of ether. After the addition was complete, the reaction was allowed to come to room temperature and was stirred for 22 hr. Hydrolysis and product isolation was conducted using the procedure of Micovic and Mihailovic.[4] Reductions in which the molar ratio of $AlCl_3$/$LiAlH_4$/amide was 1:1:1 were conducted in a similar fashion. Analyses were carried out by glpc on column A (Table VI) at 210°.

Partial Reduction of *N*-Methyl-*p*-chloroanilides.—Into 3 mmol of the anilide in 10 ml of tetrahydrofuran was injected with stirring at 0° 0.83 ml of 1.2 *M* lithium aluminum hydride in tetrahydrofuran. The reaction mixture was stirred at 0° for 10 hr and was then added to 100 ml of a saturated solution of 2,4-dinitrophenylhydrazine in 2 *M* hydrochloric acid. The resultant solution was diluted with 100 ml of 2 *M* hydrochloric acid and allowed to stand for 5 hr; the resultant 2,4-DNP was isolated, dried, and weighed.

Acknowledgments.—The authors thank the Chemistry Department and the Research Council of the University of Dayton for financial support. Helpful discussions with Professor Paul G. Gassman of The Ohio State University during the preparation of this manuscript are gratefully acknowledged. The authors are also indebted to Mr. Kenneth Fey, who conducted the studies with the mixed hydride reagents as his senior research project.

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. VIII. Isomerization of Vinylic Halides in Acetic Acid Catalyzed by Palladium(II) Chloride[1,2]

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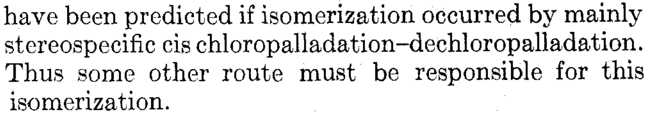
The palladium(II)-catalyzed isomerization of *cis*- and *trans*-1-chloropropene was found to obey the three-term rate expression rate = $(k_1[Li_2Pd_2Cl_6]/[LiCl] + k_2[Li_2Pd_2Cl_6] + k_3[Li_2Pd_2Cl_6]^{1/2})$[1-chloropropene]. 1-Bromopropene isomerization displayed mainly the k_2 and k_3 terms. The k_2 term most likely results from nonstereospecific chloropalladation–dechloropalladation in which the chloride adds to the carbon carrying the methyl and the palladium to the carbon carrying the halide. The k_1 and k_3 terms correspond to formation of monomer and dimeric π complexes, respectively. Isomerization is then accomplished through the π complexes without the intervention of an external reagent. A possible mechanism is rearrangement of the π complex to a Pd(II) σ-bonded carbonium ion which undergoes rotation before reverting to the π complex.

Paper IV[4] of this series describes a study of the radioactive chloride exchange of vinylic chlorides with radioactive lithium chloride. The rate expression for this exchange is given by eq 1.

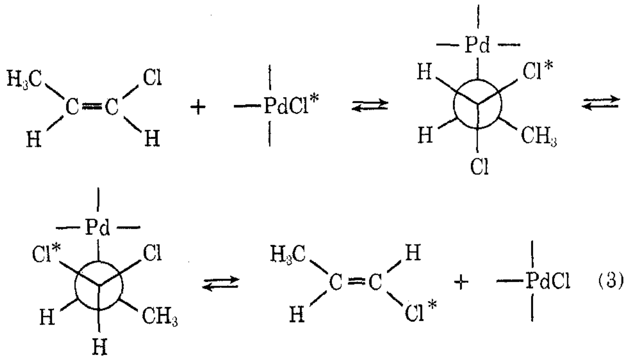
$$\text{rate} = k[Li_2Pd_2Cl_6][\text{vinylic chloride}] \quad (1)$$

The mechanism which best fits all the experimental facts consists of chloropalladation followed by dechloropalladation to give exchange. Chloropalladation is not completely stereospecific but the main mode is apparently cis chloropalladation from the coordination sphere of Pd(II).


(2)

During the course of this work it was found that *cis*- or *trans*-1-chloropropene isomerized into the other isomer considerably faster than exchange with radioactive chloride. As shown in eq 3, this result would not have been predicted if isomerization occurred by mainly stereospecific cis chloropalladation–dechloropalladation. Thus some other route must be responsible for this isomerization.

This paper will describe a study of this reaction using vinylic chlorides and bromides as reactants.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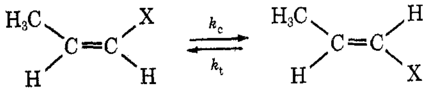
In paper VII of this series the study of a similar isomerization of enol propionates was described.[1] The rate expression for the isomerization is given by eq 4.

$$\text{rate} = \frac{k[Li_2Pd_2Cl_6][\text{enol propionate}]}{[LiCl]} \quad (4)$$

Effects of structure on rate as well as other mechanistic work showed that π-allylic or palladium hydride routes for this isomerization were very unlikely.[1,2]

Results

All runs were made at 25° in acetic acid solvent. The values of k_{obsd} for a given run are the sum of the pseudo-first-order rate constants, k_t and k_c for the reaction given by eq 5 (X = Cl or Br). The values of


(5)

k_c and k_t can readily be calculated from the composition of the equilibrium mixture, which was 74% cis when X is Cl and 70% cis when X is Br. For most

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[1] Paper VII: P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 7316 (1972).

[2] For a preliminary account of this work, see P. M. Henry, *ibid.*, **93**, 3547 (1971).

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[4] P. M. Henry, *J. Org. Chem.*, **37**, 2443 (1972).

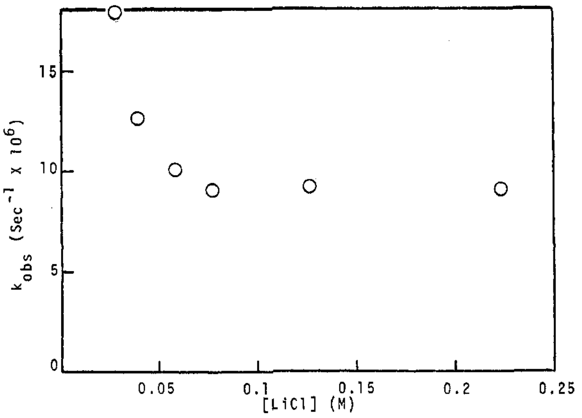

Figure 1.—Plot of k_{obsd} *vs.* [LiCl]; [$Li_2Pd_2Cl_6$] = 0.015 ± 0.0004 *M*.

runs the vinylic chloride concentration was 0.2 *M*. Under the same reaction conditions runs starting with either *cis*- or *trans*-1-halopropene gave the values of k_{obsd}. For almost all runs the trans isomer was used, since it gave the biggest change in composition and therefore the most accurate values of k_{obsd}.

As in previous work the concentrations of the various Pd(II) and chloride species were determined from the total Pd(II) concentration, [Pd(II)$_t$], and total chloride concentrations, [Cl]$_t$, making use of the previously determined[5] values of K_1 (0.1 M^{-1}) and K_D (2.6 M^{-1}) for the equilibria shown in eq 6 and 7.

$$Li_2Pd_2Cl_6 + 2LiCl \overset{K_1}{\rightleftharpoons} 2Li_2PdCl_4 \qquad (6)$$

$$2LiCl \overset{K_D}{\rightleftharpoons} Li_2Cl_2 \qquad (7)$$

Vinylic Chloride Isomerization.—The rate expression for isomerization was determined using *cis*- and *trans*-1-chloropropene. The dependence on 1-chloropropene concentration was determined under several reaction conditions. Typical results are given in Table I.

TABLE I
DEPENDENCE OF k_{obsd} ON 1-CHLOROPROPENE CONCENTRATION[a]

[*trans*-1-Chloropropene], *M*	k_{obsd}, sec^{-1} × 10^6
0.01	17.5
0.05	17.7
0.2	17.8
0.5	16.6

[a] [Pd(II)]$_t$ = 0.02052 *M*; [Cl]$_t$ = 0.0908 *M*.

Since the first-order rate constant, k_{obsd}, does not change with 1-chloropropene concentration, the reaction is first order in vinylic chloride.

The order in Pd(II) species and [LiCl] proved to be complicated. As shown in Figure 1, at low [LiCl] addition of more LiCl decreased the rate. However, above about 0.04 *M* LiCl, addition of LiCl did not affect the rate. Furthermore, if at the lowest [LiCl], a mole of $HgCl_2$ is added per mole of Pd(II) the rate is increased fivefold. That this acceleration resulted from further decrease in chloride resulting from formation of $HgCl_3^-$ species was demonstrated by running the isomerization in the presence of excess solid NaCl in the presence and absence of $HgCl_2$. In this case, where the NaCl concentration was the saturation value[5] of 0.013 *M* for both runs, the rates were identical.

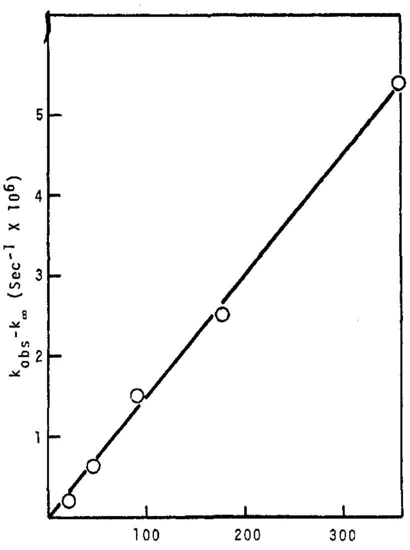

Figure 2.—Plot of $k_{obsd} - k_\infty$ *vs.* 1/[LiCl]; [$Li_2Pd_2Cl_6$] = 0.0036 ± 0.0002 *M*.

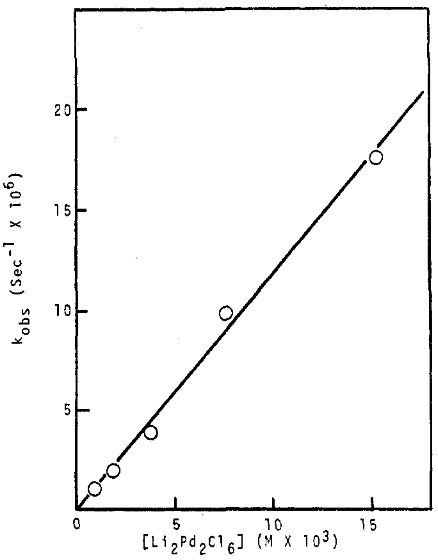

Figure 3.—Plot of [$Li_2Pd_2Cl_6$] *vs.* k_{obsd} at low chlorides; [LiCl] = 0.011 ± 0.0003 *M*.

The nature of the chloride inhibition was determined in the following way. From the values of k_{obsd} at various [LiCl] was subtracted the value of k_{obsd} when the rate became unaffected by chloride (k_∞). These values were then plotted against 1/[LiCl]. As shown in Figure 2, the plot is linear and goes through the origin, indicating a first-order chloride inhibition. The order in [$Li_2Pd_2Cl_6$] was then determined by plotting k_{obsd} *vs.* [$Li_2Pd_2Cl_6$] at 0.011 *M* LiCl, a chloride concentration at which k_{obsd} consists almost exclusively of the chloride inhibited reaction; as shown in Figure 3, the plot is linear and goes through the origin. The rate expression for the reaction at low [LiCl] is thus given by eq 8.

$$\text{rate} = \frac{k[Li_2Pd_2Cl_6][\text{1-chloropropene}]}{[LiCl]} \qquad (8)$$

The reaction was then studied at higher chloride, where the chloride-dependent reaction is negligible.

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

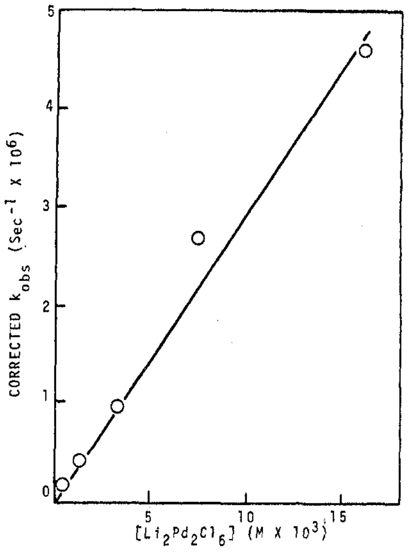

Figure 4.—Plot of corrected k_{obsd} *vs.* $[Li_2Pd_2Cl_6]$; [LiCl] = 0.207 ± 0.007 *M*.

An example of the dependence of rate on $[Li_2Pd_2Cl_6]$ is shown in Table II. The rate varies by a factor of a 8.5 while $[Li_2Pd_2Cl_6]$ varies by a factor of almost 30 and $[Li_2Pd_2Cl_6]^{1/2}$ varies by a factor of 5.5. Thus the dependence is not strictly first or $^1/_2$ order in $[Li_2Pd_2Cl_6]$. Thus result suggests two terms, one first order and one $^1/_2$ order. The contribution of each to k_{obsd} was calculated in the following fashion. The $^1/_2$-order term should predominate at low $[Li_2Pd_2Cl_6]$ because the first-order term decreases more rapidly with decreasing $[Li_2Pd_2Cl_6]$. As a first approximation the k_{obsd} at lowest $[Li_2Pd_2Cl_6]$ was assumed to consist entirely of the $^1/_2$-order term. The contribution of the $^1/_2$ term at the other $[Li_2Pd_2Cl_6]$ could then be readily calculated and substrated from the values of k_{obsd} to give the first-order contributions. From the first approximation for the first-order contribution at the highest chloride the small contribution of the first-order term at the lowest $[Li_2Pd_2Cl_6]$ was calculated and substracted from k_{obsd} to give a second approximation for the $^1/_2$-order contribution at lowest $[Li_2Pd_2Cl_6]$. The process was then repeated. After only three iterations the first- and $^1/_2$-order contributions to k_{obsd} remained constant. They are given in the last two columns of Table II. A plot of the first-order contributions *vs.* $[Li_2Pd_2Cl_6]$, shown in Figure 4, is linear with zero intercept indicative of a first-order reaction.[6]

TABLE II

DEPENDENCE OF k_{obsd} ON $Li_2Pd_2Cl_6$ CONCENTRATION AT APPROXIMATELY 0.2 *M* LiCl[a]

$[Li_2Pd_2Cl_6]$, $M \times 10^3$	$[Li_2Pd_2Cl_6]^{1/2}$, $M^{1/2} \times 10^2$	k_{obsd}, sec^{-1} × 10^6	Contribution to k_{obsd}: 1st order, sec^{-1} × 10^6	Contribution to k_{obsd}: $^1/_2$ order, sec^{-1} × 10^6
16.2	12.8	10.9	4.71	6.20
7.45	8.63	6.83	2.67	4.16
3.3	5.73	3.74	0.99	2.76
1.39	3.72	2.22	0.42	1.80
0.548	2.34	1.29	0.16	1.13

[a] [LiCl] = 0.207 ± 0.007 *M*.

The complex rate expression for $[Li_2Pd_2Cl_6]$ range of 0.00058 to 0.0162 *M* and a [LiCl] range of 0.0028 to 0.38 *M* is given by eq 9. Values of the rate constants are summarized in Table VI.

$$\text{rate} = \left(\frac{k_1[Li_2Pd_2Cl_6]}{[LiCl]} + k_2[Li_2Pd_2Cl_6] + k_3[Li_2PdCl_6]^{1/2}\right) \times [\text{vinylic halide}] \quad (9)$$

The effect of acetate and water on the rate exchange at two $[Cl]_t$ levels was determined. Data are given in Table III.

TABLE III

EFFECT OF LITHIUM ACETATE AND WATER ON RATE OF ISOMERIZATION[a]

$[Cl]_t$	[LiOAc]	$[H_2O]$	k_{obsd}, sec^{-1} × 10^6
0.0908	0	0	17.8
	0.1	0	13.5
	0.5	0	11.5
	0	2.5	14.8
0.4908	0	0	6.83
	0.5	0	6.42
	0	2.5	4.7

[a] $[Pd(II)]_t$ = 0.02052 for all runs. Rates measured using trans isomer.

The effect of acid on the rate of isomerization was tested. At $[Pd(II)]_t$ = 0.048 *M* and a $[Cl]_t$ of 0.37 *M*, the rate of isomerization is 8.9×10^{-6}. Under the same conditions except that the reaction mixture was now 1 *M* in CF_3COOH the value of k_{obsd} is 1.23×10^{-5} sec^{-1}.

cis-1-Chloropropene was isomerized to an equilibrium mixture in CH_3COOD which was 0.05 *M* in $[Pd(II)]_t$ and 0.3 *M* in $[Cl]_t$. The trans isomer was collected and analyzed by mass spectrometry. It was found to contain less than 0.2% deuterium.

1-Bromopropene Isomerization.—*cis*- and *trans*-1-bromopropene were isomerized to an equilibrium mixture of the two isomers without detectable quantities of 1-chloropropene being formed. Only upon long standing are materials with vpc retention times identical with those of *cis*- and *trans*-1-chloropropene found.

The effect of chloride concentration on rate is given in Table IV. The fact that the ratio in the last column remains almost constant even at [LiCl] = 0.0028 *M* indicates no appreciable chloride inhibition.

TABLE IV

VALUES OF k_{obsd} FOR ISOMERIZATION OF *trans*-1-BROMOPROPENE AT LOW CHLORIDE CONCENTRATIONS[a]

$[Cl]_t$, $M \times 10^2$	$[Li_2Pd_2Cl_6]$, $M \times 10^3$	[LiCl], $M \times 10^2$	k_{obsd}, sec^{-1} × 10^5	$k_{obsd}/[Li_2Pd_2Cl_6]$, M^{-1} sec^{-1} × 10^3
2.62	3.85	0.28	3.85	10.0
2.92	3.82	0.56	4.82	12.0
3.52	3.77	1.11	3.40	9.0
4.72	3.66	2.12	3.49	9.5
5.92	3.59	3.06	3.29	9.2

[a] Value of $[Pd(II)]_t$ for all runs was 0.00776 *M*; concentrations of Li_2PdCl_4 and Li_2Cl_2 can readily be calculated from concentrations of other species.

Dependence of rate on $Li_2Pd_2Cl_6$ concentration is given in Table V. In this case the total rate variation

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[6] Of course the values of the first-order contribution at the highest and lowest $[Li_2Pd_2Cl_6]$ are arranged to give a straight line through the origin. The important point is that the other three points fall on this straight line within experimental error.

Table V

Dependence of k_{obsd} on $Li_2Pd_2Cl_6$ Concentration at Approximately 0.2 M LiCl[a]

$[Li_2Pd_2Cl_6]$, $M \times 10$	$[Li_2Pd_2Cl_6]^{1/2}$, $M \times 10^2$	k_{obsd}, $sec^{-1} \times 10^5$	Contributions to k_{obsd}: 1st order, $sec^{-1} \times 10^5$	Contributions to k_{obsd}: $^1/_2$ order, $sec^{-1} \times 10^5$
10.1	10.05	6.91	5.65	1.26
4.55	6.74	3.03	2.19	0.84
1.95	4.46	1.36	0.80	0.56
0.78	2.8	0.78	0.44	0.35

[a] [LiCl] = 0.200 ± 0.002 M.

is about 9 while $[Li_2Pd_2Cl_6]$ varies by 13 and $[Li_2Pd_2Cl_6]^{1/2}$ varies by 3.6. Thus the first-order term is most important for 1-bromopropene. By procedures similar to those described earlier, the contribution of each term to k_{obsd} was calculated. They are listed in the last two columns of the table. The values of the rates constants are summarized in Table VI.

Table VI

Values of the Rate Constants for Isomerization and Exchange

	1-Chloropropene	1-Bromopropene
k_1	4.3×10^{-6} sec^{-1}	$<10^{-6}$ sec^{-1}
k_2	2.9×10^{-4} M^{-1} sec^{-1}	5.2×10^{-3} M^{-1} sec^{-1}
k_3	4.8×10^{-5} $M^{-1/2}$ sec^{-1}	1.25×10^{-4} $M^{-1/2}$ sec^{-1}
k_{ex}[a]	2.3×10^{-6} M^{-1} sec^{-1}	

[a] Rate of radioactive chloride exchange from ref 4. This value is for an equilibrium mixture of cis and trans isomers.

cis-1-Bromopropene was isomerized in CH_3COOD in the same fashion as *cis*-1-chloropropene. The *trans*-1-bromopropene formed contained less than 0.2% deuterium.

Discussion

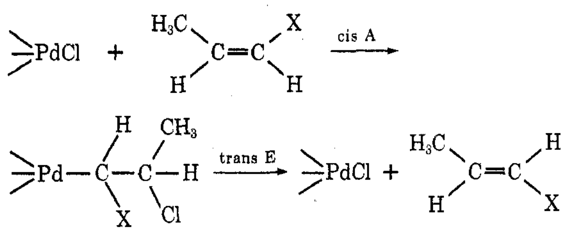
The general rate expression for isomerization of vinylic halides is given by eq 9 with rate constants listed in Table VI. The rate of radioactive chloride exchange for 1-chloropropene is included for purposes of comparison. In the case of isomerization of 1-chloropropene all three terms are detected, while, for 1-bromopropene, the k_2 term is by far the most important with the k_3 term barely detectable. This does not mean that k_1 and k_3 have lower values for 1-bromopropene than they do for 1-chloropropene. Rather, the value of k_2 for 1-bromopropene is about 20 times higher than that for 1-chloropropene. In fact k_3 for 1-bromopropene is approximately twice that for' 1-chloropropene.

The various terms can readily be interpreted in terms of mechanism. The k_1 and k_3 terms correspond to the formation of π complexes without the intervention of any other external reagent to cause isomerization. The k_1 term results from π-complex formation *via* eq 10 and the k_3 term *via* eq 11 (VH = vinylic halide).

$$Li_2Pd_2Cl_6 + VH \overset{K_1}{\rightleftharpoons} LiPd_2Cl_5(VH) + LiCl \tag{10}$$

$$Li_2Pd_2Cl_6 + 2VH \overset{K_3}{\rightleftharpoons} 2LiPdCl_3(VH) \tag{11}$$

The k_2 term is identical with that previously found for radioactive chloride exchange,[4] which apparently proceeds *via* a chloropalladation–dechloropalladation type mechanism as shown in eq 3. Thus, at least in the 1-chloropropene case, the k_2 term most likely results from nonstereospecific chloropalladation–dechloropalladation in the direction opposite from that shown in eq 3 (X = Cl or Br; A = addition, E = elimination).



(12)

It is necessary to postulate this mode of addition rather than the mode shown in eq 3 because the latter type of addition would predict rates of isomerization by this type of mechanism which would be close to the rate of exchange. In fact, as demonstrated by eq 3, since chloropalladation is mainly cis[4,7] the value of k_2 and rate of exchange should be very close. However, as shown in Table VI, the value of k_2 is much higher than k_{ex}. At a $Li_2Pd_2Cl_6$ concentration of about 0.0075 M, the rate of chloride exchange was only 5% of the rate of isomerization. According to the data in Table II, about 40% of the isomerization proceeds according to the k_2 term at this $Li_2Pd_2Cl_6$ concentration. Thus, most isomerization is proceeding according to eq 12 rather than eq 3.

Ih the case of 1-bromopropene little is known about the mode of addition, since chloropalladation in the mode of eq 3 does not have to give exchange of chloride for bromide if chloride is eliminated much more readily than bromide. Certainly the reason that 1-bromopropene isomerizes more readily than 1-chloropropene is not immediately apparent. The differences in rate would not be expected to result from steric effects if isomerization occurred *via* eq 12, since the addition of bulkier groups to the double bond decreases the rate of chloropalladation.[4] It is difficult to predict the effect on rate of changing from a chloro to a bromo group if isomerization occurs by chloropalladation in the fashion opposite to eq 12.

As mentioned earlier, the k_1 and k_3 terms correspond to π-complex formation *via* eq 10 and 11, respectively. The π complex must then perform the isomerization without the intervention of any external reagent. The exact mechanism or mechanisms whereby the isomerization occurs is uncertain. One possibility is that chloropalladation can have rate expressions corresponding to k_1 and k_3 terms as well as the k_2 term. This seems very unlikely, since the earlier study of chloride exchange *via* chloropalladation no k_1 or k_3 terms were detected.[4]

As mentioned in the introduction, π-allylic or Pd(II) hydride mechanisms were eliminated by nonkinetic experiments.[1,2] Thus, a new mechanism must be operative. As discussed in a previous paper,[1] one possibility is rearrangement of the π complex to a σ-bonded diradical type intermediate analogous to those postulated for metal carbonyl catalyzed photoisomerization of olefins.[8]

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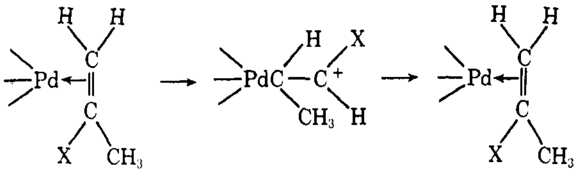
[7] P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 7311 (1972).

[8] M. Wrighton, G. S. Hammond, and H. B. Grey, *ibid.*, **93**, 3285 (1971).

Another possibility is rearrangement of the π complex to a Pd(II) σ-bonded carbonium type intermediate which can reverse either to the cis or trans isomer (X = Cl or Br).



(13)

One prediction of the last mechanism is that it should display a large negative Hammett ρ. This prediction is being checked using systems in which steric factors can be separated from electronic factors. In any case more mechanistic work is required before a definite mechanism can be proposed.

Two points deserve comment. First, the isomerization of enol propionates displayed only the k_1 term while 1-chloropropene gave all three terms and 1-bromopropene gave mainly the k_2 term. Such wide differences in structure can cause considerable differences in reactivity.

Second, this is the first time the monomeric π complex (the k_3 term) has been found to be reactive, although the π complex was detected in previous exchange studies (papers III[9] and V[10]). The reason given for its lack of reactivity previously was the larger concentration of negative charge on the Pd(II) containing the olefin in this complex as compared with the dimeric π complex. This negative charge discouraged the approach of the nucleophiles necessary for exchange. In the present case no nucleophile is required for isomerization; so it is reasonable that the monomeric π complex is reactive.

Finally, the effect of acetate and H_2O on the isomerization rate shown in Table III is explicable on the basis of other studies. Thus, at the lower chloride, the replacement of chloride by acetate to give vinylic acetate occurs at a rate comparable to isomerization and the cis isomer reacts several times faster than the trans isomer.[7] Thus, the preferential reaction of the *cis*-1-chloropropene gives an apparent slower rate of isomerization of the trans isomer. At the higher chloride the effect of added acetate is much less, since the exchange reaction is strongly retarded by increasing chloride concentration.

In other studies[11] it was found that the addition of water shifts the equilibrium shown in eq 5 to the left; so for a given chloride concentration, addition of water will decrease the dimer concentration and thus decrease the rate of exchange. As expected, the retardation is important at both high and low chlorides.

Experimental Section

Materials.—The source of the *cis*- and *trans*-1-chloropropenes has been described previously,[4] as has the preparation and analysis of Pd(II) stock solutions.[5] The mixture of *cis*- and *trans*-1-bromopropenes was purchased from K & K Laboratories. Pure samples of the cis and trans isomers were obtained by preparative vpc using a 20 ft 20% Lac 446 on Chromosorb W (60–80 mesh). Temperature was 60° and helium flow rate was 100 ml/min.

Kinetic Runs.—The reaction mixtures were prepared by mixing known amounts of the Pd(II) and LiCl stock solutions and diluting to a known volume, usually 5 ml. The run was then started by adding the vinylic halide. The progress of the isomerization was followed by vpc analysis. For the 1-chloropropene run the Lac 446 column at 50° was used. For the 1-bromopropene runs the same column at 60° was used.

The data were treated in the usual fashion for runs approaching equilibrium.[12] The equilibrium mixture for 1-chloropropene contained 74% cis isomer while that for 1-bromopropene contained 74% cis isomer while that for 1-bromopropene contained 70% cis isomer.

Registry No.—Palladium, 7440-05-3; palladium(II) chloride, 7647-10-1; *cis*-1-chloropropene, 16136-84-8; *trans*-1-chloropropene, 16136-85-9; *cis*-1-bromopropene, 590-13-6; *trans*-1-bromopropene, 590-15-8; lithium acetate, 546-89-4; $Li_2Pd_2Cl_6$, 31183-05-8.

Acknowledgment.—The author gratefully acknowledges helpful discussions with Professor H. Taube and H. Goering. The author is also grateful to Mr. F. J. Kriss for his excellent technical assistance.

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[9] P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 5200 (1972).

[10] P. M. Henry, *Inorg. Chem.*, **11**, 1876 (1972).

[11] P. M. Henry, submitted for publication.

[12] A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, Wiley, New York, N. Y., 1960, p 186.