

# Palladium(II)-Catalyzed Exchange and Isomerization Reactions.

## VI. Vinylic Chloride Exchange with Acetate in Acetic Acid Catalyzed by Palladium(II) Chloride<sup>1</sup>

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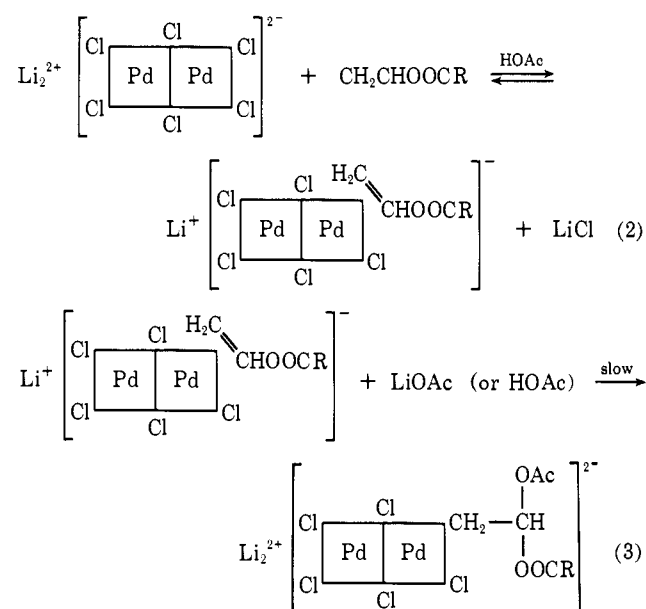
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**Abstract:** The exchange of the chloride of vinyl chloride for acetate to give vinyl acetate was found to have the rate expression:  $\text{rate} = ([\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{vinyl chloride}]/[\text{LiCl}]^2)(k' + k''[\text{LiOAc}])$ . *cis*- and *trans*-propenyl chloride exchanged to give mainly the propenyl acetate of the same configuration as the starting chloride. A mechanism compatible with the rate equation and stereochemical results as well as with the previous exchanges studied in this series involves reversible fast trans acetoxy-palladation, with *cis* dechloropalladation the slow step in the exchange. The dechloropalladation step requires that a coordination position on the Pd(II) be open to accept the chloride. This requirement accounts for a second [LiCl] inhibition not observed in other exchanges. Substitution on the olefinic carbons strongly inhibits exchange, a result in keeping with steric effects on other exchanges. However, 1-chlorocyclopentene did exchange, a result consistent with opposite stereochemistries for acetoxy-palladation and dechloropalladation.

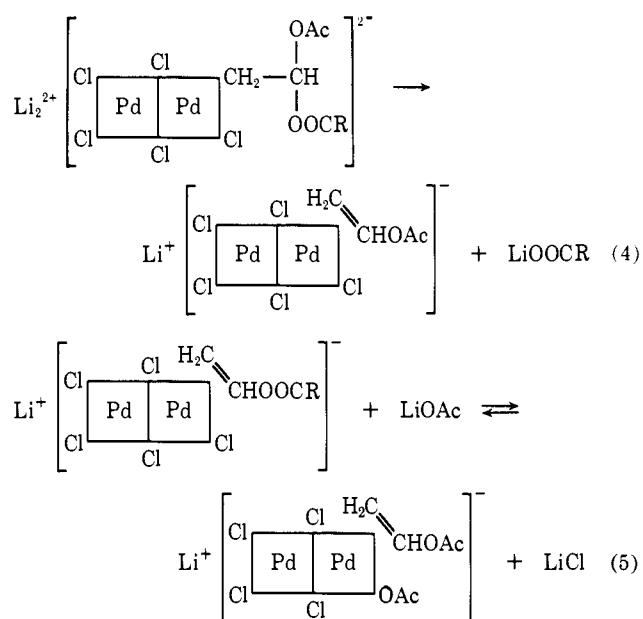
Previous papers of this series have considered vinyl ester<sup>3a</sup> and allylic ester<sup>3b</sup> exchange with acetic acid, allylic ester isomerization,<sup>3c</sup> and vinyl chloride<sup>3d</sup> and allyl trifluoroacetate<sup>2</sup> exchange with lithium chloride. The rate expression for both ester exchanges, shown in eq

$$\text{rate} = \frac{[\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{olefin}]}{[\text{LiCl}]}(k_1 + k_2[\text{LiOAc}]) \quad (1)$$

1, is consistent with an acetoxy-palladation-deacetoxy-palladation type of mechanism. For example, the vinyl ester exchange mechanism is shown in eq 2-4.



The rate expression does not have a second [LiCl] inhibition, which would have indicated acetate complexing prior to attack on the olefin as shown in eq 5. This



result<sup>4</sup> suggests that acetate is attacking *trans* from outside the coordination sphere, a type of addition consistent with independent stereochemical evidence.<sup>6</sup>

The rate equation for vinyl chloride and allyl trifluoroacetate exchange is shown in eq 6 in the form

$$\text{rate} = [\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{olefin}][\text{LiCl}]/[\text{LiCl}] \quad (6)$$

which is believed to be most indicative of the mechanism involved. The reaction path is believed to be analogous to that proposed for acetate exchange with the difference that the *main* mode of chloropalladation is *cis* chloropalladation from the coordination sphere of the Pd(II). The [LiCl] term in the numerator is believed to result from the need for LiCl from the solution to fill the incipient vacant coordination position of Pd(II) to complete the exchange. The reaction scheme is shown in eq 7.

(4) The [Cl<sup>-</sup>]<sup>2</sup> inhibition term was found for the oxidation of ethylene by Pd(II) in water<sup>5</sup> and indicated that in this case both olefin and nucleophile were coordinated to Pd(II) before attack.

(5) P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964).

(6) P. M. Henry, *ibid.*, **93**, 1494 (1971).

(1) Paper V: P. M. Henry, *Inorg. Chem.*, **11**, 1876 (1972).  
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 (3) (a) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971); (b) *ibid.*, **94**, 1527 (1972); (c) *ibid.*, **94**, 5200 (1972); (d) *J. Org. Chem.*, **37**, 2443 (1972).

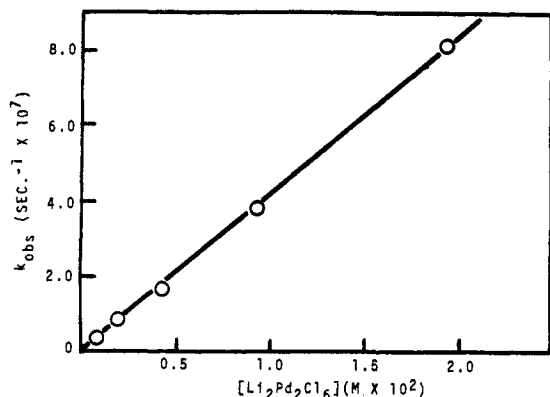


Figure 1. Plot of  $k_{\text{obsd}}$  vs.  $[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ ;  $[\text{LiCl}] = 0.125 \pm 0.005 \text{ M}$ ;  $[\text{LiOAc}] = 1.0 \text{ M}$ .

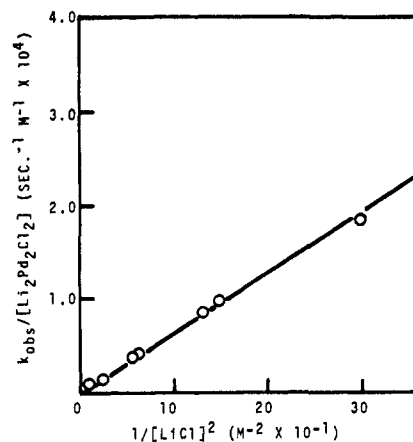
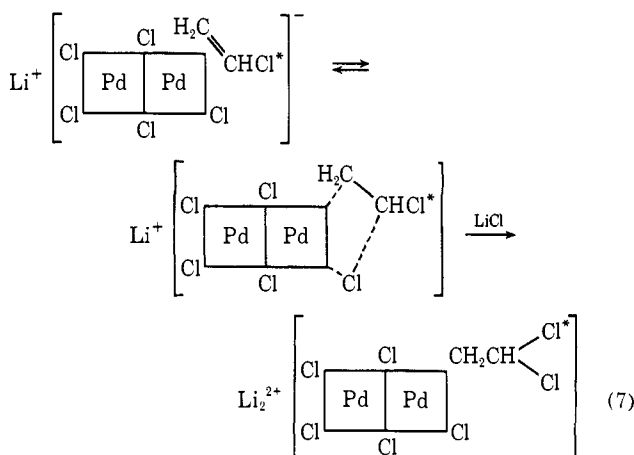


Figure 2. Plot of  $k_{\text{obsd}}/[\text{Li}_2\text{Pd}_2\text{Cl}_6]$  vs.  $1/[\text{LiCl}]^2$ ;  $[\text{LiOAc}] = 1.0 \text{ M}$ .



This paper will report a study of the Pd(II)-catalyzed exchange of vinylic chloride for acetate aimed at determining whether the kinetics of this exchange are consistent with the kinetics of the exchanges previously studied. This exchange has been reported by several workers,<sup>7-9</sup> and a mechanism involving acetoxypalladation-dechloropalladation has been suggested.<sup>9,10</sup>

## Results

All kinetic runs were made at 25° in dry acetic acid containing various amounts of palladium(II) chloride, lithium or sodium chloride, and lithium or sodium acetate. The lithium salts, because of their high solubility, were used to define the kinetics, but in some runs sodium salts were employed. As in earlier studies<sup>1,3</sup> the previously determined<sup>11</sup> values of  $K_1$  ( $0.1 \text{ M}^{-1}$ ) and  $K_D$  ( $2.56 \text{ M}^{-1}$ ) were used to determine the con-



centrations of the various species under any set of reaction conditions from a knowledge of total Pd(II),  $([\text{Pd(II)}]_t)$ , and chloride  $([\text{Cl}]_t)$  concentrations.

(7) E. W. Stern, M. L. Spector, and H. P. Leftin, *J. Catal.*, **6**, 152 (1966).

(8) C. F. Kohll and R. Van Helden, *Recl. Trav. Chim. Pays-Bas*, **87**, 481 (1968).

(9) H. C. Volger, *ibid.*, **87**, 501 (1968).

(10) Discussions: Homogeneous Catalytic Reactions Involving Palladium, E. W. Stern and H. C. Volger, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (4), F4 (1969).

(11) P. M. Henry and O. Marks, *Inorg. Chem.*, **10**, 373 (1971).

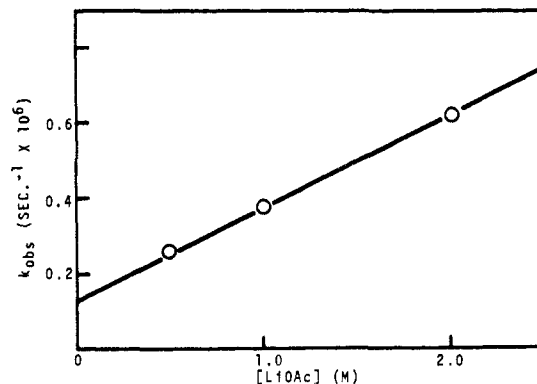


Figure 3. Plot of  $k_{\text{obsd}}$  vs.  $[\text{LiOAc}]$ ;  $[\text{Pd(II)}]_t = 0.0224 \text{ M}$ ;  $[\text{Cl}]_t = 0.2808 \text{ M}$ .

One problem in studying this exchange reaction is the fact that acetate is consumed and chloride is formed as the reaction proceeds. Since these ingredients almost certainly appear in the rate expression, the pseudo-first-order rate constant will change as the reaction proceeds. To overcome this problem, the reactions were carried only to very small conversions based on vinylic chloride present, usually less than 1% so that not enough chloride was produced or acetate consumed to affect the kinetics.

The rate expression was defined by use of saturated vinyl chloride solutions at atmospheric pressure. The vinyl chloride concentration was *ca.* 1.5 M. Since, in the previous studies, the dimer,  $[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ , was found to be the reactive species, the rate was plotted against  $[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ . Such a plot of  $k_{\text{obsd}}$ , the rate constant obtained for a reaction first order in vinyl acetate, vs.  $[\text{Li}_2\text{Pd}_2\text{Cl}_6]$  at constant  $[\text{LiCl}]$  and  $[\text{LiOAc}]$  is shown in Figure 1. It is linear with zero intercept indicating a reaction first order in  $[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ . The value of  $k_{\text{obsd}}$  was found to decrease very markedly with increasing  $[\text{LiCl}]$ , suggesting a  $[\text{LiCl}]^2$  inhibition term. To test this possibility,  $k_{\text{obsd}}/[\text{Li}_2\text{Pd}_2\text{Cl}_6]$  at constant  $[\text{LiOAc}]$  was plotted against  $1/[\text{LiCl}]^2$ . Such a plot, shown in Figure 2, is linear with zero intercept confirming the second-order LiCl inhibition. Next the  $[\text{LiOAc}]$  dependence was determined by plotting the value of  $k_{\text{obsd}}$  at constant  $[\text{Li}_2\text{Pd}_2\text{Cl}_6]$  and  $[\text{LiCl}]$  vs.  $[\text{LiOAc}]$ . Such a plot, shown in Figure 3, indicates a term zero order in  $[\text{LiOAc}]$  and a term first order in  $[\text{LiOAc}]$ .

Finally, the first-order dependence on the vinyl chloride was confirmed. Since it is inconvenient to vary the concentration of a gas such as vinyl chloride, isopropenyl chloride was used for this purpose. However, substitution on the double bond inhibits exchange much more than it does decomposition of the enol acetate to give carbonyl compound,<sup>12-14</sup> so that with substituted vinylic chlorides, as was reported previously,<sup>8</sup> this decomposition becomes a serious side reaction. This problem can be avoided by using very low chloride since, because of the differing chloride dependencies under these conditions, exchange is fast compared with decomposition. However, at low chloride even small conversions give appreciable change in [LiCl]. If the reaction is run with sodium salts and a solution saturated with NaCl, the chloride salt remains at a low (0.013 M<sup>11</sup>) but constant value because the chloride formed is precipitated as NaCl. As shown in Table I, values of the first-order rate constant,  $k_{\text{obsd}}$ ,

Table I. Effect of Isopropenyl Chloride Concentration on the First-Order Rate Constant<sup>a</sup>

Isopropenyl chloride	$10^8 k_{\text{obsd}}$ , sec <sup>-1</sup>
0.2	9.1
1.0	10.2

<sup>a</sup> [Na<sub>2</sub>Pd<sub>2</sub>Cl<sub>6</sub>] = 0.0177 M; [NaCl] = 0.013 M; [NaOAc] = 1.0 M.

remain constant with changing isopropenyl chloride concentration, confirming that the reaction is first order in vinylic chloride.

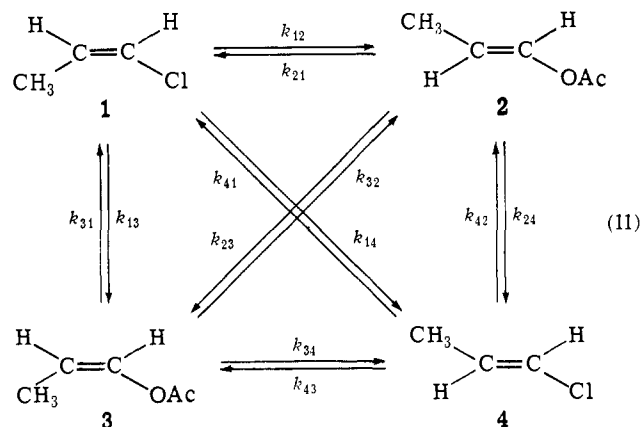
The complete rate expression is thus

rate =

$$\frac{[\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{vinyl chloride}]}{[\text{LiCl}]^2}(k_1 + k_2[\text{LiOAc}]) \quad (10)$$

where  $k_1 = 2.3 \times 10^{-7}$  M sec<sup>-1</sup> and  $k_2 = 4.6 \times 10^{-7}$  sec<sup>-1</sup>.

To determine whether exchange occurs with retention or inversion of configuration, samples of *cis*- and *trans*-propenyl chlorides were exchanged and the rates of formation of *cis*- and *trans*-propenyl acetates determined from each. As shown by the scheme in eq 11, the complete reaction is complicated, requiring 12 rate constants to define the system completely. However, this scheme is analogous to reaction schemes found in earlier work, which were solved by computer programs. Thus  $k_{21}$ ,  $k_{24}$ ,  $k_{31}$ , and  $k_{34}$  are zero because acetates do not exchange with chlorides under the reaction conditions. Furthermore,  $k_{41}$ ,  $k_{14}$ ,  $k_{23}$ , and  $k_{32}$  can be measured independently. The remaining four rate constants are determined by systematically substituting values of the rate constants in the computer program until calculated product distribution change with time matches the experimental distributions. In practice, since reactions were carried to very low conversions during the time the run was followed, very little isomerization of one propenyl chloride into the



other occurred so both  $k_{41}$  and  $k_{14}$  could be presumed to be zero.

Runs starting with either *trans*- or *cis*-1-chloropropene indicated that exchange occurred *mainly* to give enol acetates of the same configuration as the starting 1-chloropropene, *i.e.*,  $k_{13} > k_{12}$  and  $k_{42} > k_{43}$ . However, exchange did not occur exclusively with retention of configuration; for instance,  $k_{12}$  and  $k_{43}$  have positive values. This fact is demonstrated by the data for the exchange of *cis*-1-chloropropene listed in Table II. The best fit to the data gives a value of  $k_{12}$  about

Table II. Exchange of *cis*-1-Chloro-1-propene. Calculated and Observed Values of the Concentrations of *cis*- and *trans*-1-Propen-1-ol Acetate<sup>a</sup>

Time, min	Enol acetate, <i>cis</i> (3)		Concn, M × 10 <sup>2</sup> , <i>trans</i> (2)	
	Calcd <sup>b</sup>	Obsd	Calcd <sup>b</sup>	Obsd
27	1.27	1.33	0.39	0.41
40	1.85	1.82	0.62	0.62
72	3.17	3.19	1.22	1.08
88	3.80	3.64	1.55	1.47

<sup>a</sup> Starting material was 97% *cis* isomer and 3% *trans* isomer; [Na<sub>2</sub>Pd<sub>2</sub>Cl<sub>6</sub>] = 0.0177 M; [NaCl] = 0.013 M; NaOAc = 1.0 M. Initial [1-chloro-1-propene] = 1.0 M. <sup>b</sup> Calculated using  $k_{13} = k_{41} = 0$ ;  $k_{12} = 6.6 \times 10^{-6}$  sec<sup>-1</sup>;  $k_{13} = 1.07 \times 10^{-6}$  sec<sup>-1</sup>;  $k_{23} = 1.83 \times 10^{-4}$  sec<sup>-1</sup>;  $k_{32} = 3.53 \times 10^{-4}$  sec<sup>-1</sup>.  $k_{23}$  and  $k_{32}$  determined by equilibrating *trans*-1-propen-1-ol acetate under the reaction conditions.  $k_{12}$  and  $k_{13}$  are the values of these rate constants which give best fit to experimental data.

six times that for  $k_{13}$ . To determine the effect of chloride concentration on this ratio, a run was also made at [LiCl] = 0.2 M. In this case, the ratio of  $k_{12}$  to  $k_{13}$  was about 10.

The values of  $k_{\text{obsd}}$  for several vinylic esters under one set of reaction conditions are given in Table III.

Table III. Values of  $k_{\text{obsd}}$  for Several Vinylic Chlorides under One Set of Reaction Conditions<sup>a</sup>

Vinylic chloride	$k_{\text{obsd}}$ , sec <sup>-1</sup> × 10 <sup>4</sup>
Vinyl chloride	1.94
<i>trans</i> -1-Chloropropene	$1.5 \times 10^{-2}$
<i>cis</i> -1-Chloropropene	$9.5 \times 10^{-2}$
Isopropenyl chloride	$1.0 \times 10^{-2}$
2-Chloro-2-butene <sup>b</sup>	$2.2 \times 10^{-4}$
1-Chlorocyclopentene	$2.6 \times 10^{-3}$

<sup>a</sup> [Na<sub>2</sub>Pd<sub>2</sub>Cl<sub>6</sub>] = 0.0177 M; [NaCl] = 0.013 M saturated; [NaOAc] = 1.0 M. <sup>b</sup> Mixture of *cis* and *trans* isomers.

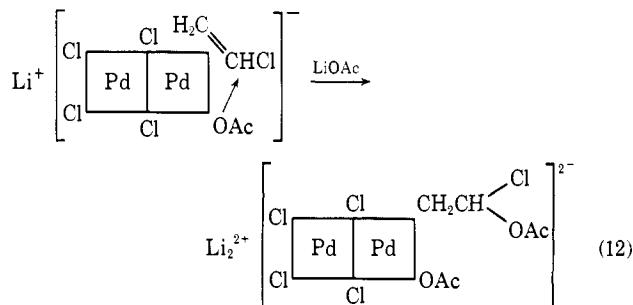
(12) W. H. Clement and C. M. Selwitz, *Tetrahedron Lett.*, 1081 (1962).

(13) R. G. Schultz and P. R. Rony, *J. Catal.*, **16**, 133 (1970).

(14) P. M. Henry, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), B15 (1969).

## Discussion

The rate expression for exchange of acetate for chloride, shown in eq 10, is interesting in that it is analogous to that found for oxidation of ethylene by Pd(II) in aqueous solution.<sup>5</sup> Without the background provided by previous papers in this series, it would be tempting to postulate that the first two steps in the reaction are those represented by eq 2 and 5, followed by attack of acetate from the coordination sphere to give the acetoxy-palladation adduct. However, the fact that acetoxy-palladations of vinyl<sup>3a</sup> and allylic<sup>3b</sup>



esters do not occur by this route, as well as the evidence that acetoxy-palladation of olefins is a trans process, argues against this mechanism. Certainly acetoxy-palladation of vinyl chloride would not be expected to occur by a route completely different from that of the other olefins studied.

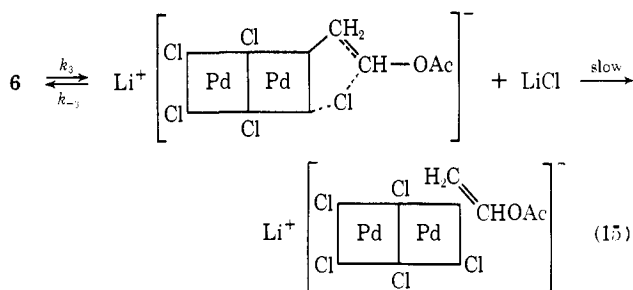
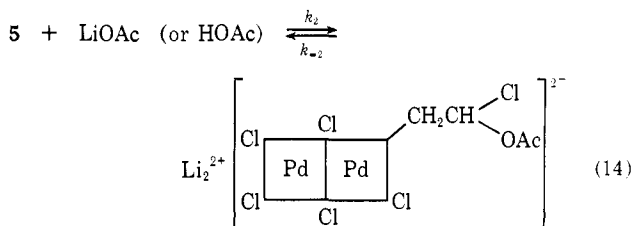
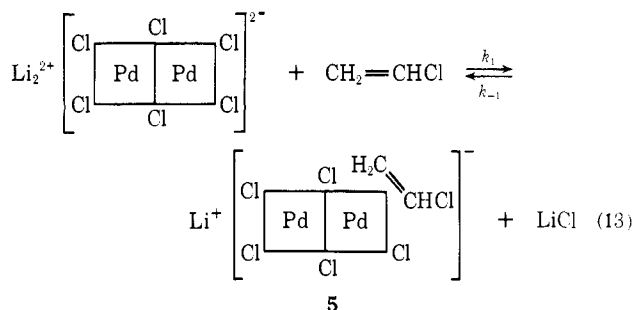
In fact, a mechanism can be written which is entirely consistent with both previous and present kinetics and stereochemical results. In regard to stereochemistry, the present study has confirmed the previous qualitative observation<sup>15,16</sup> that exchange of acetate for chloride gives mainly an enol acetate with the same configuration as the starting chloride. As discussed previously,<sup>10</sup> this result is consistent with acetoxy-palladation and dechloropalladation having different stereochemistries. In regard to kinetics, the rate expression for chloropalladation (eq 6) has a [LiCl] term in the numerator which would not be expected for cis chloropalladation unless chloride is required to fill the vacant coordination site left by the chloride adding to the olefin. From the principle of microscopic reversibility, the reverse type of chloride dependence would be expected for dechloropalladation. The net result is that if acetoxy-palladation-dechloropalladation is fast compared with dechloropalladations, then an added [LiCl] inhibition would be expected. This is exactly what is found. The complete reaction scheme is shown in eq 13-15.

The first-order terms in [Li<sub>2</sub>Pd<sub>2</sub>Cl<sub>6</sub>] and [C<sub>2</sub>H<sub>3</sub>Cl] in the numerator, as well as one [LiCl] term in the denominator, result from eq 13, while the [LiOAc]-dependent and [LiOAc]-independent terms result from eq 14. Finally the second [LiCl] inhibition term results from eq 15.

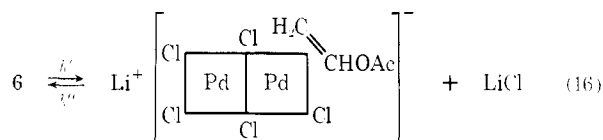
It is worthwhile noting that the kinetics are *not* consistent with trans elimination of chloride followed by readdition, since once the LiCl leaves, exchange is complete. The readdition would merely amount to the first step in the reverse reaction: exchange of acetate for chloride. The fact that *cis*-1-chloro-1-propene does not give exclusively *cis*-1-propen-1-ol acetate

(15) E. W. Stern, *Catal. Rev.*, **1**, 73 (1967); see p 125.

(16) A. Sabel, J. Smidt, R. Jira, and H. Prigge, *Chem. Ber.*, **102**, 2739 (1969).



must now be considered in light of the above mechanism. The simplest explanation is that chloride is leaving by a trans elimination to give *trans*-1-propen-1-ol acetate. However, as shown by eq 16, this type of

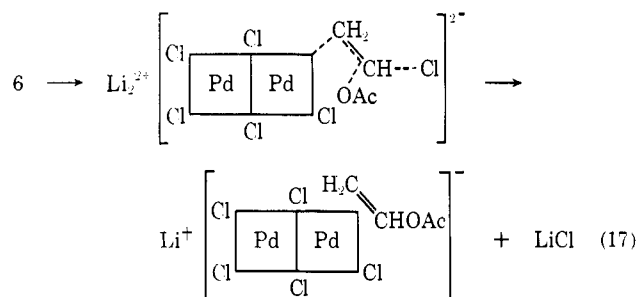


elimination does not require an empty coordination sphere on the Pd(II). The net result is that exchange involving cis dechloropalladation should have the rate expression given by eq 10, while exchange involving trans dechloropalladation should have the rate expression given by eq 1.

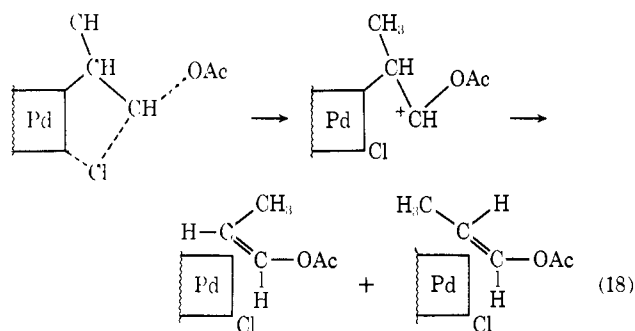
This would mean that the ratio of *cis*-to-*trans*-1-propen-1-ol acetate from *cis*-1-chloropropene should *decrease* as chloride increases. Actually the ratio *increased* slightly in going from [NaCl] = 0.013 M to [LiCl] = 0.2 M. Thus simple trans dechloropalladation cannot explain the presence of *trans*-1-propen-1-ol acetate.

The source of the *trans*-1-propen-1-ol acetate from the *cis*-1-chloropropene is not readily apparent. It is possible that the breaking of the Pd(II)-carbon and Cl-carbon bond in dechloropalladation is not well synchronized so a carbonium ion is formed permitting some rotation about the carbon-carbon bond.

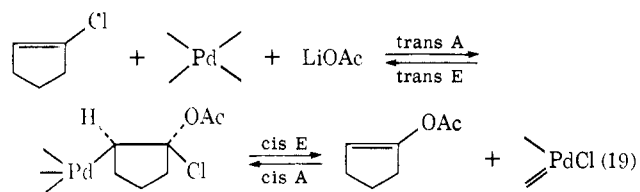
Although not detected kinetically in the present study, some trans dechloropalladation most likely does occur according to eq 17 since this type of elimination is required to explain the exchange of 1-chlorocyclopentene with radioactive LiCl.<sup>3d</sup> Elim-



ination according to eq 18 would not predict the exchange of cyclic vinylic chlorides.



With the exception of 1-chlorocyclopentene, the effect of vinylic chloride structure on rate is quantitatively very similar to that found for vinyl ester exchange.<sup>3a</sup> This result is not surprising since both exchanges involve an acetoxy-palladation step which is quite sensitive to steric factors. However, 1-chlorocyclopentene exchanges while 1-acetoxycyclopentene did not exchange within the limit of detection. This result would be expected if acetoxy-palladation and dechloropalladation have different stereochemistries (A = addition; E = elimination).



The fact that 1-chlorocyclopentene exchanges appreciably faster than 2-chloro-2-butene is interesting in light of the fact that 2-acetoxy-2-butene exchanges with acetate while 1-acetoxycyclopentene does not exchange within the limit of detection. Thus the fact that 1-acetoxycyclopentene does not exchange cannot be attributed to steric factors.

The ratio  $k_1/k_2$  is much higher than it was for either

enol<sup>3a</sup> or allylic<sup>3b</sup> ester exchange. Thus at  $[\text{LiOAc}] = 1.0 M$  the ratio of rates of the neutral and acetate-catalyzed reactions is 0.5 for chloride exchange while for ester exchange it was *ca.* 0.01. The difference may result from the preequilibrium represented by eq 14 for chloride exchange which was not present for the ester changes.

### Experimental Section

**Materials.** Sources of most chemicals and preparation and analysis of stock solutions have been described previously.<sup>1,3,11</sup>

**Kinetic Runs.** The vinyl chloride runs were carried out on a 5-ml scale in capped polymerization tubes in the same fashion as for radioactive chloride exchanges<sup>3d</sup> except that in the present case 0.05-ml samples were withdrawn periodically and analyzed for vinyl acetate using 6-ft 20% Carbowax 20M on ABS (70-80 mesh) programmed from 80 to 200° at 7.5°/min. The helium flow rate was 60 ml/min. Toluene was used as an internal standard. Since the conversions were less than 1%, the data were plotted in a linear fashion to obtain the rate constant as shown below. The usual first-order rate expression can be written ( $C_0$  = initial [vinyl chloride] and  $x$  is [vinyl acetate] formed)

$$\ln(C_0 - x)/C_0 = kt \quad (20)$$

$$\ln(C_0 - x) = -kt + \ln C_0 \quad (21)$$

but

$$\ln(C_0 - x) = \ln C_0 +$$

$$2 \left[ \frac{-x}{2C_0 - x} + \frac{1}{3} \left( \frac{-x}{2C_0 - x} \right)^3 \dots \right] \quad (22)$$

At low conversion only the first term is important. Since  $x \ll C_0$ , we have

$$\ln(C_0 - x) = \ln C_0 - x/C_0 \quad (23)$$

Substituting in eq 23 and cancelling  $\ln C_0$  on both sides, we have

$$x/C_0 = kt \quad (24)$$

Thus a plot of  $x/C_0$  vs.  $t$  gives the rate constant,  $k$ .

The runs with the other vinylic chlorides were carried out in a similar fashion except that the chloride was added as a liquid. Runs were on a 5-ml or 25-ml scale. The larger scale was used for the slower runs. In this case 2-ml aliquots were worked up by extracting the enol acetate into  $\text{CH}_2\text{Cl}_2$  and washing with water to remove the acetic acid. The organic extract was then dried and concentrated and the entire sample injected for vpc analysis. Either the Carbowax column or a 20-ft 20% Lac 446 on Chromosorb (60-80 mesh) column (flow rate = 100 ml/min) was used. A temperature of 150° was used for the 2-butanone enol acetates and 120° for the propionaldehyde enol acetates. This column easily separated the *cis* and *trans* isomers of each. Either toluene or *m*-xylene was used as internal standard.

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