Acknowledgment. We thank the Spanish DGICYT (PB 88-0467) for financial support.

Registry No. **1a**, 38173-71-6; **1b**, 56811-95-1; **1c**, 70749-13-2; **2a**, 136182-90-6; **2b**, 141753-30-2; **2c**, 141753-31-3; **3a**, 136182-94-0; **3b**, 141753-35-7; **3c**, 136182-93-9; **3d**, 136182-91-7; **3e**, 136182-92-8; **3f**, 141753-33-5; **3g**, 141753-36-8; **3h**, 141753-34-6; **3i**, 141753-37-9; **4**, 136182-95-1; $[Mn_2(bpy)_2(CO)_6]$, 128927-36-6; *fac*-$[Mn(bpy)(CO)_3(THF)]^-$, 141753-32-4; CN-^{t}Bu, 7188-38-7; CN-2,6-Xyl, 2769-71-3; $P(OMe)_3$, 121-45-9; PEt_3, 554-70-1; *fac*-$[Mn(bpy)(CO)_3H]$, 141753-38-0.

Supplementary Material Available: Tables of structural data, positional and thermal parameters, bond lengths and bond angles, anisotropic temperature factors, hydrogen atom parameters, torsion angles, and least-squares planes (9 pages). Ordering information is given on any current masthead page.

OM910657G

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. 15.[1] Kinetics and Stereochemistry of the Isomerization of 2-(Methyl-d_3)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol in Aqueous Solution Catalyzed by $PdCl_4^{2-}$ at High Chloride Concentrations

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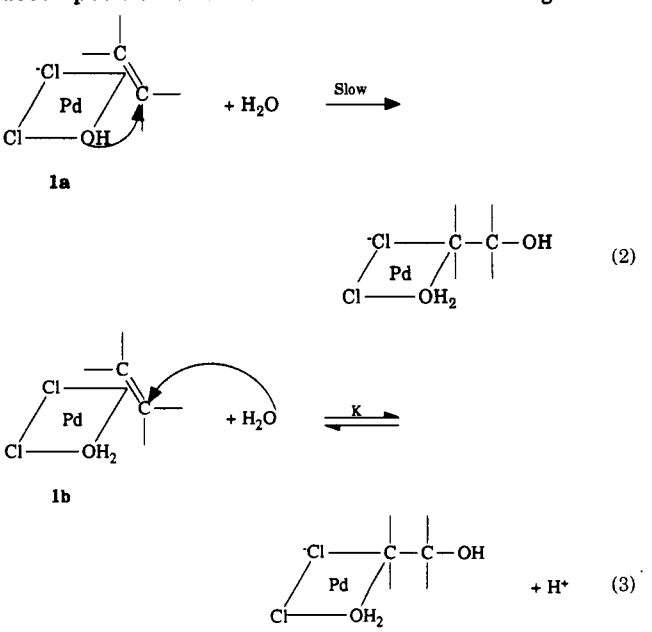
The isomerization of 2-(methyl-d_3)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol (**2a**) into an equilibrium mixture of **2a** and 2-methyl-4-(methyl-d_3)-1,1,1,5,5,5-hexafluoro-3-penten-2-ol (**2b**) in aqueous solution was studied by ^1H and ^2H NMR spectroscopy under conditions of high chloride (>2.0 M) concentration used previously in the presence of $CuCl_2$ to determine the stereochemistry of hydroxypalladation. The rate expression under these conditions is rate = $k_i[PdCl_4^{2-}][\mathbf{2a}]/[Cl^-]$, with $k_i = 1.1 \times 10^{-3}$ s^{-1}. This rate expression at high chloride concentrations is identical to the rate expression found for the nonoxidative isomerization of allyl alcohol under the same reaction conditions and is consistent with an equilibrium π-complex formation followed by trans attack of water to give the oxypalladation intermediate, which reverses the process to give exchange. The fact that the attack is from outside the coordination sphere of the palladium(II) explains the single-chloride inhibition. Stereochemical studies were conducted with chiral (*E*)-**2a**. The observed result was the formation of chiral **2b** with the same configuration as the initial **2a** but with the *Z* geometric configuration. This result is also consistent only with trans hydroxypalladation; thus, both the kinetic and stereochemical studies give the same result. This result also agrees with earlier stereochemical studies at high chloride concentrations which used quite a different technique. The important point is that since the exchange stereochemical studies carried out in the previous paper of this series showed the hydroxypalladation to have stereochemistry opposite from that at high chloride concentrations, the previous stereochemical studies at high $[Cl^-]$ are *not* a valid indication of the stereochemistry at low $[Cl^-]$.

Introduction

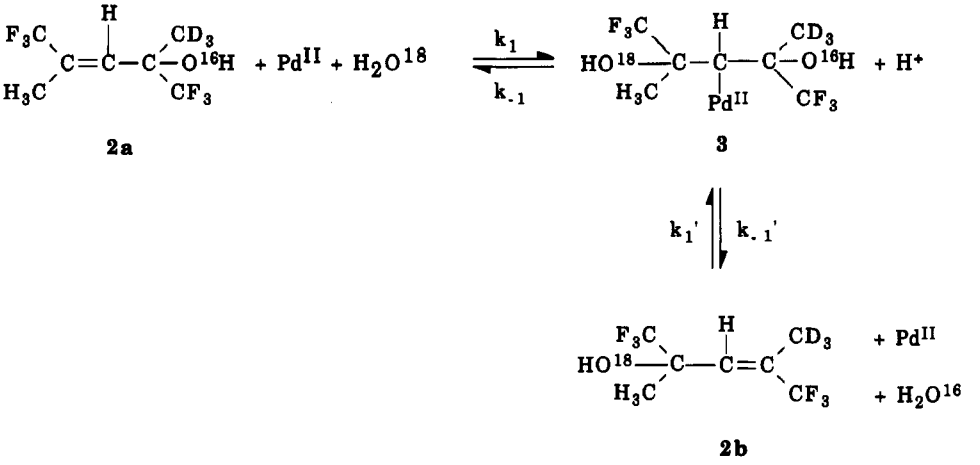
The fact that most catalytic reactions involve several steps makes the interpretation of kinetic data in terms of mechanisms ambiguous in such complicated systems. For instance, in the Wacker process for the oxidation of olefins to aldehydes and ketones in aqueous solution by $PdCl_4^{2-}$, the kinetic rate expression, given by eq 1, can be interpreted in several ways. Although most workers agree the $[Cl^-]^2$ inhibition results from displacement of two chlorides by olefin and water in the Pd(II) coordination sphere in rapid preequilibria, there is considerable disagreement as to the source of the proton inhibition. The kinetics are consistent with (a) cis addition by coordinated hydroxyl in the slow step (eq 2) or (b) trans attack by external water in an equilibrium step (eq 3).[2] In the second mechanism, decomposition of the adduct is rate-determining.

$$\text{rate} = \frac{k[PdCl_4^{2-}][\text{olefin}]}{[H^+][Cl^-]^2} \quad (1)$$



(1) Part 14: Francis, J. W.; Henry, P. M. *Organometallics* **1991**, *10*, 3498.

Scheme I



2a **3** **2b**

The arguments in favor of the cis route are kinetic in nature, involving isotope effects[3,4] and demonstration of the rate-determining step.[5] The arguments favoring trans addition are all stereochemical in nature.[6-8] However, since the usual carbonyl products do not give stereochemical information, the reaction conditions must be changed drastically to obtain the type of products which have chiral centers. There is a strong possibility that such changes in conditions may alter the mode of hydroxypalladation. For example, in the study closest to the conditions of the Wacker reaction, (*E*)- and (*Z*)-ethene-d_2 was oxidized in the $CuCl_2$-promoted reaction to give 2-chloroethanol-d_2. The configurations of the chloroethanols obtained from the two deuteriated ethenes were consistent only with trans hydroxypalladation. However, in order to form 2-chloroethanols, it was necessary to use high chloride concentrations (>3 M), which are much higher than are employed in Wacker chemistry. It is possible the mode of addition is changed at these high chloride concentrations. In fact there is evidence the reactions are different at high and low chloride concentrations. Allyl-*1,1*-d_2 and allyl-*3,3*-d_2 alcohols, which are oxidized to Wacker products by the rate expression given by eq 1 at low [Cl^-], undergo a nonoxidative isomerization and solvent exchange at high [Cl^-] which obeys the rate expression given by eq 4.[9]

$$\text{rate} = \frac{k[PdCl_4^{2-}][\text{olefin}]}{[Cl^-]} \qquad (4)$$

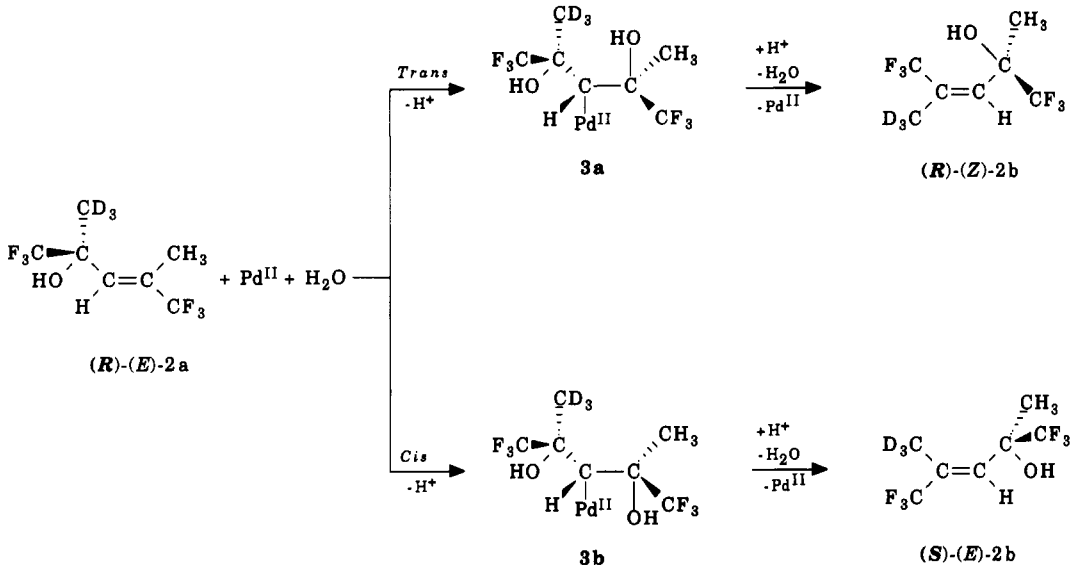
Thus, there is a need for mechanistic probes for determining the kinetics and stereochemistry of oxypalladation without the complication of oxidation. The design of these probes was discussed in detail in the last paper[1] of this series and will only be outlined here. The strategy for designing a kinetic probe involves studying the kinetics of a mechanistically very simple reaction for which the rate-determining step is known to be hydroxypalladation. This reaction is the isomerization and water exchange[10] of a tetrasubstituted allylic alcohol made unsymmetrical by substituting methyl-d_3 for a regular methyl group at one end of the allylic alcohol. This alcohol cannot undergo oxidation by Wacker chemistry to give carbonyl products. 2-(Methyl-d_3)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol (**2a**) gave the required hydrolytic stability under the acid conditions of the Wacker reaction. As discussed previously,[1] the rate-determining step for exchange is k_1 in Scheme I.

The stereochemical probe involves the determination of the optical and geometric configuration of the isomerization product formed from one geometric isomer of a chiral allylic alcohol which has a high barrier to free rotation. The allyl alcohol chosen for the present studies was actually the *E* isomer of chiral **2a**. The trifluoromethyl groups which were required for hydrolytic stability also provided steric hindrance, which resulted in restricted rotation. Computer calculations of energies show that the OH group is restricted to a position facing one plane of the molecule, since the OH and CF_3 groups are forced into a configuration in which they are furthest from the CH_3 group.[11] The face to which the Pd(II) is directed will depend on the absolute configuration of the starting alcohol. The directing influence of the hydroxyl group has been demonstrated for several epoxidation reactions[12,13] and has been shown to exist for several reactions.[14] In one study, on the Simmons–Smith reaction with cis allylic alcohols, over 99% stereoselectivity was found.[15]

The possible reaction sequences for the (*R*)-(−)-(*E*)-2 isomer are outlined in Scheme II. Trans hydroxy-

(2) For general discussion and references, see: Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, Holland, 1980; pp 41–84.
(3) (a) Henry, P. M. *J. Am. Chem. Soc.* **1964**, *86*, 3246. (b) Henry, P. M. *J. Organomet. Chem.* **1973**, *38*, 2415. (c) Kosaki, M.; Isemura, M.; Kitaura, Y.; Shinoda, S. *J. Mol. Catal.* **1977**, *2*, 351.
(4) Saito, Y.; Shinoda, S. *J. Mol. Catal.* **1980**, *9*, 461.
(5) Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal.* **1982**, *16*, 81.
(6) Stille, J. K.; James, D. E. *J. Organomet. Chem.* **1976**, *108*, 401.
(7) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.
(8) Stille, J. K.; Divakarumi, R. *J. Organomet. Chem.* **1979**, *169*, 239.
(9) Gregor, N.; Zaw, K.; Henry, P. M. *Organometallics* **1984**, *3*, 1251.
(10) The simultaneous H_2 ^{18}O exchange is studied to eliminate possible π-allyl mechanisms.[1] It was not measured in this work because it was measured in the very similar isomerization of deuterated allyl alcohols and it was shown that the reaction must be proceeding by the route shown in Scheme I.[9]
(11) Obtained from the "MMX PC Model" by Serena Software, Bloomington, IN, 1989.
(12) (a) Heathcock, C. H.; Flippin, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 1667. (b) Chautemps, P.; Pierre, J. L. *Tetrahedron* **1976**, *32*, 549.
(13) (a) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63. (b) Rissiter, B. E.; Verhoeven, T. R.; Sharpless, K. B. *Tetrahedron Lett.* **1979**, 4733. (c) Michelich, E. D. *Tetrahedron Lett.* **1979**, 4729.
(14) 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) For hydroboration, see: Brown, J. M.; Naik, R. G. *J. Chem. Soc., Chem. Commun.* **1982**, 348. (d) For isomerization, see: Smadja, W.; Ville, G.; Georgoulis, C. *J. Chem. Soc., Chem. Commun.* **1980**, 584. (e) Stork, G.; Kahn, M. *Tetrahedron Lett.* **1983**, 3951. (f) For oxidation, see: Sha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron Lett.* **1983**, 3943, 3947. (g) For alkoxy- and azidomercuration, see: Czernecki, S.; Georgoulis, C.; Provelenghiou, C. *Tetrahedron Lett.* **1975**, 2623; **1979**, 4841.
(15) Ratier, M. C.; Castaing, M.; Godet, J.-Y. G.; Pereyre, M. *J. Chem. Res., Miniprint* **1978**, 2309.

Scheme II



palladation gives the adduct **3a**, which by the principle of microscopic reversibility would undergo dehydroxypalladation to give **2b**, which has the same *R* configuration corresponding to the starting alcohol but is the *Z* geometric isomer. On the other hand, cis addition gives the intermediate **3b**, which decomposes to the product **2b** with the *S*-(+) configuration and the *E* geometric configuration.

At this point it seems instructive to consider the requirements for a valid stereochemical determination in a metal-catalyzed system such as this. They would be the following: (1) The absolute configurations of the starting allylic alcohol and final product must be known. (2) The *E* or *Z* geometry of the starting allylic alcohol must be known with certainty. (3) The directing influence of the hydroxyl group must be demonstrated for Pd(II) additions. (4) It must be shown that addition to only one face of the olefin occurs. In regard to requirement 1, note that the determination of absolute configuration is not crucial to this study since the two chiral centers are chemically the same except for the small effect of the substitution of methyl-d_3 for a non-deuterated methyl group. This difference would not have an appreciable effect on rotation or GLC retention times of their esters. Thus, all that is needed is a knowledge of whether retention or inversion of the chiral center has occurred and if geometric isomerization takes place. In regard to requirement 2, the geometric isomerism of the starting allylic alcohol has been established definitely by NOE experiments as well as other spectroscopic properties of the two isomers.[1] In regard to requirement 3, as mentioned above, there are many examples of the directing influence of the hydroxyl group in metal-catalyzed reactions of allylic alcohols. In regard to palladium specifically, partial 1,2-chirality transfer has been demonstrated for the palladium(II)-catalyzed addition of a phenyl group (Heck reaction) to chiral 3-methylbut-3-en-2-ol.[16] Perhaps the most definitive demonstration comes in the oxidation of 2-cyclohexenol-*1-d*. The isotopic distribution of deuteriated Wacker-type products could only be explained by hydroxypalladation with Pd(II) being directed to the same side of the cyclohexane ring as the hydroxyl.[17] Also, there is precedent for Pd(II) adding to allylic alcohols with hindered rotation from the most stable rotamer as shown in Scheme II. In the oxidation of (*R*)-(*Z*)-3-penten-2-ol, which would have an appreciable barrier to rotation, by phenylpalladium(II) reagent the isomer formed in excess is (*R*)-4-phenyl-2-pentanone.[16] Since phenylpalladation is known to be a cis process,[18] the only way the main product could have been formed is by the hydroxyl directing the Pd(II) from the most stable rotamer. Finally, in regard to requirement 4, the amount of isomerization, as determined by NMR spectroscopy, will be compared with the amount of *S*-(+) isomer formed. Since reisomerization would give back the starting configuration by both types of addition, with cis addition the amount of isomerization should equal the amount of *S*-(+) isomer formed. For trans addition, the *R*-(−) configuration should be formed but geometric isomerization should be observed. It is important to emphasize that the experiment requires that the rate of optical and/or geometric change be the same as the rate of isomerization since this result ensures only one type of hydroxypalladation is occurring. Thus, assume that rotation is not restricted to any extent. In that case either trans or cis hydroxypalladation, which could occur at both faces of the olefin, would also give eventual racemization because both will give the (*R*)- and (*S*)-**2b** isomers. However, both types of addition would give a rate of formation of (*S*)-**2b** which is half that of isomerization because each time (*S*)-**2b** is formed an equal amount of (*R*)-**2b** is formed.

The last paper in this series used these probes to study the mode of hydroxypalladation under Wacker conditions.[1] The exchange kinetics was identical in form to eq 1, which indicated proton release occurred *before* the rate-determining step, a result that strongly supported the cis addition mechanism. The stereochemical results were consistent only with cis hydroxypalladation and thus were consistent with the kinetic results. This paper will examine the reaction at high chloride concentrations to determine the reason for the previously reported trans stereochemistry.

Results

All kinetic runs were carried out at 25 °C. Preliminary control experiments revealed that there was no oxidation evident over 24 h under all reaction conditions. There was no acid- or chloride-catalyzed isomerization observed in

(16) Smadja, W.; Czernecki, S.; Ville, G.; Georgoulis, C. *Organometallics* **1987**, *6*, 166.
(17) Zaw, K.; Henry, P. M. *Organometallics* **1992**, *11*, 2008.
(18) (a) Heck, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6707. (b) Henry, P. M.; Ward, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 673.

Table I. Rates of Isomerization of 2-(Methyl-d_3)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol at High Chloride Concentrations[a]

run no.	$[PdCl_4^{2-}]$, M	$[H^+]$,[b] M	$[Cl^-]$,[c] M	10^6k_{obsd}, s^{-1}	10^3k_i, s^{-1}
1	0.016	0.05	2.0	8.4	1.1
2	0.016	0.05	2.5	6.7	1.1
3	0.016	0.05	3.0	5.5	1.0
4	0.016	0.10	2.0	8.3	1.0
5	0.016	0.15	2.0	8.4	1.1
6	0.008	0.05	2.0	4.1	1.0
7	0.032	0.05	2.0	17	1.1
8	0.064	0.05	2.0	34	1.1
9	0.016	0.05	4.0	4.4	1.1
10	0.016	0.05	3.5	5.1	1.1
11	0.016	0.20	2.0	8.2	1.0
12	0.016	0.40	2.0	8.4	1.1
					1.1 (av)

[a] All runs are in aqueous solution at 25 °C; quinone (0.10 M) was added to all runs to prevent the formation of Pd(0). In all runs initial $[C_7H_5D_3F_6O]$ = 0.044 M. $LiClO_4$ was added to bring the ionic strength (μ) to 2.0 M. [b] Added as $HClO_4$. [c] Added as LiCl. [d] k_i was calculated for runs 1–12 by assuming the rate expression given in eq 5 is operative and $[PdCl_4^{2-}]$, $[H^+]$, and $[Cl^-]$ are constant for each run.

the absence of $PdCl_4^{2-}$. Under all reaction conditions dehydration of the alcohol species was not observed.

The isomerization data are given in Table I. The data clearly indicate the absence of an acid inhibition term. In runs 1, 4, and 5, for which $[PdCl_4^{2-}]$ and $[Cl^-]$ remain constant, the rate remains constant as $[H^+]$ increases. The fact that the values of k_i, which were calculated using eq 5, remain constant indicate the rate expression is of the form of eq 4 rather than eq 1. The value of k_i is 1.1×10^{-3} s^{-1}.

$$\text{rate} = \frac{k_i[PdCl_4^{2-}][C_7H_5D_3F_6O]}{[Cl^-]} \qquad (5)$$

The enantiomers of **2** were resolved by preparative GLC of their (*S*)-(+)-α-(trifluoromethyl)phenylacetate ((+)-MTPA) esters. Their absolute configuration was assigned by the induced chemical shift of the methoxy proton signals by Eu(fod)$_3$ shift reagent.[19] The *E* configuration of **2** was assigned on the basis of ^1H NOE experiments on the ketone from which **2** was prepared as well as differences in the NMR and IR spectra of the two geometric isomers due to the more hindered rotation in the *Z* isomer. The product, **2a**, was resolved as above and the absolute configuration of the enantiomers assigned in the same fashion. The two optical isomers of **2** were regenerated by reaction with $LiAlH_4$ and isomerized under the conditions of the Wacker reaction. The product, **2b**, was isolated, the (*S*)-(+)-MTPA esters were again prepared, and the optical purity was determined by analytical GLC and ^1H NMR methods. The results are summarized in Table II. These results clearly indicate that isomerization occurs with retention of configuration. According to Scheme II, this result is consistent only with trans hydroxypalladation under the conditions of the isomerization. These are the same as those used to determine the stereochemistry of hydroxypalladation from which the mode of addition under Wacker conditions was inferred.

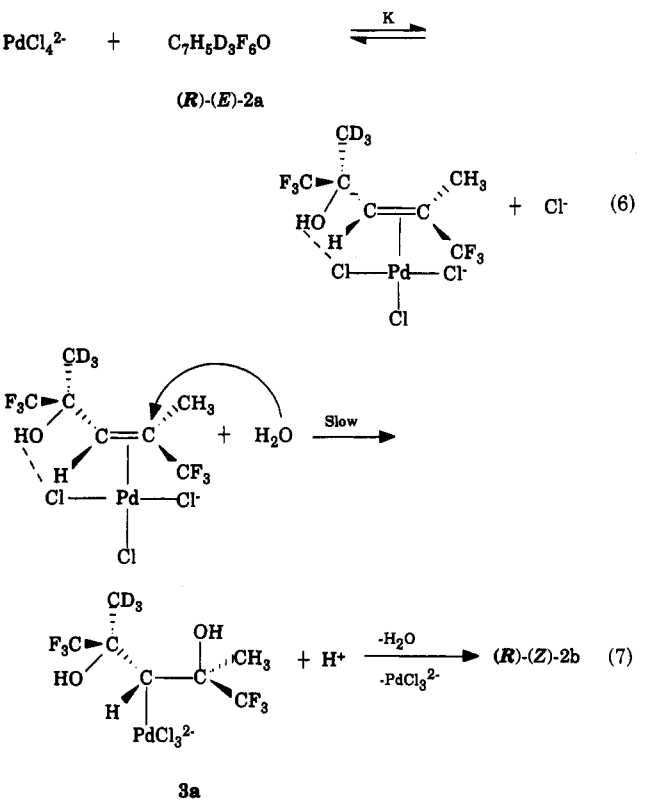
Discussion

The first time in mechanistic studies of catalytic palladium(II) chemistry that both kinetics and stereochemistry were determined under the same reaction conditions was in the last paper of this series.[1] In that study the two separate measurements reinforced each other. The present study is the second time that both types of determinations were made, and again they reinforce each other. Thus, the rate expression is consistent with a an equilibrium π-complex formation, as shown in eq 6, followed by trans

Table II. Stereochemistry of the Isomerization of (*E*)-2-(Methyl-d_3)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol at High Chloride Concentrations[a]

substrate			product		
confign	% ee[b]	$[Cl^-]$, M	% isomerizn[c,e]	% *S*[d]	% *R*[d]
R	100	2.0	31 (30)	0.0	100
R	100	3.5	27 (25)	0.0	100
S	100	2.0	35 (32)	100	0.0
S	100	3.5	45 (45)	100	0.0

[a] Acid and $PdCl_4^{2-}$ concentrations were kept constant at 0.20 and 0.05 M, respectively. [b] Determined by ^1H NMR spectroscopy of the OCH_3 singlet of the MTPA ester, and GC peaks of the *RR* and *RS* diastereomers, respectively. [c] Determined by ^2H NMR spectroscopy of the CD_3 resonance. [d] Determined by GC retention times of the MTPA diastereomers. [e] Values given in parentheses indicate percentage obtained as the *Z* geometric isomer.



attack of water, which is depicted in eq 7, to give the oxypalladation intermediate, which reverses the process to give exchange. This mechanism is consistent with the kinetics, since the single chloride inhibition only allows for incorporation of olefin into the coordination sphere to give π-complex formation, which is always a requirement for catalytic reactions of olefins with transition metals. It is *not* consistent with formation of an aquo π-complex, which would be a requirement for cis addition, since an aquo π-complex would require that two chlorides be replaced, giving a second-order chloride inhibition in the kinetic expression. The stability of the intermediate, analogous to **3a** in the nonoxidative isomerization of allyl-*1,1*-d_2 and allyl-*3,3*-d_2 alcohols, can be explained by the extra chloride in the coordination sphere as compared to the intermediates in eqs 2 and 3. This extra chloride must prevent decomposition by a β-hydride shift to give carbonyl products.

(19) (a) Yamaguchi, S.; Yasuhara, F.; Kabuto, K. *Tetrahedron* **1976**, *32*, 1363. (b) Yamaguchi, S.; Yasuhara, F. *Tetrahedron Lett.* **1977**, 89. (c) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1963**, *34*, 2543. (d) Dale, D. L.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

As depicted in eqs 6 and 7, the rotamer with the CF_3 on the same side as the olefinic hydrogen is the most stable one. This causes the hydroxyl in (*R*)-(*E*)-**2a** to direct the $PdCl_3^{2-}$ to the olefin face of the double bond which gives the intermediate **3a** by trans addition. This intermediate reverses the hydroxypalladation process to give (*R*)-(*Z*)-**2b** as the exchange product. As in the previous paper, the stereochemical results support the kinetic rate expression, not a surprising result if one appreciates the power of kinetic arguments. The stereochemical results of the work are in complete agreement with those of Bäckvall, Åkermark, and Ljunggren, who, using $CuCl_2$ to trap the intermediate hydroxypalladation adduct to give 2-chloroethanol, showed that the addition was trans by the configuration of the product from ethene-*1,2-d*$_2$.[7] Thus, their work is a confirmation of the results of this study. In fact, it is because of the elegant studies of these workers that the absolute stereochemical results of this and the previous paper in the series[1] are not vital to the arguments concerning the stereochemistry of hydroxypalladation under Wacker conditions.[20] Since these workers showed that the addition is trans at high chloride concentrations, all that is necessary is to demonstrate that the stereochemistries of addition are different at high and low chloride concentrations. This and the previous paper in this series[1] prove that the stereochemistries of addition under the conditions of low and high chloride concentration are in fact different, demonstrating that the extrapolation from high to low chloride concentration, which is the basis for the generally accepted trans addition under Wacker conditions is invalid. It follows that, since the stereochemistries are different, the addition must be cis at low chloride concentration. The obvious conclusion is that transition-metal catalysis is much too complicated for extrapolations from one set of reaction conditions to another. Thus, stereochemical studies in nonaqueous or mixed aqueous solvents or with olefins other than acyclic olefins that obey the Wacker kinetics given in eq 1 are not valid indicators of the stereochemistry under Wacker conditions.

The important point is that general statements to the effect that oxygen nucleophiles attack olefins in a trans fashion are meaningless because the mode of addition could depend on the olefin and reaction conditions. The final proof of the mechanism of the Wacker reaction must be stereochemical studies under the conditions of the rapid olefin oxidation to aldehydes and ketones. This will not be a simple task because the products are carbonyls, but in order to be valid, the stereochemical studies must be carried out with an olefin which has been shown to obey the Wacker kinetics given in eq 1.

Experimental Section

Starting Materials. Palladous chloride was purchased from AESAR. 1,1,1-Trifluoroacetone, sodium (pellets in xylene), phosphorus pentoxide, and (methyl-*d*$_3$)magnesium iodide (Aldrich, Sure-Seal) were purchased from Aldrich Chemicals and used without further purification. All other chemicals were of reagent grade.

Isomerization Kinetics. The isomerization of 2-(methyl-*d*$_3$)-4-methyl-1,1,1,4,4,4-hexafluoro-3-penten-2-ol was monitored by ^{2}H NMR spectroscopy using a Varian 300 VXR NMR instrument. The experimental procedures have been described.[1]

Preparation of 2-Oxo-4-methyl-1,1,1,5,5,5-hexafluoro-4-pentanol.[22] This was prepared by the self condensation of 1,1,1-trifluoroacetone. The experimental procedure has been described.[1]

Preparation and Characterization of (*E*)- and (*Z*)-4-Methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-one. These were prepared by the dehydration of 2-oxo-4-methyl-1,1,1,5,5,5-hexafluoro-4-pentanol with 20% oleum. The conformers were separated by preparative GLC methods and characterized by ^{13}C and ^{1}H NMR and IR spectra and elemental analyses. The configurations of the conformers were assigned on the basis of ^{1}H NOE experiments as well as others characteristics of the spectra.[1]

Preparation of (*E*)-2-(Methyl-*d*$_3$)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol. This was prepared by the addition of (methyl-*d*$_3$)magnesium iodide to (*E*)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-one. Its preparation and characterization have been described.[1]

Resolution of (*E*)-2-(Methyl-*d*$_3$)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol. (*E*)-2-(Methyl-*d*$_3$)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-yl α-methoxy-α-(trifluoromethyl)phenylacetate was prepared, the diastereomers were separated by preparative GLC methods, and absolute configurations were assigned by Eu(fod)$_3$ shift studies. The experimental procedures have been described.[1]

Preparation and Resolution of (*Z*)-2,4-Dimethyl-1,1,1,5,5,5-hexafluoro-3-penten-2-yl α-Methoxy-α-(trifluoromethyl)phenylacetate. The alcohol 2,4-dimethyl-1,1,1,5,5,5-hexafluoro-3-penten-2-ol was prepared in the usual manner by Grignard reaction of CH_3MgI with (*Z*)-4-methyl-1,1,1,5,5,5-hexafluoro-3-penten-2-one and resolved as described above. The assignments were made by Eu(fod)$_3$ shift studies. The procedures have been described.[1]

Analysis of Stereochemical Reaction Mixtures. The reactions were run on a 10-mL scale as for the kinetic runs. However, for the stereochemical studies the entire reaction mixture was worked up. The MTPA esters were prepared and analyzed by GLC methods to determine the distribution of optical and geometric isomers. In addition, the ^{1}H NMR spectra of the esters were taken to confirm the distributions.

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(20) It is important to emphasize that the major stereochemical result of this paper is the finding that the mode of addition at high [Cl$^-$] is different from that at low [Cl$^-$] reported in the previous paper.[1] Thus, a reviewer has pointed out that cis addition from the unstable isomer followed by cis elimination would give the same stereochemical result. Addition of Pd(II) from an unstable π-complex was previously found for asymmetric hydrogenation.[21] As mentioned in the Introduction, there is precedent for Pd(II) addition from the most stable rotamer for allylic alcohols with hindered rotation. However, more important is the fact that in the present system there is independent evidence for trans addition so that the determination of absolute stereochemistry is not vital. The stereochemical results would be invalid only in the very unlikely event in which the addition is from the stable isomer at low [Cl$^-$] and the unstable isomer at high [Cl$^-$].

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