Articles

Oxidation of Olefins by Palladium(II). 13.[1] Product Distribution and Kinetics of the Oxidation of 2-Cyclohexenol and 2-Cyclohexenol-*1*-*d* by $PdCl_4^{2-}$ in Aqueous Solution

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The rate expression for the oxidation of 2-cyclohexenol, rate = $k[PdCl_4^{2-}][C_6H_{10}]/[Cl^-]$, is *different* from that previously found for the oxidation of acyclic olefins but the same as that found for the nonoxidative isomerization of allyl alcohol at high chloride concentrations. The product distribution under one set of reaction conditions ($[Li_2PdCl_4]$ = $[Cl^-]$ = $[H^+]$ = 0.1 M) consisted of 19% 2-cyclohexenone (**5**), 45% cyclohexanone (**6**), and 36% 3-hydroxycyclohexanone (**7**). While **5** and **7** were oxidation products, **6** must have arisen from a nonoxidative rearrangement of 2-cyclohexenol. The rate expression is consistent with a mechanism involving equilibrium formation of an olefin π-complex followed by external attack of water in the slow step to give a hydroxypalladation adduct which decomposed to **7**. To obtain further insight into the detailed route, 2-cyclohexenol-*1*-*d* (**4a**) was oxidized. Under the oxidation conditions **4a** was isomerized into its allylic isomer 2-cyclohexenol-*3*-*d* (**4b**), at appreciable rates. The rate expression was found to be rate = $k_i[C_6H_{10}O][H^+]$. When the reaction was run at low acid ($[H^+]$ = 0.05 M) and chloride concentrations ($[Cl^-]$ = 0.05 M), this complication could be avoided. The isomer of **7** that was formed had the deuterium on the alcoholic carbon, so the hydride shift to form **7** had to have occurred from the carbon to which the hydroxyl was added to form the hydroxypalladation adduct. This is consistent only with the original hydroxyl directing the palladium to the same side of the ring as the hydroxyl followed by trans attack of water. Only the hydrogen on the carbon to which the hydroxyl has been added is in position for a cis hydride migration to give **7**. Next, **4a** was equilibrated with aqueous acid to give a 50:50 mixture of **4a** and **4b**. The oxidation of **4b** would only give **7** with hydrogens on the alcoholic carbon, so the **7** formed by the oxidation of **4a** did not interfere with the analysis of the ^1H NMR spectra. This analysis showed that the alcoholic hydrogen and the hydrogen on the carbon between the alcoholic carbon and the carbonyl were in a cis configuration. This result was also only consistent with trans hydroxypalladation of a π-complex with the Pd(II) on the same side as the hydroxyl. The **5** formed contained deuterium, which indicated it arose from dehydration of **7** rather than direct deuteride extraction from the alcoholic carbon.

Introduction

The rate expression for the oxidation of acyclic olefins by aqueous $PdCl_4^{2-}$ to aldehydes and ketones (eq 1) follows the rate expression given by eq 2. It is generally agreed

$$PdCl_4^{2-} + C_nH_{2n} + H_2O \rightarrow Pd(0) + C_nH_{2n}O + 2HCl + 2Cl^- \quad (1)$$

$$\frac{-d[\text{olefin}]}{dt} = \frac{k[PdCl_4^{2-}][\text{olefin}]}{[H^+][Cl^-]^2} \quad (2)$$

that the mechanism involves conversion of an olefin π-bonded to palladium(II) to a palladium(II)-2-hydroxyalkyl species (**1**), a process called hydroxypalladation.[2] The previous three papers in this series have described the products and kinetics of the oxidation of allyl alcohol[3] and 3-buten-2-ol and 2-buten-1-ol.[1] The kinetics obeyed eq 2. The products could be explained by hydroxypalladation to place the Pd(II) either next to the hydroxyl to give **1a** or on the olefinic carbon opposite from the hydroxyl to give **1b** (eq 3). Thus, the oxidation of allyl alcohol gave

$$R_1CH{=}CHCH(OH)R_2 + Pd(II) + H_2O \xrightarrow{-H^+} \underset{\mathbf{1a}}{R_1CH(OH)CH(-Pd^{II})CH(OH)R_2} + \underset{\mathbf{1b}}{R_1CH{-}(Pd^{II})CH(OH)CH(OH)R_2} \quad (3)$$

$HOCH_2CH_2CHO$ (**2**; 40%), $CH_3C(=O)CH_2OH$ (**3**; 12%), acrolein (30%), and propanone (15%). The main product, **2**, resulted from decomposition by hydride shift of an intermediate analogous to **1a** (R_1 = R_2 = H), while **3** was formed in the same fashion from an intermediate analogous to **1b** (R_1 = R_2 = H). The acrolein did not result from a hydroxypalladation intermediate such as **1** but, rather, by direct hydride abstraction from the alcohol carbon, while the propanone must have resulted from reduction of the acrolein by Pd^{II}-H from acrolein production.[3a] When steric factors were equivalent, such as was the case with crotyl alcohol (**1**: R_1 = CH_3; R_2 = H), the hydroxyl strongly directed the mode of addition to give **1a**. The kinetics of oxidation of all three allylic alcohols obeyed eq 2, indicating their mechanism of oxidation is similar to that of other acyclic olefins. One important result of these studies was the demonstration that 3-buten-2-ol and 2-buten-1-ol did not isomerize into an equilibrium mixture of the two allylic isomers under the reaction conditions.

The oxidation of 2-cyclohexenol is of interest for several reasons. First, the kinetics of oxidation of cyclohexene does

(1) Part 12: Zaw, K.; Henry, P. M. *J. Org. Chem.* **1990**, *55*, 1842.
(2) For a general discussion and references, see: Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, Holland, 1980; pp 41-84.
(3) (a) Zaw, K.; Lautens, M.; Henry, P. M. *Organometallics* **1985**, *4*, 1286. (b) Wan, W. K.; Zaw, K.; Henry, P. M. *Organometallics* **1988**, *7*, 1677.

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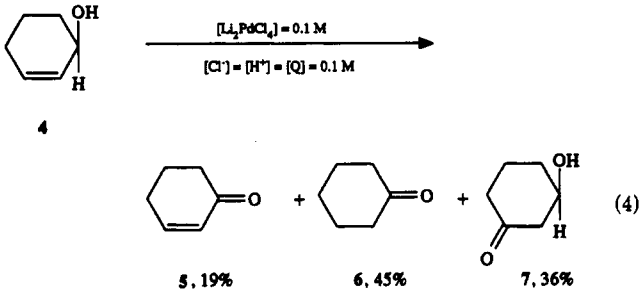
not display a proton inhibition and thus does not obey the rate expression given by eq 2. This implies that its detailed mechanism of oxidation must be different from that of acyclic olefins.[4,5] However, the exact chloride inhibition has not been defined, apparently because of solubility limitations. Since the kinetics of oxidation of allylic alcohols is identical with that for other acyclic olefins, the kinetics of oxidation of 2-cyclohexenol, by analogy, would also not be expected to obey eq 2 and, since solubility would not be a problem, a complete kinetic expression could be defined. Second, the directing influence of the hydroxyl group should be very important with this olefin. Third, since 2-cyclohexenol is a cyclic olefin, the stereochemistry of hydroxypalladation can, in principle, be determined by using specifically deuteriated samples. Finally, cyclohexene structures have been used to infer stereochemistry for acyclic olefins under Wacker conditions.[6] Thus, it is important to know the kinetics and stereochemistry of 2-cyclohexenol oxidation under Wacker conditions.

Results

Yields and Product Distributions. All yields and product distributions were determined at 25 °C. Product distributions were first determined with nonlabeled 2-cyclohexenol. The conditions were $[Li_2PdCl_4] = [Cl^-] = [H^+] = [Q] = 0.1$ M (Q = *p*-benzoquinone). The reaction was allowed to run for 2–4 h. The product distribution was determined by preparing the 2,4-DNP derivatives of the reaction mixture and running the ^1H NMR spectrum of the mixture. Relative yields were measured from integration of the intensities of certain resonances of each of the products. The mixture was then separated into individual components by column chromatography and the individual 2,4-DNP's identified by comparison with authentic samples. The distribution shown in eq 4 is the average of four determinations.



(4)

5, 19% 6, 45% 7, 36%

Oxidation Kinetics. All kinetics runs were carried out at 25 °C in the presence of *p*-benzoquinone (Q), which reoxidized the Pd(0) formed back to Pd(II) while being reduced itself to hydroquinone so that the reaction was catalytic in Pd(II) and the formation of π-allylic palladium(II) species was avoided. The reaction is shown in eq 5. The kinetics were studied using a potentiometric

$$H_2O + C_6H_{10}O + Q \xrightarrow{Li_2PdCl_4} \text{products} + H_2Q \quad (5)$$

procedure based on the quinone–hydroquinone redox couple. Lithium salts were used for the kinetics runs, and the ionic strength was maintained at 2.0 using lithium perchlorate as inert electrolyte.

The data are summarized in Table I. Runs 1–7 test the effect of palladium(II) concentration, while runs 8–13

Table I. Rates of Oxidation of 2-Cyclohexenol[a]

run no.	$[Li_2PdCl_4]$, M	$[H^+]$,[b] M	[Cl],[c] M	10^6k_{obs}, s^{-1}	10^5k,[d] s^{-1}
1	0.025	0.2	0.6	1.3	3.1
2	0.035	0.2	0.6	1.9	3.3
3	0.050	0.2	0.6	2.7	3.2
4	0.060	0.2	0.6	3.0	3.0
5	0.080	0.2	0.6	3.7	2.8
6	0.100	0.2	0.6	5.2	3.1
7	0.125	0.2	0.6	6.6	3.2
8	0.050	0.2	1.2	1.6	3.8
9	0.050	0.2	0.90	1.9	3.4
10	0.050	0.2	0.5	3.4	3.4
11	0.050	0.2	0.33	5.0	3.3
12	0.050	0.2	0.25	6.5	3.2
13	0.050	0.2	0.2	7.7	3.1
14	0.050	0.4	0.2	7.7	3.1
15	0.050	0.6	0.2	7.6	3.0
16	0.050	0.8	0.2	8.0	3.2
17	0.050	1.0	0.2	8.0	3.2

[a] All runs in aqueous solution at 25 °C. $LiClO_4$ was added to bring the ionic strength to 2.0. Initial allyl alcohol and quinone concentrations are 0.005 M. Data are treated as a first-order reaction in allyl alcohol. [b] Added as $HClO_4$. [c] Added as LiCl. [d] Calculated by assuming the rate expression given by eq 6 is operative.

Table II. Variation of k_{obs} with Temperature[a]

T, °C	10^3K^{-1}	10^5k_{obs}, s^{-1}	T, °C	10^3K^{-1}	10^5k_{obs}, s^{-1}
13.5	3.49	1.9	25.0	3.35	7.7
18.5	3.43	3.3	30.0	3.30	12.2

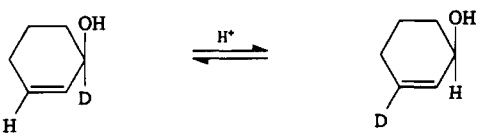
[a] Conditions: $[Li_2PdCl_4] = 0.05$ M; $[H^+] = 0.2$ M; $[Cl^-] = 0.2$ M.

determine the order in $[Cl^-]$ and runs 10 and 14–17 determine the order in $[H^+]$. The fact that the values of k calculated by assuming a rate expression of the form of eq 6 remain relatively constant indicate this rate expression

$$\frac{-d[C_6H_{10}O]}{dt} = \frac{k[PdCl_4^{2-}][C_6H_{10}O]}{[Cl^-]} \quad (6)$$

is indeed the correct one with a value of $k = 3.1 \times 10^{-5}$ s^{-1}. The rate under one set of reaction conditions was measured at four different temperatures. Data are given in Table II. A plot of ln k_{obs} vs $1/T$ yielded a straight line, giving the values of enthalpy and entropy of activation of 19.9 kcal/mol and −15.0 eu.

Deuterium Labeling Studies—Isomerization of 2-Cyclohexenol-*1*-*d*. It was found that when an aqueous acid solution of 2-cyclohexene-*1*-*d* (**4a**) is allowed to sit at 25 °C, it isomerizes into its allylic isomer **4b** (eq 7). The



(7)

4a 4b

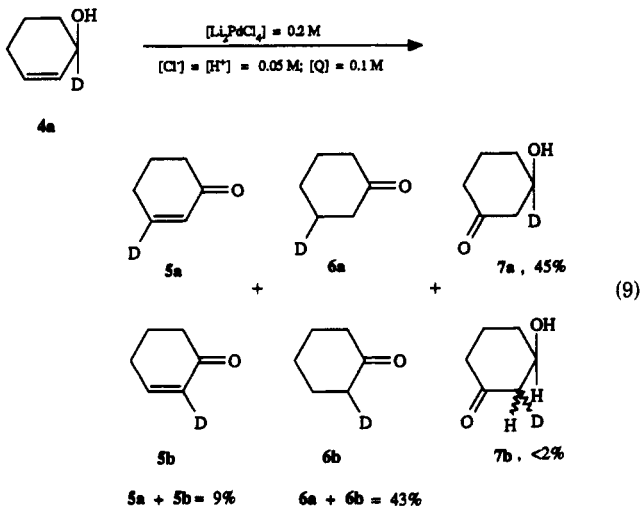
kinetics were studied at 25 °C under various reaction conditions. Data are given in Table III. Runs 18–23 test the effect of acid, while runs 18, 24, and 25 test the effect of $[Cl^-]$ and runs 18 and 26–28 test the effect of [Pd(II)]. The rate depends only on $[H^+]$, so the reaction is not Pd(II)-catalyzed. A plot of k_{obs} vs $[H^+]$ for runs 18–23 is linear with an intercept of zero. Thus, the rate expression for allylic isomerization is given by eq 8, where $k_i = 7.5 \times 10^{-4}$.

$$\text{rate of isomerization} = k_i[C_6H_{10}O][H^+] \quad (8)$$

Deuterium Labeling Studies—Product Distributions. The reactions were run with **4a** or a mixture of **4a** and **4b**, the products isolated as their 2,4-DNP (2,4-di-

(4) Vargaftik, M. N.; Moiseev, I. I.; Syrkin, Y. K. *Dokl. Akad. Nauk SSSR* **1961**, *139*, 3196.
(5) Bratz, E.; Prauser, G.; Dialer, K. *Chem.-Ing.-Tech.* **1974**, *46*, 161.
(6) Åkermark, B.; Söderberg, B. C.; Hall, S. S. *Organometallics* **1987**, *6*, 2608.

nitrophenylhydrazone) derivatives, and the mixtures analyzed by a combination of ^1H and ^2H NMR spectra. Every possible product could be detected by this procedure. First, the olefin was oxidized at low $[H^+]$ and short reaction times to prevent isomerization. The concentrations of reactants were $[Li_2PdCl_4]$ = 0.2 M, $[H^+] = [Cl^-]$ = 0.05 M, and [Q] = 0.1 M. The product distribution is shown in eq 9. It was found that the proportion of **6a** plus **6b** increased steadily as the acid concentration increased. At $[H^+]$ = 0.4 M, **6a,b** were 70% of the total product. Next, **4a** was equilibrated with acid to give a 50:50 mixture of **4a** and **4b**. This mixture was oxidized using the same concentrations of reactants as in the first run. The product distribution is given in eq 10.



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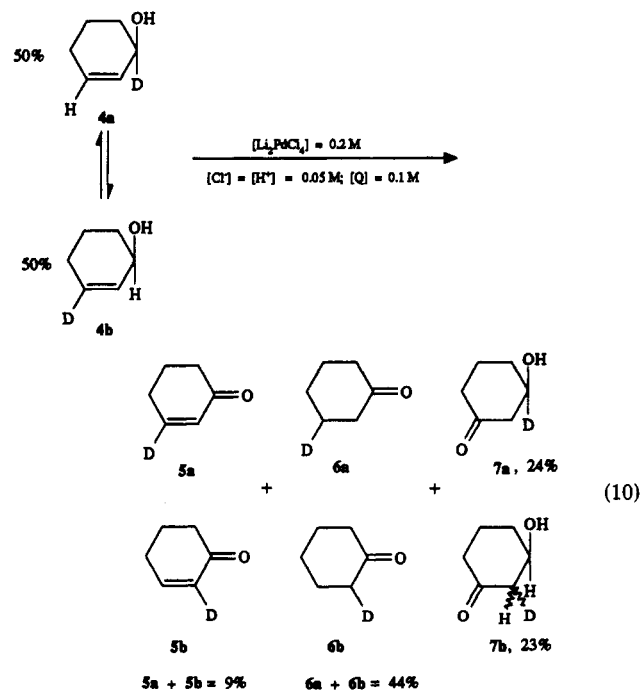

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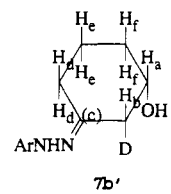
Deuterium Labeling Studies—Structure of 7b. It was now necessary to determine if **7b** had the protons in a cis (**7b′**) or a trans (**7b″**) arrangement. A combination of homonuclear selective decoupling, COSY, ^1H–^{13}C heteronuclear correlation (HETCOR), and NOESY spectra on the undeuteriated 3-hydroxycyclohexanone (**7**) gave the ^1H and ^{13}C assignments shown below using **7b′** as substrate. The resonance at 4.1 ppm was a multiplet because of the splitting by the adjacent protons. In the deuteriated sample this resonance was also a broad multiplet. Irradiation at 2.0 ppm gave a broad triplet (expected doublet of doublets). Irradiation at 1.8 ppm gave a broad doublet at 2.0 ppm (J = 3–4 Hz), which is clearly in the range of a cis coupling constant in the cyclohexane system.[7] The structure of **7b** must thus be **7b′**, which is the structure shown (Ar = 2,4-$C_6H_3(NO_2)_2$).

Table III. Rates of Isomerization of 2-Cyclohexenol-*1*-*d*[a]

run no.	$[Li_2PdCl_4]$, M	$[H^+]$,[b] M	$[Cl^-]$,[c] M	10^3k_{obs}, s^{-1}	10^4k,[d] M s^{-1}
18	0.050	0.2	0.2	1.5	7.5
19	0.050	0.4	0.2	3.6	9.0
20	0.050	0.6	0.2	4.4	7.3
21	0.050	0.8	0.2	6.8	8.5
22	0.050	1.0	0.2	8.0	8.0
23	0.050	1.6	0.2	11.5	7.2
24	0.050	0.3	0.6	2.6	7.8
25	0.050	0.3	1.4	2.7	8.1
26	0.00	0.3	0.2	2.7	8.1
27	0.0050	0.3	0.2	2.8	8.4
28	0.0010	0.3	0.2	2.6	7.8

[a] All runs in aqueous solution at 25 °C. $LiClO_4$ was added to bring the ionic strength to 2.0. Initial allyl alcohol and quinone concentrations are 0.005 M. Data are treated as a first-order reaction in allyl alcohol. [b] Added as $HClO_4$. [c] Added as LiCl. [d] Calculated by assuming the rate expression given by eq 8 is operative.



7b′

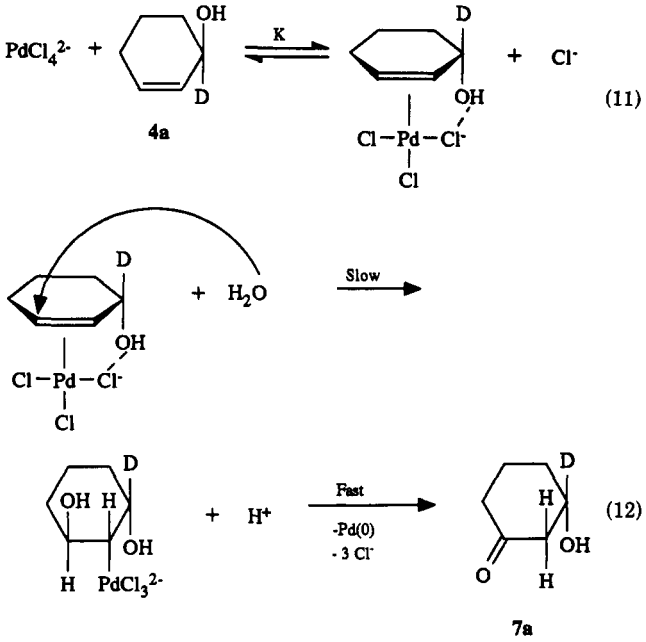
^1H, ppm		^{13}C, ppm	
H_a	4.1	C_a	67.7
H_b	2.0	C_b	34.0
		C_c	160
H_d	2.8	C_d	31.4
H_e	2.4	C_e	23.0
H_f	1.8	C_f	33.0

Discussion

The kinetic expression for oxidation of 2-cyclohexenol (**4**) is identical with that previously found for the isomerization of allyl alcohol-*1,1*-d_2 in aqueous solution at high $[Cl^-]$. It was proposed that the single chloride inhibition and absence of an acid inhibition was consistent only with external attack of water on an olefin–Pd(II) π-complex. This resulted in the trans stereochemistry for hydroxypalladation observed by other workers under the same conditions of high $[Cl^-]$. The same situation exists with 2-cyclohexenol. The single chloride inhibition only allows for formation of a π-complex; it does not permit water also in the coordination sphere for internal attack. Also, the lack of an acid inhibition indicates water has to be the attacking species. The proposed reaction pathway for **4a** is given in eqs 11 and 12. In the formation of the π-complex in eq 11, Pd(II) is held on the same side as the hydroxyl group by bonding between the hydroxyl hydrogen and chlorine bonded to Pd(II). Note that in this scheme the addition is the slow step, for if hydroxypalladation were an equilibrium process, there would be a proton inhibition in the rate expression.

Further support for this mechanism comes from the deuterium distribution studies and also gives information as to the directing influence of the hydroxyl group. The possible reaction pathways for the unequilibrated **4a** are

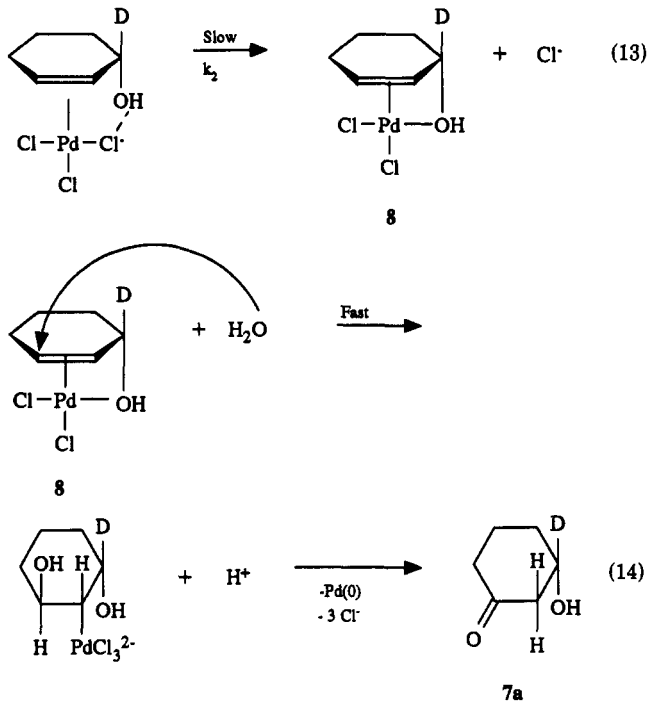
(7) Booth, H. *Progr. Nucl. Magn. Reson. Spectrosc.* **1969**, *5*, 149.



shown in Scheme I. Cis addition to put the Pd(II) on the opposite side from the hydroxyl gives only **7b**. Addition to the opposite side gives no reaction. Trans addition to put the Pd(II) opposite the hydroxyl gives a hydroxypalladation that decomposes to a mixture of **7a** and **7b**. Although deuterium isotope effects would favor **7a**, these isotope effects are not large ($k_H/k_D \approx 2$ in analogous systems[1,3a]), so about a third of the mixture would be **7b**. Only trans addition of the Pd(II) and water with the Pd(II) directed to the same side as the original hydroxyl (bottom pathway) will explain the formation of only **7a**. Thus, the results strongly support the addition shown in eq 12 as occurring exclusively and give quantitative information on the directing influence of the hydroxyl group toward Pd(II).

Even more evidence for the proposed trans addition sequence comes from the oxidation of the 50:50 mixture of **4a** and **4b**. Since oxidation of **4a** gave only **7a**, **7b** resulting from the oxidation of the mixture must arise from the oxidation of **4b**. Scheme II shows the possible reaction sequences with **4b**, which are analogous to those shown in Scheme I for **4a**. In this case **7b** would be formed by trans addition with the Pd(II) on the opposite side from the hydroxyl or on the same side as the hydroxyl. In the former case the trans isomer (**7b″**) is formed, while in the latter case the cis (**7b′**) isomer is formed. A distinction can be made on the basis of coupling constants. For the cis structure $J \approx 3$–5 Hz, while for the trans structure $J \approx$ 7–12 Hz. The actual J was 3–4 Hz, indicating **7b′** was the structure of the oxidation product from **4b**. This result supports the conclusion of trans addition made previously from the fact that **7a** was the only product from the oxidation of **4a**.

A basic question which must be addressed is whether it is something inherent in the cyclohexene system which is causing the difference in kinetics and thus in mechanism as compared to the acyclic system or whether the hydroxyl is causing a minor variation in mechanism and thus in rate expression. Thus, another pathway consistent with the rate expression is rate-determining loss of chloride to form a coordinated hydroxyl species, **8**, which decomposes to products in the fast step.[8] The scheme is shown in eqs 13 and 14. This reaction scheme can be discussed in terms



of its inherent likelihood as well as the basic differences between cyclohexene and acyclic olefins. With regard to feasibility considerations the replacement of chloride on a labile species such as Pd(II) would be a very rapid process. Rates of replacement of chloride from $PdCl_3(H_2O)^-$ are on the order of 10 s^{-1} and would probably be higher for **8** because of the trans effect of the olefin.[10] Using the value of 10 s^{-1} for k_2, the maximum value of K in eq 13 which will give the experimental rate constant can be calculated. According to the reaction scheme in eqs 11–13, the overall rate of reaction is equal to $k_2[8]$, where $[8] = K[PdCl_4^{2-}][C_6H_{10}O]/[Cl^-]$. Thus, the overall rate of reaction is given by eq 15. Equating eq 15 to eq 6 gives the

$$\frac{-d[C_6H_{10}O]}{dt} = \frac{k_2K[PdCl_4^{2-}][C_6H_{10}O]}{[Cl^-]} \qquad (15)$$

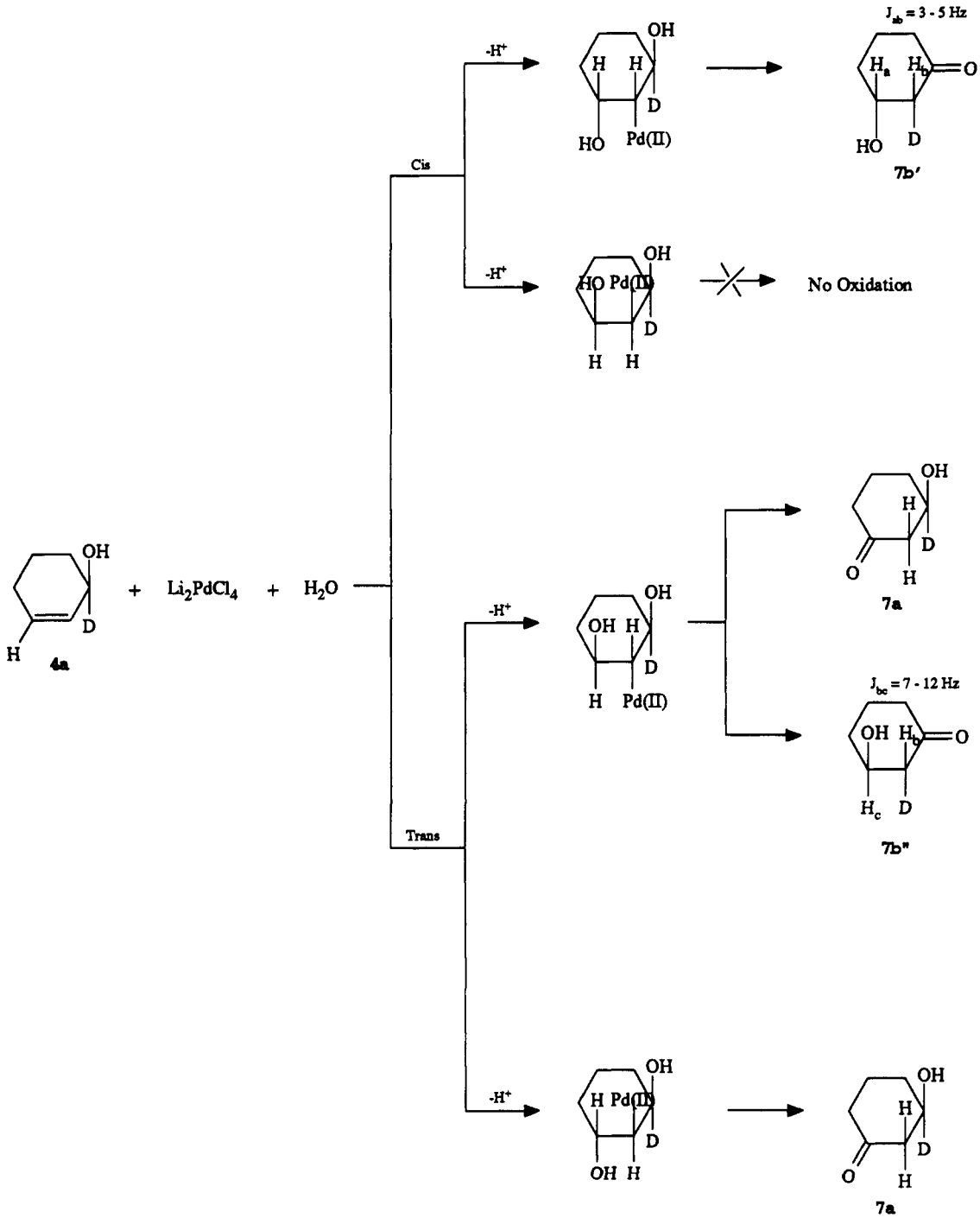
expression $k = k_2K$ or $K = k/k_2$, where $k = 3 \times 10^{-5}$ s^{-1} and $k_2 = 10$ s^{-1}. These values require that K in eq 11 have a value no higher than 3×10^{-6}. This value is at least 5 orders of magnitude less than would be expected on the basis of other π-complex formation constants in aqueous solution. Although the equilibrium for cyclohexene itself has not been measured, the value for *cis*-2-butene, for instance, is 8.7.[1] Stable cyclohexene π-complexes of Pt(II) were prepared a number of years ago,[11] and NMR evidence for π-complexes between Pd(II) and 1,2-dimethyl-1,4-cyclohexadiene, which coordinates as a monoolefin, indicates that cyclohexene does form π-complexes readily.[6] Although electron-withdrawing groups decrease K, the effects are not large. Thus, allyl alcohol has a value of K about one-third of that for propene.[1]

With regard to inherent differences between the cyclic and acyclic systems, as mentioned in the Introduction, cyclohexene itself does not follow the oxidation kinetics of acyclic olefins given by eq 2, so the allylic hydroxyl

(8) This route was suggested by a reviewer. A similar rate-determining loss of chloride has previously been postulated to explain the isotope effects in the ethene oxidation.[9]

(9) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.
(10) Bekker, P. v. Z.; Robb, W. *J. Inorg. Nucl. Chem.* **1975**, *37*, 829.
(11) (a) Kharasch, M. S.; Ashford, T. A. *J. Am. Chem. Soc.* **1936**, *58*, 1733. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

Scheme I

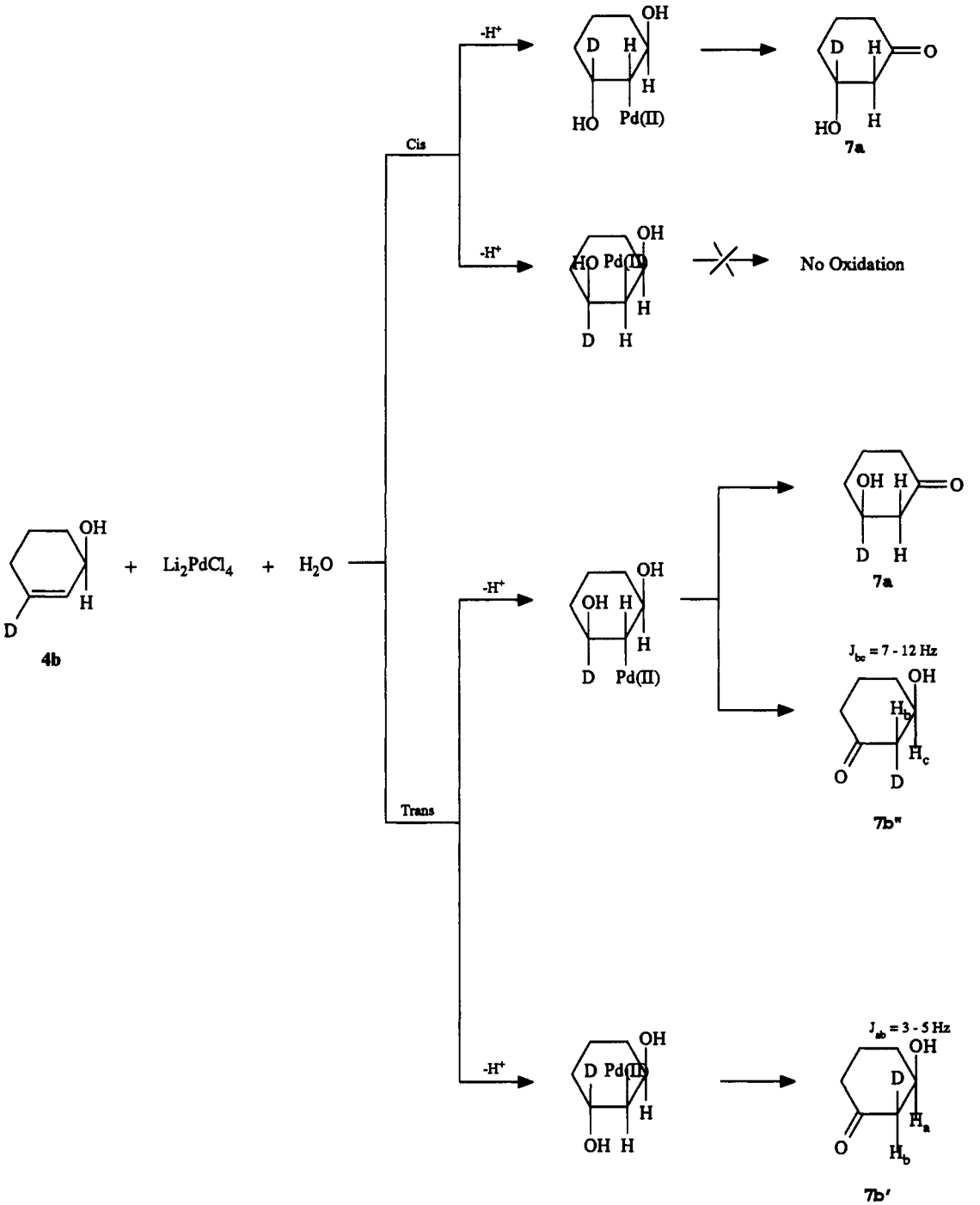


cannot be the only reason the cyclohexene system behaves differently from the acyclic one. Also, as mentioned in the Introduction, acyclic allyl alcohols and other acyclic olefins obey the oxidation rate expression given by eq 2, indicating the acyclic allylic alcohols are not oxidized by the reaction pathway given by eqs 13 and 14 but rather by the same mechanism as other acyclic olefins. Finally, a recent kinetic and stereochemical study of the exchange of a tetrasubstituted allylic alcohol, which cannot undergo oxidation, indicated hydroxypalladation was also directed by the hydroxyl group. The kinetics of exchange obeyed eq 2, and the stereochemical results were consistent with cis hydroxypalladation. Thus, the preponderance of evidence indicates that the cyclohexene system is oxidized by the rate expression given by eq 6 because it undergoes trans hydroxypalladation, while acyclic olefins are oxidized by the rate expression given by eq 2 because they undergo cis hydroxypalladation.

The reason cyclohexene behaves differently from acyclic olefins is, of course, related to the conformational energies of the cyclic system. In at least one other Pd(II)-catalyzed reaction, allylic exchange, the cyclohexene system behaved differently from acyclic olefins.[12] The present results underline the care that must be taken in extrapolating from one system to another. As mentioned in the Introduction, cyclohexene type systems have been used to infer the stereochemistry of hydroxypalladation under Wacker conditions for acyclic olefins.[6] The present results clearly indicate this is not a valid comparison. Also, chelating

(12) Ng, F. T. T.; Henry, P. M. *J. Org. Chem.* **1973**, *38*, 3338.

Scheme II



cyclic diolefins have been used as models for Wacker chemistry.[13] This is also not a valid comparison in light of the present results.

A comparison of the product distributions obtained from 2-cyclohexenol with those obtained from acyclic olefins gives some further insights into the effects of structure on product distribution in Pd(II) catalysis. With acrolein, deuterium labeling studies showed its mechanism of formation involved direct hydride extraction for the alcohol carbon rather than dehydration of the initial β-hydroxylpropanal (2) product. Since the yield of acrolein was appreciable and the overall kinetics of oxidation obeyed eq 2 very closely, it was assumed that acrolein formation also obeyed eq 2. In the case of 2-cyclohexenol, in the first run the unsaturated ketones **5a** and **5b** constitute about 20% of the oxidation product and could affect the overall kinetics if they are also formed by the rate expression given by eq 2. However, they could not have been formed by direct hydride extraction since, in the case of **4a**, that would have resulted in deuteride extraction and the product **5** from **4a** would contain no deuterium. The only explanation for this result is that **5** arises from dehydration of **7** and thus its formation would not affect the kinetics. Further evidence is the fact that the yield of **7** increased and that of **5** decreased at shorter reaction times (eqs 4 and 9). The equilibrium ratio of **5**/**7** is reported to be 2.4 at 25 °C, and the rate of dehydration of **7** depends on acid concentration.[14] At $[H^+]$ = 0.05 M the half-life for deh-

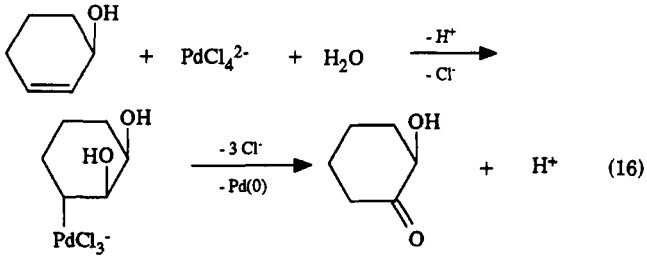
(13) Stille, J. K.; James, D. E. *J. Organomet. Chem.* **1976**, *108*, 401.

(14) Stiles, M.; Longroy, A. *Tetrahedron Lett.* **1961**, 337.

ydration is 72 h. This seems too large to explain the amount of **5a** formed, but the rate constants are approximate and the Pd(II) may also catalyze the dehydration. The presence of small amounts of **5b** is less readily explained. It would be formed by the dehydration of **7b** formed by oxidation of **4b**. However, in the first run **4b** was not supposed to be present to any extent and no **7b** was detected in the reaction mixture. Since **5b** was present to the extent of only 2%, its determination has a high degree of error and so explanations for its presence cannot be taken too seriously.

In the allyl alcohol oxidation some propanal was detected. This was postulated to arise from the addition of Pd^{II}–H, which arose from the oxidation of allyl alcohol to acrolein, across the double bond of acrolein followed by attack of a second Pd^{II}–H to complete the reduction. This is a valid proposal only if the amount of propanal is half or less of the total of acrolein plus propanal. In the case of allyl alcohol oxidation this was true, since yields of acrolein and propanal were 30% and 15%, respectively. With the oxidation of 2-cyclohexenol this is not the case, since the saturated ketone product is formed in higher amounts than the unsaturated ketone. Also, as mentioned above, deuterium labeling indicates Pd–H extraction from the 2-cyclohexenol alcoholic carbon cannot be the mechanism for 2-cyclohexenone formation, so Pd–H would not be present. The reaction is, no doubt, a Pd(II)-catalyzed isomerization of the allylic alcohol to the saturated ketone. It is well-known that the isomerization of allylic alcohols to the corresponding aldehydes and ketones is catalyzed by a variety of transition-metal species[15] and there is at least one example with a Pd(II) catalyst.[16] The 1,3-hydrogen transfer has been shown to be stereospecific with a $RuCl_3$ catalyst,[15] and a mechanistic study on this system has indicated that the reaction proceeds via an oxo–π-hydro–ruthenium complex.[17] Such a 1,3-hydrogen shift would predict **6a** as the major saturated ketone product and, although the analysis did not permit a quantitative determination, **6a** was present in much larger amounts than **6b**. Also, some oxotropic rearrangement was found to occur in the $RuCl_3$ system, which could explain the formation of **6b**. The fact that acid increased the yield of **6a** plus **6b** suggests acid may be taking part in the catalysis to give these saturated products.

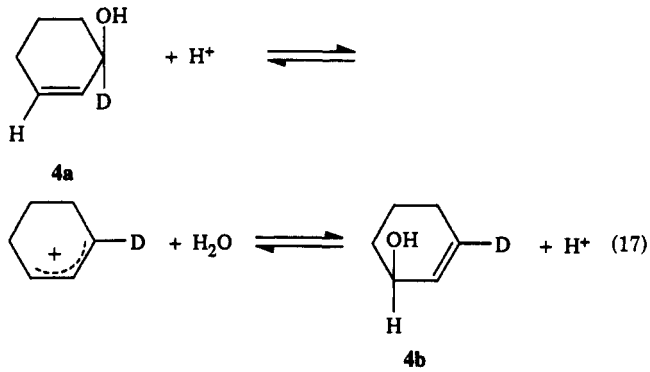
Allyl alcohol gave a 12–15% yield of hydroxyacetone arising from the intermediate **1b**. In the cyclohexene system this would be equivalent to the addition shown in eq 16 followed by decomposition to give 2-hydroxycyclohexanone (**9**). Since no **9** was observed, this type of addition must not have occurred. Actually this is not surprising, since in the crotyl system only about 2% of the product arises from hydroxypalladation, which puts the Pd(II) at the carbon removed from the hydroxyl.[1] This is another indication of the directing ability of the hydroxyl group.



(16)

9

With allyl alcohol the isomerization of one deuteriated allylic isomer into the other was too slow to be detected, and with the crotyl and 3-buten-2-ol systems isomerization was much slower than oxidation. As might be expected, however, with the cyclohexene system isomerization was a serious side reaction and short reaction times had to be employed to avoid complications from it. The isomerization must proceed through the allylic carbonium ion mechanism shown in eq 17.



(17)

The directing influence of the hydroxyl group is certainly not surprising. There is an early report that the known trans hydroxymercuration of 2-cyclohexenol followed by removal of mercury with sodium borohydride gave mainly trans 1,3-diol.[18] The directing influence of the hydroxyl group has been demonstrated for several epoxidation reactions[19,20] and has been shown to exist for several other reactions.[21] In one study on the Simmons–Smith reaction with cis allylic alcohols over 99% stereoselectivity was found.[22] Partial 1,2-chirality transfer was shown for the Pd(II)-catalyzed addition of a phenyl group (Heck reaction) to chiral 3-methylbut-3-en-2-ol.[23] Recently, crystal structure data for analogous, but more stable, Pt(II) π-complexes of allylic alcohols with amino acid ligands indicated possible hydrogen bonding between the OH and the nitrogen or oxygen of the amino acid ligands.[24] On the other hand, crystal structure data for $[PtCl_2(PMe_2Ph)(CH_2{=}CHCH_2OH)]$ indicated that an intramolecuar O–H···Cl hydrogen bond is not present in the crystal.[25]

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(21) For recent diastereofacial selection occurring with olefinic alcohols, see: (a) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 1072. (b) Thompson, H. W.; Shah, N. V. *J. Org. Chem.* **1983**, *48*, 1325. (c) Brown, J. M.; Naik, R. G. *J. Chem. Soc., Chem. Commun.* **1982**, 348 (for hydroboration). (d) Smadja, W.; Ville, G.; Georgoulis, C. *J. Chem. Soc., Chem. Commun.* **1980**, 584 (for isomerization). (e) Stork, G.; Kahn, M. *Tetrahedron Lett.* **1983**, 3951. (f) Sha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron Lett.* **1983**, 3943, 3947 (for oxidation). (g) Czernecki, S.; Georgoulis, C.; Provelenghiou, C. *Tetrahedron Lett.* **1975**, 2623; **1979**, 4841 (for alkoxy- and azidomercuration).
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Table IV. ^2H NMR Data for the (2,4-Dinitrophenyl)hydrazone Derivatives of the Carbonyl Products[a]

product	chem shift, ppm	product	chem shift, ppm
5a	6.4	**6b**	2.4
5b	6.6	**7a**	4.1
6a	1.7	**7b**	2.0

[a] In $CHCl_3$. Chemical shifts were measured with respect to $CDCl_3$ at 46 MHz on a VXR-300 NMR spectrometer.

The activation parameters of the present work can be compared with those previously measured for the ethene oxidation, which were $\Delta H^* = 19.8$ kcal and $\Delta S^* = -8.7$ eu.[26] However, for ethene these activation parameters were for k in eq 12 since the value of K in eq 11 was measured for ethene. In the present case the activation parameters are for kK. Although the two sets of activation parameters are in the same range, no great significance can be placed on this fact since the mechanisms are different.

In conclusion the most significant result of this study is the demonstration that 2-cyclohexenol is oxidized by Pd(II) by a different rate expression and thereby a different mechanism than acyclic olefins. Deuterium labeling experiments demonstrated that this mechanism involved trans attack of water on a Pd(II) π-complex in which the Pd(II) is directed to the same side of the cyclohexene ring as the hydroxyl. This is the first quantitative demonstration of the directing influence of the hydroxyl group in Pd(II) chemistry.

Experimental Section

Materials. Palladous chloride was purchased from Engelhardt, Inc. The 2-cyclohexenol was prepared by the reduction of 2-cyclohexenone (Aldrich) with $CeCl_3/NaBH_4$ or $CeCl_3/LiAlH_4$ by following a literature procedure.[27] 2-Cyclohexenol-*1-d* (**4a**) was prepared in the same fashion using $LiAlD_4$ as reducing agent. ^1H NMR spectroscopy indicated its isotopic purity was 99.5%. The 50:50 mixture of **4a** and 2-cyclohexenol-*3-d* (**4b**) was prepared by equilibrating **4a** in 0.4 M aqueous acid overnight followed by neutralization with Na_2CO_3. The ratio of the two isomers in the aqueous solution was determined as described below for the isomerization kinetics. 3-Hydroxycyclohexanone was prepared by the acid-catalyzed hydration of cyclohexanone.[14] All other chemicals were of reagent grade.

Physical Measurements. All ^1H and ^2H NMR spectra were recorded on a Varian VXR-300 NMR spectrometer.

Kinetics Studies. The oxidation reactions were run in the presence of *p*-benzoquinone (Q), which oxidized the Pd(0) formed in the oxidation back to Pd(II). The benzoquinone is reduced to hydroquinone (QH_2) in the process. The extent of reaction was determined by measuring the emf of the cell: Pt/Q, QH_2, Pd(II), HCl, $LiClO_4$, olefin/Pd(II), HCl, $LiClO_4$, Q, QH_2/Pt. The apparatus and procedure have been described.[1] Since the concentrations of all reagents but 2-cyclohexenol remained constant during a run, the data were treated as a reaction first order in the allylic alcohol. Linear plots were obtained for all runs.

All the isomerization kinetic runs contained 0.1 M Q to prevent the formation of π-allyl complexes. At various times aliquots of the reaction mixture were extracted with ether, the ether was dried with anhydrous $MgSO_4$, and 0.1 mL of phenyl isocyanate was added. After the mixture stood overnight, the ether was evaporated. The residue was chromatographed over silica gel using methylene chloride as eluant. The isomerization was followed by ^2H NMR spectroscopy by measuring the decrease in intensity of the peak at 5.3 ppm due to **4a** and the increase in the intensity of the peak at 6.0 ppm due to **4b**. The data were treated as a reaction approaching equilibrium. For all runs, straight lines were obtained from which values of k_{obs} for isomerization could be calculated.

Product Identification and Analysis. After the oxidation reaction was completed, the reaction mixture was treated with zinc to precipitate Pd(0) and filtered. The mixture was then treated with a freshly prepared solution of (2,4-dinitrophenyl)-hydrazine. A portion of the precipitate was dissolved in $CDCl_3$ for proton NMR analysis. The remaining portion was chromatographed on neutral alumina eluted first with benzene and then with a benzene–ethyl acetate mixture to separate each pure component, which was identified by comparison with authentic samples. Each product had a resonance different from those of the other products, which allowed for quantitative analysis in the mixture. In the case of the products from 2-cyclohexenol-*1-d* the identification and quantitative analysis of the various products were complicated by the fact that the resonances in the ^2H NMR spectrum of the entire reaction mixture overlapped. The ^2H resonances in Table IV give the chemical shifts for each of the deuteriated products. In the unseparated reaction mixture the ratios **5a**:**5b**, **7a**:**6a**, and **6b**:**7b** could be determined by the ratio of the integrations of the 6.4–6.6, 4.1, and 1.7–2.4 ppm regions of the spectrum. Next the reaction mixture was chromatographed as described above. The fraction containing **7a** and **7b** was then analyzed by ^1H NMR spectroscopy. The integral at 4.1 ppm was compared with the integral at 2.8 ppm, which is completely separated from the other ring protons, to obtain the fraction of **7b** in the total **7** fraction. The integration in the 1.7–2.4 ppm region of the ^2H NMR spectrum of the total reaction mixture was then corrected for the amount of **7b** present to give the actual amount of **6a** plus **6b** present.

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Registry No. **4**, 822-67-3; **4a**, 55282-88-7; **4b**, 73741-72-7; **5a** (hydrazone deriv.), 140225-59-8; **5b** (hydrazone deriv.), 140225-60-1; **6a** (hydrazone deriv.), 140225-61-2; **6b** (hydrazone deriv.), 140225-62-3; **7a** (hydrazone deriv.), 140225-63-4; **7b′** (hydrazone deriv.), 140225-64-5; Li_2PdCl_4, 15525-45-8.

OM9105785

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