlations than that obtained by using all alkenes. Comparison with analogous plots for other reactions indicates that the mechanism for this reaction has similarities to that for hydroboration, the major difference being that the lines in the plots for hydroboration have positive slopes, indicating an electrophilic rate-determining step involving the π electrons, while those for the title reaction have small negative slopes, indicating a nucleophilic rate-determining step. Of the two reaction mechanisms proposed for the title reaction, only one has a nucleophilic attack at the complexed alkene as the rate-determining step, and therefore, this work supports that reaction mechanism.

I. Introduction

We have developed a technique[1] for correlating measurable characteristics in addition reactions with alkenes in order to gain information which is useful mechanistically and synthetically. We have applied this technique to several reactions: hydroboration,[1a] oxymercuration,[1a] bromination,[1a,g,h] diimide addition,[1b] oxidation with permanganate,[1c] epoxidation,[1d] sulfenyl halide addition,[1d] mercuric chloride complexation,[1d] silver ion complexation,[1d,h] carbene addition,[1e] nitrosyl chloride addition,[1e] oxidation with osmium tetroxide,[1e] chlorination,[1g,h] and complexation with iodine.[1g,h] This technique offers (1) a procedure to determine relative magnitudes of steric and electronic effects in the rate-determining step, (2) a relatively simple way to predict the effects of substituents on reaction rates for synthetic purposes, and (3) a method to choose between alternative proposed reaction mechanisms in some cases. In investigations[1] of other additions to alkenes, we applied this simple method by correlating the logs of the relative reaction rates (log k_{rel} values) with the alkene ionization potentials (IPs), with their highest occupied molecular orbital energies (HOMOs), and in some cases with their lowest unoccupied molecular orbital energies (LUMOs). In those investigations, reactions with similar mechanisms gave correlation plots which were similar in appearance. To develop further this new technique and to elucidate synthetically and mechanistically important information from experimental or from computational data, we apply the technique to important reactions with a variety of mechanisms. For nucleophilic addition reactions, such as $PdCl_2$ oxidation and other transition metal additions, which are characterized by inhibition of rate by alkyl substitution and nonselective mode of addition, there have been no clear measures of the relative importance of electronic and steric effects; this technique provides such quantitative information.[2] Thus, it is desirable to investigate similarly the $PdCl_2$ oxidation of representative functionalized alkenes, because this is an important reaction for which is indicated a mechanism of a type which we have not treated previously, and the reaction is suited to our analysis method.

II. Background

There has been much interest[3−12] in the mechanism of palladium chloride ($PdCl_2$) oxidation (eq 1) of acyclic alkenes.

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[2] We are grateful to a reviewer for making this point.

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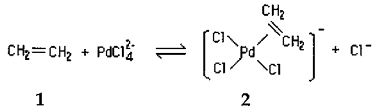
10.1021/ja002190j CCC: $20.00

This is in part due to the industrial importance[3,4] of the reaction in the synthesis of carbonyl compounds from corresponding alkenes (the Wacker oxidation[3a,b]) and in part due to the interest in its mechanistic pathway.[3−12]

$$C_nH_{2n} + PdCl_2 + H_2O \rightarrow C_nH_{2n}O + Pd(0) + 2HCl \quad (1)$$

The steps of the reaction are now generally considered to be those shown below (eqs 2−7), although there has been disagreement over some mechanistic details and over the identity of the rate-determining step.[4−12] The first step (eq 2) of the reaction is alkene coordination to give a palladium(II) complex **2**. The next step (eq 3) in the reaction sequence is generally accepted to be the nucleophilic replacement of a second chloride by water to give intermediate **3**. There seems to be agreement that the previous equilibrium steps (eqs 2 and 3) in the reaction sequence are fast relative to the rates of the subsequent steps.[4−12] However, two different pathways have been suggested for the following step (**3** → **5**) (eqs 4 and 4′). In the first pathway,[4] the alkene complex **3** deprotonates first to a negative hydroxymetal complex ion **4** (eq 4), followed by rate-determining conversion of the palladium(II) alkene π-complex into a palladium(II) β-hydroxyalkyl species **5**, a process called hydroxypalladation (eq 4).[4] The second proposed pathway[7a,b] is a rapid equilibrium in which a H_2O molecule attacks the C═C double bond directly to give the palladium β-hydroxyalkyl intermediate 5 (eq 4′), with the rate-determining step following. The palladium β-hydroxyalkyl intermediate **5** then loses a chloride ion (eq 5) to yield another β-hydroxyalkyl intermediate **6**. The next step (eq 6) is β-hydrogen elimination of the intermediate **6** to give a palladium enol π-complex **7**. Compound **7** then undergoes β-hydrogen addition to give the palladium α-hydroxyalkyl species **8**. Finally, the carbonyl product **9** is produced by deprotonation and dissociation (eq 7).



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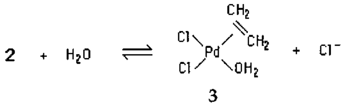

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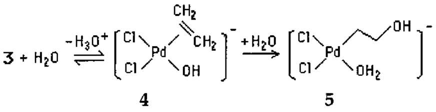

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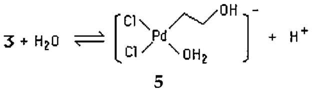

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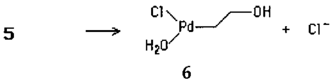

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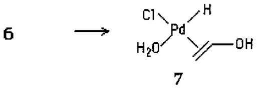

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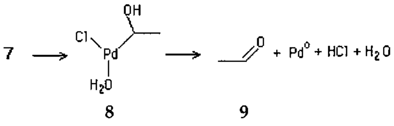
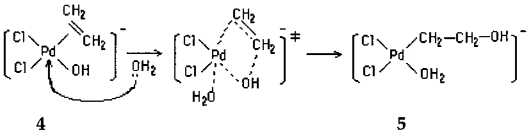


(7)

Much debate surrounding the identity of the rate-determining step has focused on whether the hydroxypalladation (**3** → **5**) is the rate-determining step or an equilibrium immediately preceding the rate-determining step (eq 5).[4−12] This is linked to a controversy over whether the attack by the nucleophile on the double bond in step 4 is internal (eq 8) or external (eq 9). The proposed mechanism which has eq 8 as the rate-determining step proceeds via internal nucleophilic attack, while the proposed mechanism which has eq 10 as the rate-determining step specifies a relatively fast thermodynamic external nucleophilic attack preceding the rate-determining step.



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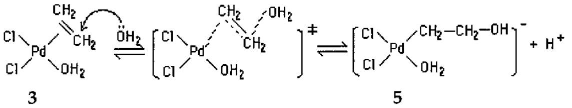

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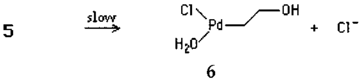

(10)

Henry proposed a concerted nonpolar four-center transition state[4a] (eq 8) in the rate-determining step, similar to an I_a process.[11b] This mechanism has been described as “a cis attack of coordinated hydroxide upon one of the double bond carbon atoms” [4b] and “a nucleophilic intramolecular attack on the coordinated alkene”.[9] Further investigation,[4] using a low concentration of chloride ion, showed that a combination of steric and electronic effects directs the mode of this hydroxypalladation step (eq 8).

In the second mechanism proposed, the hydroxypalladation step (eq 8) is not the rate-determining step but is a reversible procedure involving a relatively rapid external attack of a water molecule upon a carbon atom of the alkene double bond (eq 9).[7a,b] Instead, the loss of a chloride ion Cl^- from the palladium

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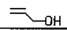
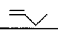
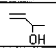
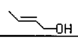
Table 1. IPs, HOMOs, LUMOs, and Relative Rates of Palladium Chloride Oxidation of Alkenes

No.	alkene	IP (eV)[a]	HOMO (eV)	LUMO (eV)	k_{rel} $PdCl_2$[b]
1		10.52	-10.17	1.32	897
2		9.74	-9.97	1.12	241
3		9.63[c]	-9.93	1.14	103
4		9.63	-9.94	1.12	100
5		9.52[d]	-9.92	1.18	35.9
6		9.24	-9.80	0.99	44.9[e]
7		9.12	-9.79	0.93	76.9
8		9.12	-9.78	0.93	87.2
9		9.01[f]	-9.75	0.96	22.3

[a] Reference 13a. [b] Reference 4c. [c] Reference 13b. [d] Calculated by applying to the IP for 1-butene a correction factor calculated as the difference between the IPs of 1-propene and 2-propen-1-ol: 9.63 eV − (9.74 eV − 9.63 eV) = 9.52 eV, ref 15. [e] Reference 4d. [f] Calculated by applying to the IP for 2-propen-l-ol a correction factor calculated as the difference between the IPs of 1-propene and *trans*-2-butene: 9.63 eV − (9.74 eV − 9.12 eV) = 9.01 eV; refs 13c and 15.

β-hydroxyalkyl intermediate **5** (eq 10) is proposed to be the rate-determining step of the reaction.[7a,b,10,11] However, data used to formulate these conclusions were obtained from reactions carried out under a high (≃3 M) chloride ion concentration, so these results may apply to a reaction other than that which is the subject of this report.

There may be some confusion surrounding the mechanism of this reaction because many of these reactions were not run under the exact conditions of the Wacker reaction.[3a,b] For example, reactants often had different ligands on palladium[5] or used different nucleophiles;[6] it has been reported[4f] that either of these can change the reaction mechanism. In addition, some studies[7] have been carried out with a much higher concentration of chloride (≃3 M) than is used in the traditional Wacker reaction (<1 M), developed by Smidt and co-workers[3a,b] (while at Wacker Chemie laboratory). Originally, it was assumed[7b] that using a chloride concentration different from that in the original Wacker oxidation would not be likely to change the steric course of the reaction. However, it was recently shown that this higher chloride concentration does indeed change the reaction mechanism, from syn addition at low [Cl^-] to anti addition at high [Cl^-].[4f] Moreover, different products are obtained with the different chloride concentrations.[4f] The relative reactivity data used for our study were obtained under the lower [Cl^-] (<1 M), so the studies[4] pertinent to this investigation are those carried out under analogous reaction conditions, including low chloride ion concentration. Therefore, only those pertinent studies[4] under analogous conditions will be used herein for comparison and analysis.

III. Results

Relative rates[4c,d] for the $PdCl_2$ oxidation of representative alkenes and alkene IPs[12] are shown in Table 1. As in our previous studies,[1] cyclic alkenes and aryl alkenes are omitted in order to avoid effects due to ring strain or conjugation with phenyl; only acyclic alkenes without aryl functionalities are included in this study. HOMOs and LUMOs, also given in Table 1, were calculated as described below.

The plot of the log k_{rel} values for $PdCl_2$ oxidation of alkenes versus their corresponding IPs (Figure 1) reveals a natural grouping of data for monosubstituted and disubstituted alkenes. Lines show a good-to-excellent correlation ($r_{monosubstituted} = 0.99$, $r_{disubstituted} = 0.43$) within each sterically similar group, with a small natural separation between the two lines so formed. The correlation obtained by considering data for all alkenes regardless of degree of substitution is $r_{all} = 0.87$. Within each group of alkenes, the relative reaction rates increase as the IPs increase, giving a line with negative slope. Figure 2 shows similar correlations of log k_{rel} values versus the HOMOs of the corresponding alkenes ($r_{monosubstituted} = 0.92$, $r_{disubstituted} = 0.66$, $r_{all} = 0.85$). Similar to the IP data, within each group of sterically similar alkenes, relative reaction rates increase as the HOMO energies decrease. The negative slopes of the lines in the plots using IP and HOMO values indicate a nucleophilic attack upon the complexed alkene in the rate-determining step. Therefore, we also determined the LUMO energies in order to ascertain whether there was a similar correlation. In Figure 3, a correlation with the alkene LUMOs shows results somewhat more definitive than those obtained with IPs or with the HOMOs ($r_{monosubstituted} = 0.88$, $r_{disubstituted} = 0.60$, $r_{all} = 0.44$). Considering the data from all three plots, the correlations within sterically similar groups are somewhat better than those obtained with all data points regardless of degree of substitution.

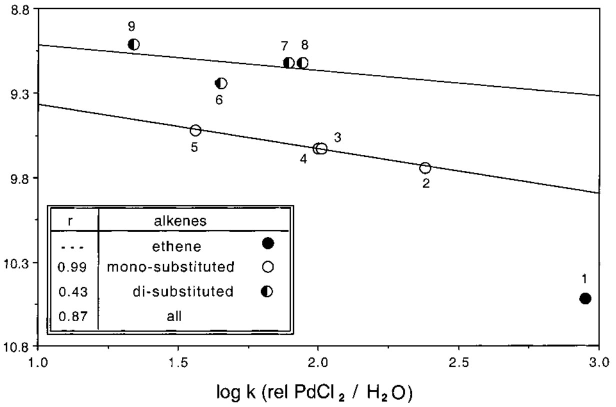


Figure 1. Plot of the log k_{rel} values for $PdCl_2$ oxidation of alkenes versus their corresponding IPs. Data are from Table 1. Lines of correlation for monosubstituted alkenes and for disubstituted alkenes are shown. Correlation coefficients *r* are given in the legend for monosubstituted alkenes, for disubstituted alkenes, and for all alkenes regardless of the degree of substitution about the double bond. The *y*-axis IP data are plotted in inverse order so that data reflecting lower π-electron energies appear at the bottom of the plot, to facilitate comparison with the plots of HOMOs and of LUMOs.

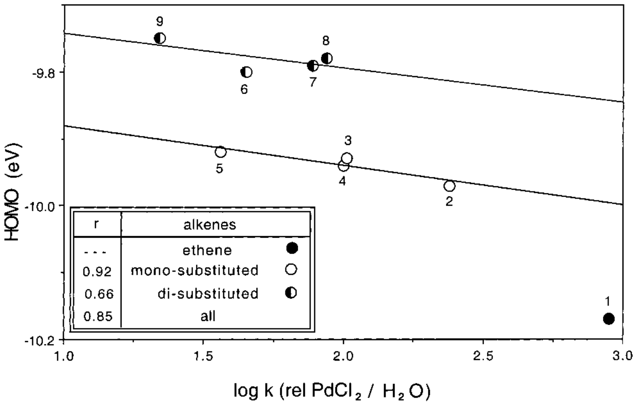


Figure 2. Plot of log k_{rel} vs HOMO analogous to that shown in Figure 1.

IV. Discussion

A. Nucleophilic vs Electrophilic. The lines of correlation in the plots (Figures 1 and 2) show an opposite (negative) slope compared to the results of most of our previous investigations,

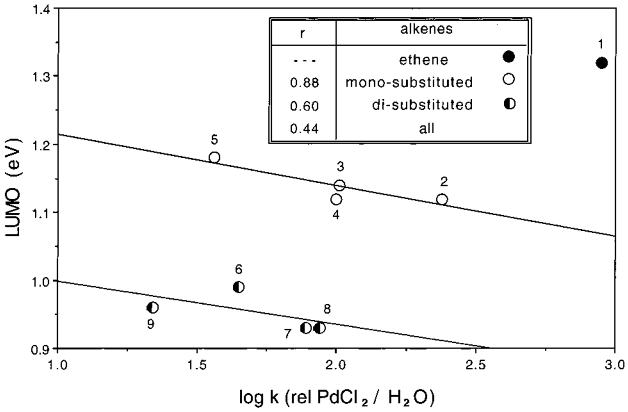


Figure 3. Plot of log k_{rel} values vs LUMO analogous to that shown in Figure 1.

which were of electrophilic reactions with positive slopes, such as bromination,[1a] hydroboration,[1a,g,h] oxymercuration,[1a] diimide reduction,[1b] and chlorination.[1g,h] These results are similar to those found for nucleophilic reactions such as permanganate oxidation[1c] and conversion of the adsorbed form of the alkene on molecular iodine or silver ion to the complexed form,[1h] although the slopes of the lines are smaller for this reaction. The negative slope, reflecting a nucleophilic attack at the alkene carbons, is in agreement with Henry's proposed rate-determining step for the $PdCl_2$ oxidation of alkenes, which invokes attack by OH^- at the complexed alkene. The small magnitude of the slope indicates that the reaction is not as dependent upon IP as other nucleophilic reactions which we have investigated previously.[1c,h] Nevertheless, this is interesting and important since we have not previously found another system which gives plots with multiple lines of negative slope.

The nucleophilicity of the rate-determining step of this reaction is relevant to the recent debate surrounding the mechanism of the $PdCl_2$ oxidation of alkenes,[4−11] i.e., whether the rate-determining step is eq 8[4,8,9] or eq 9.[7a,b,10,11] Henry's most recent mechanistic studies[4f,g] indicate that the rate-determining step is eq 8, the nucleophilic hydroxypalladation step leading from the π-complex. Our results support this conclusion, since the lines in our plots each have a negative slope, characteristic of a nucleophilic reaction.[1c,g]

The other proposed rate-determining step, the dissociation of Cl^- (eq 5), has no direct relation to the π-bond in the alkene. Our results, which indicate a correlation with molecular orbital energies, disfavor that step as the rate-determining step. They are inconsistent with the mechanism proposed by Bäckvall and co-workers, in which the hydroxypalladation is an equilibrium process, and the rate-determining step is loss of chloride from the hydroxypalladation adduct **5** (eq 5). These conclusions, which account for the appearance of the plots for this reaction and for Henry's findings,[4] also fit the patterns which were established by our previous studies.

B. Mechanism of Formation of the C−O Bond. There have been conflicting proposals for the mechanism by which the C−O bond is formed in eq 4 or 4′; some reports propose an internal migration of OH to a carbon of the complexed alkene (eq 4),[4,8,9] and some propose an external attack by H_2O upon a carbon of the complexed alkene (eq 4′).[7a,b,10,11] Our work cannot differentiate between external vs internal attack directly. However, our work does show that the rate-determining step for the reaction with low $[Cl^-]$ is a nucleophilic addition to an alkene, and in the proposed mechanism involving nucleophilic addition to an alkene (eq 8), the C−O bond is formed via internal migration. Conversely, the step involving external attack is proposed to be a rapid equilibrium[7a,b,10,11] (eq 9) preceding a rate-determining step (eq 10), which neither is nucleophilic nor involves the alkene π-electrons. Therefore, our work indirectly supports internal migration of OH to the complexed alkane.

C. Relative Magnitudes of Steric versus Electronic Effects. Additional patterns drawn from our previous studies of additions to alkenes can be used for comparison to help differentiate between eqs 8 and 10 as the rate-determining step for the palladium chloride oxidation of alkenes. In previous studies of single-step reactions leading to three-center products or reactions involving three-center intermediates, we often find two types of plots of log k_{rel} values vs alkene IPs. Type 1: If the rate-determining step leads *to* a three-center intermediate or product, a correlation involving all alkenes regardless of steric effects is indicated by a single line of correlation in the analogous plot of log k_{rel} vs IP or HOMO.[1] Type 2: If the rate-determining step leads *from* a three-center π-complex, then plotted data appear in groups dependent upon the steric requirements of the alkenes.[1d]

Since plotted data for palladium chloride oxidation of alkenes appear in groups dependent upon the steric requirements of the alkenes, these results support a reaction mechanism[4] more similar to the type 2 mechanism, with the rate-determining step leading *from* the π-complex, as depicted in eq 8. A correlation with all alkenes regardless of steric effects would favor formation of a π-complex, similar to the reaction shown in eq 2, as the rate-determining step of this reaction. The natural separation into two sterically similar groups supports the postulation that the rate-determining step of this reaction is dependent upon both steric and electronic effects. These conclusions, regarding the rate-determining step and the steric and electronic effects upon it, are similar to those reported by Henry et al.[4c,f]

The log k_{rel} values for substituted alkenes **6**−**9** are faster than would be predicted on the basis of IP alone. Because the IP reflects the electronic but not the steric effects of the substituents, the steric effects in palladium chloride oxidation may be responsible for the reaction rate being different than would have been expected solely on the basis of the IP. If this is the case, then the steric effects of the substituents on the double bond carbon atoms do not decelerate the decomposition of the Pd(II) β-hydroxyalkyl, but accelerate it. The steric effects of the alkenes might be expected to affect the rate of the hydroxypalladation step (eq 8), since the Pd(II) group complexed to the alkene is quite large and could therefore create steric congestion. Steric acceleration in the rearrangement from the π-complex would occur when the complex is more sterically congested than the transition state structure which follows. A similar analysis of hydroboration or of oxymercuration reveals steric deceleration, which indicates a transition from a less to a more sterically hindered structure. This might indicate that the π-complex in hydroboration is looser and less sterically congested (eqs 10 and 11).[14]

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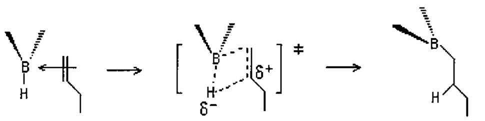
(13) (a) Masclet, P.; Grosjean, D.; Mouvier, G.; Dubois, J. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 225−237. (b) Katrib, A.; Rabalais, J. W. *J. Phys. Chem.* **1973**, *77*, 2358−2363. (c) Klasnic, L.; Ruscic, B.; Sabljie, A.; Trinajstic, N. *J. Am. Chem. Soc.* **1979**, *101*, 7477−7482.

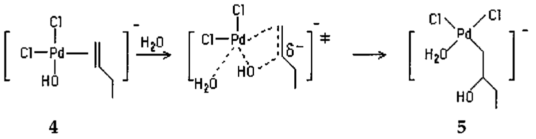
(14) (a) Brown, H. C. *Hydroboration*; W. A. Benjamin, Inc.: New York, 1962; p 13. (b) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1075−1082. (c) Sundberg, K. R.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1979**, *101*, 2863−2869. (d) Nagase, S.; Ray, N. K.; Morokuma, K. *J. Am. Chem. Soc.* **1980**, *102*, 4536−4537. (e) Clark, T.; Schleyer, P.v. R. *J. Organomet. Chem.* **1978**, *156*, 191−202. (f) Dasgupta, S.; Datta, M. K.; Datta, R. *Tetrahedron Lett.* **1978**, *15*, 1309−1312. (g) Seyferth, D. *Prog. Inorg. Chem.* **1962**, *3*, 210. (h) Streitwieser, A. J.; Verbit, L.; Bittman, R. *J. Org. Chem.* **1967**, *32*, 1530−1532.

D. Compare and Contrast Similar Reactions. The $PdCl_2$ reaction has similarities to and differences from hydroboration and oxymercuration: (1) The plot for each shows a separation into groups of sterically similar alkenes, with each group dependent upon the steric requirements of the alkenes. (2) Increased substitution on the alkene causes a rate decrease in all three reactions. (3) The slopes of the lines in the plots are negative in $PdCl_2$ oxidation but positive in hydroboration and oxymercuration. (4) In each reaction, the π-electrons are complexed to the metal via a dative bond which changes to a formal σ bond through the transition state. (5) A four-center transition state in the rate-determining step preceded by a three-center π-complex has been proposed for each reaction.[1,4a,14] (6) However, palladium chloride oxidation demonstrates effects consistent with steric acceleration in rearrangement from the π-complex while hydroboration and oxymercuration results are consistent with steric deceleration.

The similarities suggest that the steric and electronic requirements of the internal migration could be analogous to those of hydroboration (eqs 10 and 11), and those of the external attack could be analogous to oxymercuration (eqs 12 and 13). The following comparison between the mechanisms involving four-center transition states in palladium chloride oxidation proposed originally by Henry (eq 11),[4a] and in hydroboration proposed originally by Brown (eq 10),[14a] is striking.[16]



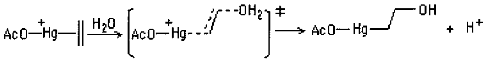
(10)



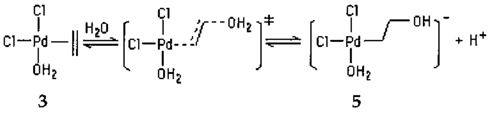
(11)

The external attack mechanism in $PdCl_2$ oxidation (eq 13) is also similar to that in oxymercuration (12), except that eq 12 is proposed to be the rate-determining step in oxymercuration, while eq 13 is *not* proposed to be the rate-determining step in $PdCl_2$ oxidation.

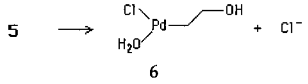
However, comparing eqs 12 and 13 is not warranted for at least three reasons: (1) the reaction shown in eq 13 is not proposed as a rate-determining step, (2) the rate-determining step in the proposed mechanism which includes step 13 is not a nucleophilic process, and (3) the mechanism by which the C−O bond is formed in eq 4 has been determined recently by Henry to be internal attack in the presence of low [Cl$^-$] and external attack with high [Cl$^-$].[4f] This conclusion fits nicely our results for this reaction using low [Cl$^-$] as well as analogies with other reactions predicted from the patterns determined in our previous studies.



(12)



(13)



(5)

The electrophilic nature of the electronic effects in hydroboration and in oxymercuration manifests itself as a slope opposite to that for oxidation by using palladium chloride, a nucleophilic reaction. However, a linear relationship of the electronic effects is apparently intact in all three reactions.

V. Theoretical Procedure

The HOMOs and LUMOs of the alkenes were calculated by using MNDO in the same manner as reported previously.[1a] In each case, the eigenvectors were examined to ensure that the HOMO and LUMO correspond to the carbon−carbon π- and π^*-orbitals, respectively. The HOMOs for the allylic alcohols each pertain to the geometry having the O−C−C=C dihedral angle equal to 0°. We found that these geometries yield the lowest-magnitude HOMO values for the allylic alcohols and give the best correlation with log k_{rel} values. For some allylic alcohols having both HOMO and IP data available, the use of HOMO values for other conformers was explored; these data were not used because the correlation between HOMO and IP values was diminished in those cases.

VI. Conclusion

Plots of log k_{rel} values vs IPs, vs HOMOs, and vs LUMOs reveal multiple nearly parallel lines of correlation with negative slopes in each, indicating that the rate-determining step of this reaction is a nucleophilic process. Although the present results cannot distinguish between anti and syn additions, they do indicate that the rate-determining step is a nucleophilic addition. This result is consistent with the mechanism proposed by Henry in which the rate-determining step is nucleophilic hydroxypalladation. It is inconsistent with the mechanism proposed by Bäckvall and co-workers, in which the hydroxypalladation is a rapid equilibrium and the rate-determining step is loss of chloride from the hydroxypalladation adduct. Comparison of the plots for $PdCl_2$ oxidation versus those for hydroboration and for oxymercuration, combined with consideration of the two mechanisms proposed for $PdCl_2$ oxidation, indicates that the mechanism for $PdCl_2$ oxidation of alkenes at low [Cl$^-$] has similarities to that for hydroboration. The method of analysis reported herein also provides a simple way to predict relative reactivities of functionalized alkenes for synthetic purposes, based on the electronic and steric characteristics of the substituents.

Acknowledgment. We are grateful to Lucent Technologies, McEvoy Financial Corp., and Sunwest Capital Corp. for financial support.

JA002190J

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(16) A reviewer noted that a similar unsymmetrical transition state has been previously proposed for nucleophilic attack upon olefins complexed to other transition metals: (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103,* 4308−4320. (b) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102,* 6148−6149.