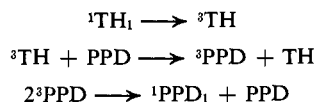


An alternate explanation of the formation of  ${}^1\text{PPD}_1$  can also be given. The failure to obtain PPD ecl in the PPD-10 MP experiment can be attributed to quenching of  ${}^3\text{PPD}$  by 10-MP. Since the triplet level for 10-MP is 2.4 eV<sup>3</sup> and that for TH is 2.6 eV, this would locate the energy level of  ${}^3\text{PPD}$  at about  $2.5 \pm 0.1$  eV. Similar quenching of an electrogenerated fluoranthene triplet intermediate by *trans*-stilbene has been observed by Freed and Faulkner.<sup>3</sup> If the  ${}^3\text{PPD}$  level is lower than that of TH, then the following sequence can be invoked to explain the emission of  ${}^1\text{PPD}_1$ .



The rapid intersystem crossing of TH to the triplet state<sup>6</sup> is consistent with this mechanism. The disappearance of the PPD emission with increasing square-wave frequency can also be associated with the formation of the emitting species,  ${}^1\text{PPD}_1$ , by secondary reac-

tions which do not have sufficient time to occur within the short pulse lengths, although quenching of  ${}^3\text{PPD}$  by the relatively higher radical ion concentrations existing during the short pulses is also possible. Possible candidates for the emission that occurs at wavelengths longer than that for TH singlet emission include excimers of TH and PPD or a PPD-TH exciplex. There appears to be no precedence for any of those species from previous spectroscopic work. Indeed, Lami and Laustriat<sup>14</sup> were unable to observe excimer emission in fluorescence of concentrated PPD, although related compounds (e.g., PPO) did show excimer formation. Similarly, no previous reports of delayed fluorescence of PPD have been found.

**Acknowledgment.** The support of the Robert A. Welch Foundation and the U. S. Army Research Office-Durham is gratefully acknowledged. We also appreciate the helpful comments and criticisms by Professors L. R. Faulkner and D. Hercules and Dr. E. A. Chandross.

## Palladium(II)-Catalyzed Exchange and Isomerization Reactions. II. Allylic Ester Exchange Catalyzed by Palladium(II) Chloride in Acetic Acid<sup>1</sup>

Patrick M. Henry<sup>2</sup>

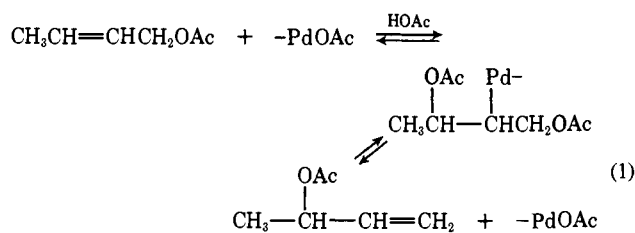
Contribution No. 1559 from the Research Center, Hercules Incorporated, Wilmington, Delaware 19899. Received May 21, 1971

**Abstract:** The exchange of allyl propionate with acetate in acetic acid to give allyl acetate has been found to obey the following rate expression:  $-d[\text{allyl propionate}]/dt = [\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{allyl propionate}]/[\text{LiCl}](k' + k''[\text{LiOAc}])$ . Unsymmetrical allylic propionates such as crotyl and 3-buten-2-ol propionates exchange and undergo allylic isomerization simultaneously. This result is consistent with a mechanism involving addition of the elements of Pd(II) and acetate across the double bond (acetoxypalladation) followed by elimination of the elements of Pd(II) and propionate. The complete reaction sequence involves formation of a  $\pi$  complex between the olefin and  $\text{Li}_2\text{Pd}_2\text{Cl}_6$  with release of LiCl to give a Pd(II) dimer  $\pi$  complex followed by attack of acetate to give the acetoxypalladation adduct in the rate-determining step,  $\text{Li}_2\text{Pd}_2\text{Cl}_6 + \text{allyl ester} \rightleftharpoons \text{Li}_2\text{Pd}_2\text{Cl}_6(\text{allyl ester}) + \text{LiCl}$ . Kinetic and ultraviolet spectral results indicate that a monomeric  $\pi$  complex is formed in larger quantities than the reactive dimeric  $\pi$  complex but is unreactive ( $\text{Li}_2\text{Pd}_2\text{Cl}_6 + 2 \text{ allyl ester} \rightleftharpoons 2\text{LiPdCl}_3(\text{allyl ester})$ ). Trifluoroacetate esters exchange faster than propionate esters. Substitution on the double bond strongly inhibits exchange, indicating that steric effects are very important in the acetoxypalladation step.

The first paper<sup>1</sup> of this series described kinetic and mechanistic studies of vinyl ester exchange. It has been reported<sup>3</sup> that Pd(II) salts will also catalyze the exchange of allylic esters. This paper will be concerned with the kinetics and mechanism of the exchange of allylic propionate and trifluoroacetate esters with acetate in acetic acid.

A reaction which may be related to allylic exchange is allylic isomerization. Thus Pd(II) is reported<sup>4,5</sup> to

catalyze the isomerization of allylic acetates, for instance, crotyl acetate to 3-buten-2-ol acetate. One mechanism that has been suggested<sup>3,4</sup> for this reaction involves an acetoxypalladation-deacetoxypalladation sequence. When crotyl acetate is the starting ester, the scheme is as follows



(1) Paper I, P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971).

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(3) A. Sabel, J. Smidt, R. Jira, and H. Prigge, *Chem. Ber.*, **102**, 2939 (1969).

(4) W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **88**, 2054 (1966).

(5) T. Matsuda, R. Mitsuyasu, and Y. Nakamura, *Kogyo Kagaku Zasshi*, **72**, 1751 (1969).

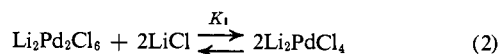
**Table I.** Values of  $k'$  and  $k''$  for Various Reaction Conditions<sup>a</sup>

[Pd] <sub>t</sub> <sup>b</sup>	[Cl] <sub>t</sub> <sup>b</sup>	[Li <sub>2</sub> Pd <sub>2</sub> Cl <sub>6</sub> ] <sup>c</sup>	[Li <sub>2</sub> PdCl <sub>4</sub> ] <sup>c</sup>	[LiCl] <sup>c</sup>	[Li <sub>2</sub> Cl <sub>2</sub> ] <sup>c</sup>	$k_{\text{obsd}}$ , sec <sup>-1</sup> × 10 <sup>5</sup>	$k'$ , sec <sup>-1</sup> × 10 <sup>5</sup>	$k''$ , M <sup>-1</sup> sec <sup>-1</sup> × 10 <sup>5</sup>
0.00667	0.0382	0.00319	0.000295	0.0165	0.0007	24.8	7.4	1.20
0.00667	0.0532	0.00308	0.00050	0.0285	0.0021	14.1	7.8	1.22
0.02668	0.1428	0.0255	0.00244	0.0483	0.0060	32.0	7.5	1.18
0.01334	0.1028	0.00606	0.00121	0.0492	0.0062	16.7	8.1	1.27
0.00333	0.0728	0.00138	0.00058	0.0496	0.0063	3.56	7.7	1.20
0.02668	0.1928	0.0120	0.0027	0.0785	0.0158	17.5	6.9	1.08
0.02668	0.2928	0.0112	0.0042	0.127	0.041	7.36	5.0	0.78
0.02668	0.4928	0.0102	0.0064	0.200	0.103	5.0	5.9	0.93

<sup>a</sup> [Allyl propionate] = 0.02 M; by varying [LiOAc] in some runs, the contribution of  $k'$  to  $k_{\text{obsd}}$  was found to be 6% at [LiOAc] = 1.0 M. In remaining runs [LiOAc] was 1.0 M and  $k'$  was calculated by assuming that its contribution to  $k_{\text{obsd}}$  was 6%. <sup>b</sup> [Pd]<sub>t</sub> = total Pd(II) concentration and [Cl]<sub>t</sub> = total chloride concentration. These values are known from analyses of stock solutions used to make runs. <sup>c</sup> The values calculated assuming the equilibria represented by eq 3 and 4, using values of 0.1 M<sup>-1</sup> from  $K_1$  and 2.56 M<sup>-1</sup> for  $K_D$ .

## Results

The rate expression for exchange was defined using the exchange of allyl propionate with acetic acid to give allyl acetate. All kinetic runs were made at 25° in acetic acid containing various amounts of PdCl<sub>2</sub>, LiCl, and LiOAc. To define the kinetics of the system completely, the mode of interaction of PdCl<sub>2</sub> with LiCl must be known. A recent spectral and molecular weight study<sup>6</sup> indicated that the following equilibria must be considered.



$K_1$  was found to have a value of 0.1 M<sup>-1</sup> and  $K_D$  a value of 2.56 M<sup>-1</sup> at 25°. For any set of reaction conditions the values of all the species present could be calculated from these equilibrium constants.

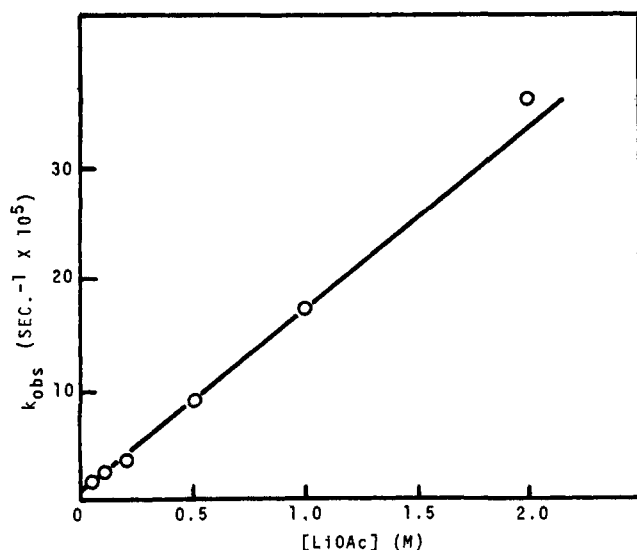


Figure 1. Plot of  $k_{\text{obsd}}$  vs. [LiOAc]; [Pd(II)]<sub>t</sub> = 0.02668 M, [Cl]<sub>t</sub> = 0.1428 M.

The LiOAc dependence was determined from kinetic runs at one set of total PdCl<sub>2</sub> and LiCl concentrations but at various LiOAc concentrations. Results are shown in Figure 1. The plot of the observed first-order rate constant ( $k_{\text{obsd}}$ ) vs. [LiOAc] is linear up to 2

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

M [LiOAc], indicating a reaction first order in [LiOAc]. However, the plot has a positive intercept, indicating that there is also a reaction zero order in [LiOAc].

The order in allyl propionate proved to be complicated. Although a given run was strictly first order, the observed first-order rate constant decreased as the initial allyl propionate concentration increased. However, below an initial concentration of about 0.05 M, the initial allyl propionate concentration had little effect on rate. Therefore, before defining this inhibition, the orders in Pd(II) and LiCl were determined using initial allyl propionate concentrations of 0.02 M. In the concentration range [Li<sub>2</sub>Pd<sub>2</sub>Cl<sub>6</sub>] = 0.0014–0.026 M, at a constant [LiCl] of 0.049 M, a plot of  $k_{\text{obsd}}$  vs. [Li<sub>2</sub>Pd<sub>2</sub>Cl<sub>6</sub>] was linear and passed through the origin, indicating a reaction first order in dimer concentration. To determine the order in [LiCl],  $k_{\text{obsd}}/[\text{Li}_2\text{Pd}_2\text{Cl}_6]$  was plotted vs. 1/[LiCl]. In the concentration range, [LiCl] = 0.015–0.2 M, this plot was also linear and passed through the origin. Thus at low initial allyl propionate the rate of exchange is given by eq 4.

$$\text{rate} = \frac{[\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{allyl propionate}]}{[\text{LiCl}]} \times (k' + k''[\text{LiOAc}]) \quad (4)$$

Values of  $k'$  and  $k''$  for some representative reaction conditions are shown in Table I.

Next the allyl propionate inhibition must be considered. As mentioned previously, the rate decreases as the initial allyl propionate concentration increases,

**Table II.** Effect of Allyl Acetate Concentration on Rate of Allyl Propionate Exchange<sup>a</sup>

[Allyl propionate], M	[Allyl acetate], M	$k_{\text{obsd}}$ , sec <sup>-1</sup> × 10 <sup>5</sup>
0.1		22.2
0.5		7.8
0.1	0.4	8.4

<sup>a</sup> [Pd(II)]<sub>t</sub> = 0.02668; [Cl]<sub>t</sub> = 0.1428.

although for a given run the reaction is strictly first order. For inhibition by allyl propionate alone, first-order kinetics would not be expected, since the concentration of the inhibitor decreases as the reaction proceeds. Thus, the value of  $k_{\text{obsd}}$  should increase as the reaction proceeds. However, first-order kinetics

**Table III.** Values of  $(k' + k''[\text{LiOAc}])$  Obtained by Correcting for Allyl Ester Inhibition<sup>a</sup>

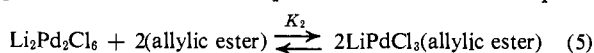
$[\text{Pd(II)}]_t$	$[\text{Cl}]_t$	[Allyl ester (ol)]	$[\text{Li}_2\text{Pd}_2\text{Cl}_6]$	$[\text{Li}_2\text{PdCl}_4]$	$[\text{LiPd}_2\text{Cl}_5\text{ol}]$	$k_{\text{obsd}}$ , $\text{sec}^{-1} \times 10^6$	$k' + k''$ , $[\text{LiOAc}]_t^b$ , $\text{sec}^{-1} \times 10^4$
0.02668	0.1428 <sup>c</sup>	0.02	0.012	0.00169	0.00104	22.9	7.8
0.02668	0.1428 <sup>c</sup>	0.1	0.0102	0.00156	0.0048	22.2	10.5
0.02668	0.1428 <sup>c</sup>	0.2	0.0083	0.00141	0.0087	17.2	10.2
0.02668	0.1428 <sup>c</sup>	0.3	0.00677	0.00128	0.012	12.4	9.0
0.02668	0.1428 <sup>c</sup>	0.5	0.0046	0.00106	0.0164	7.8	8.3
0.00667	0.0828 <sup>d</sup>	0.02	0.00270	0.000809	0.00050	5.19	9.5
0.00667	0.0828 <sup>d</sup>	0.1	0.00200	0.00070	0.00196	4.56	11.3
0.00667	0.0828 <sup>d</sup>	0.2	0.00129	0.00056	0.00353	2.87	11.0
0.00667	0.0828 <sup>d</sup>	0.3	0.00089	0.00047	0.00442	1.87	10.4
0.00667	0.0828 <sup>d</sup>	0.5	0.000473	0.00034	0.00538	1.1	11.5
0.02668	0.2928 <sup>e</sup>	0.02	0.0108	0.00415	0.00097	7.36	8.7
0.02668	0.2928 <sup>e</sup>	0.1	0.00914	0.00383	0.00456	6.96	9.7
0.02668	0.2928 <sup>e</sup>	0.2	0.00747	0.00347	0.00828	5.72	9.7
0.02668	0.2928 <sup>e</sup>	0.3	0.00612	0.00314	0.0113	4.49	9.4
0.02668	0.2928 <sup>e</sup>	0.5	0.00420	0.00261	0.0157	3.0	9.1

<sup>a</sup>  $[\text{LiOAc}] = 1.0 M$  for all runs. <sup>b</sup> This value =  $k_{\text{obsd}}[\text{LiCl}]/[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ . <sup>c</sup>  $[\text{LiCl}] = 0.049 \pm 0.005 M$  for this  $[\text{Pd(II)}]_t$  and  $[\text{Cl}]_t$ . <sup>d</sup>  $[\text{LiCl}] = 0.0492 \pm 0.003 M$  for this  $[\text{Pd(II)}]_t$  and  $[\text{Cl}]_t$ . <sup>e</sup>  $[\text{LiCl}] = 0.127 \pm 0.001 M$  for this  $[\text{Pd(II)}]_t$  and  $[\text{Cl}]_t$ .

would be expected if the product, allyl acetate, is also an inhibitor. This point was checked by making runs in which allyl acetate was initially present. Results are given in Table II. The value of  $k_{\text{obsd}}$  is seen to depend on total allylic ester concentration, so allyl acetate is approximately as effective as allyl propionate as an inhibitor.

Next the nature of the inhibition must be considered. The kinetics (see Discussion) require that the initial step in the reaction sequence is the formation of a dimeric  $\pi$  complex. One explanation is that  $\pi$  complex formation to give the initial dimeric  $\pi$  complex is occurring to an appreciable extent. If the formation constants for the propionate and acetate esters are approximately the same, first-order kinetics would be predicted, but a plot of  $1/k_{\text{obsd}}$  vs. allyl ester concentration should give a straight line at constant  $[\text{Pd(II)}]_t$  and  $[\text{Cl}]_t$  (see Experimental Section). However, as shown in Figure 2, these plots were not linear but curved upward.

The only other likely possibility appeared to be  $\pi$ -complex formation *via* eq 5. The kinetics require



that this monomeric  $\pi$  complex be unreactive, for if it were reactive, at low [allyl ester] the order in  $[\text{Li}_2\text{Pd}_2\text{Cl}_6]$  would be one-half.

To confirm that  $\pi$ -complex formation *via* eq 5 was occurring, an ultraviolet spectral study of the interaction of allyl propionate with  $\text{Li}_2\text{Pd}_2\text{Cl}_6$  in acetic acid was undertaken (see Experimental Section). The results were consistent only with this type of equilibrium. The value of  $K_2$  was found to be  $0.25 M^{-1}$ . Using this value of  $K_2$  to determine the actual concentration of  $[\text{Li}_2\text{Pd}_2\text{Cl}_6]$ , the value of  $k' + k''[\text{LiOAc}]$  now remains constant with changing [allyl propionate] at various  $[\text{Pd(II)}]_t$  and  $[\text{Cl}]_t$ , as shown in Table III.

The values of  $k'$ ,  $k''$ , and  $K_2$  for several allylic esters are shown in Table IV. For all but allyl propionate,  $K_2$  was calculated from the change in  $k_{\text{obsd}}$  with allylic ester concentration. An attempt was made to measure the rate of exchange of 2-cyclohexen-1-ol propionate. However, its exchange was very slow. Furthermore, it did not follow the rate expression given by eq 4. This system is presently under investigation.

**Table IV.** Values of  $k'$ ,  $k''$ , and  $K_2$  for Several Allylic Esters

Allylic ester	$K_2$ , $M^{-1}$	$k'$ , $\text{sec}^{-1}$ $\times 10^4$	$k''$ , $\text{sec}^{-1}$ $\times 10^3$
$\text{CH}_2=\text{CHCH}_2\text{O}_2\text{CC}_2\text{H}_5$	0.25	0.70	1.08
$\text{CH}_2=\text{CHCH}_2\text{O}_2\text{CCF}_3$	0.13	1.7	6.04
$\text{H}_3\text{CC}(\text{O}_2\text{CC}_2\text{H}_5)\text{HCH}=\text{CHCH}_3$	0.07	$2.4 \times 10^{-2}$	$2.3 \times 10^{-2}$
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{O}_2\text{CC}_2\text{H}_5$	0.14	$7 \times 10^{-4}$	$3.6 \times 10^{-4}$

Finally, the exchange of the propionate esters of crotyl alcohol and 3-buten-2-ol was studied as mentioned in the introduction; allylic isomerization of these unsymmetrical esters has been postulated to

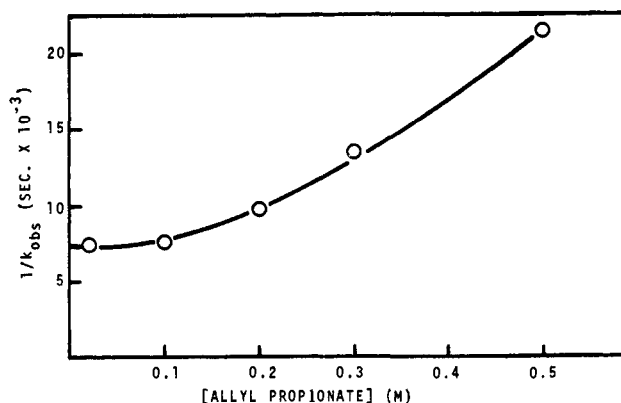
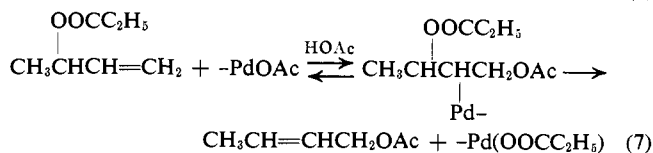
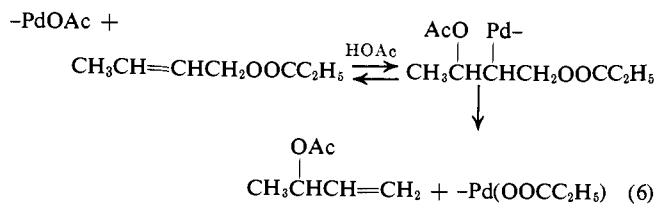


Figure 2. Plot of  $1/k_{\text{obsd}}$  vs. [allyl propionate];  $[\text{Pd(II)}]_t = 0.02668 M$ ,  $[\text{Cl}]_t = 0.1428 M$ .

proceed *via* an acetoxypalladation-deacetoxypalladation mechanism. If exchange occurs by the same mechanism, exchange should occur when, and only when, there is isomerization.

Actually, the reaction proved to be more complicated than that represented by eq 6 and 7. It was found that isomerization occurred both with exchange of acetate for propionate and without this exchange.<sup>7</sup> The important point for the purposes of the present study is that the exchange reaction, which has the rate expression represented by eq 4, follows eq 6 and 7.

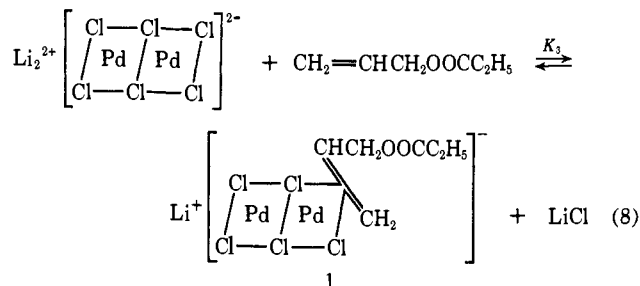
(7) The complete definition of this complicated system is the subject of the following paper in the series.



### Discussion

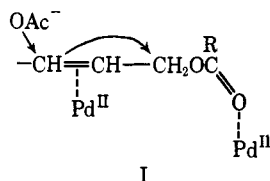
The rate expression for allylic exchange is identical with that previously found for vinyl acetate exchange.<sup>1</sup> The stereochemistry results for vinyl ester exchange indicate that it proceeds *via* an acetoxy-palladation-deacetoxy-palladation route. This similarity in rate expressions suggests that both reactions occur by analogous mechanisms. Further evidence that allylic exchange occurs by the addition-elimination mechanism is provided by the results with unsymmetrical allylic esters. Thus, as shown by eq 6 and 7, this mechanism predicts that exchange would occur when, and only when, isomerization occurs. This is the observed result. In addition to providing strong evidence for the acetoxy-palladation type of mechanism, this result eliminates  $\pi$ -allyl intermediates or SN2 attack. The last possibility could not be conclusively eliminated as a possibility for vinyl ester exchange.<sup>1</sup>

The first step in the reaction sequence is most likely the formation of a  $\pi$  complex in a rapid preequilibrium (eq 8). This would explain the chloride inhibition.

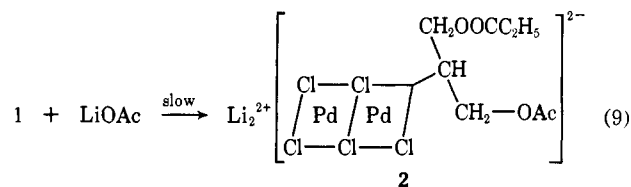


The next step would then be the addition of the elements of Pd(II) and acetate across the double bond to give 2.<sup>8</sup>

(8) A referee has suggested an interesting push-pull type of mechanism (I) involving attack of acetate on an olefinic carbon simultaneous with a double bond shift. The second Pd(II) of the dimer would assist in removing the propionate by complexing the propionate in an axial position. Although this mechanism explains the results with unsym-

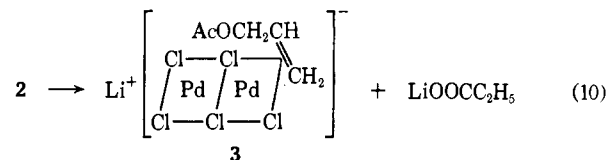


metrical esters, we believe it very unlikely, not only because it is inconsistent with other Pd(II) chemistry, but also for the following reasons. (1) Vinyl ester exchange, which cannot proceed by this mechanism, also requires the dimer to be the reactive species.<sup>1</sup> (2) Acetate ion in Pd(II) solutions containing chloride is, at most, very weakly complexed to Pd(II),<sup>1,6</sup> and organic acetate would have even less tendency to complex. (3) It would be difficult to rationalize the effect of allylic ester structure on rates shown in Table IV. Thus, why should methallyl propionate

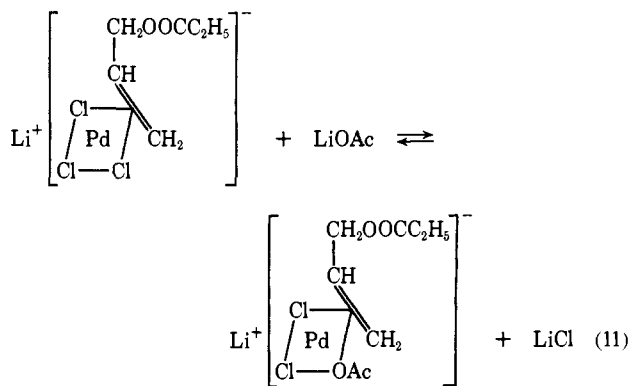


The exact nature of the LiOAc attack is not known. Since there is no second chloride inhibition as in the aqueous ethylene oxidation,<sup>9</sup> the complexing of the nucleophile acetate is not required. As discussed previously,<sup>1</sup> the acetate could be complexing by breaking a chloride dimer bridge prior to attack, the acetate could be complexing in a fifth coordination position on the Pd(II), or the acetate simply could be attacking from outside the coordination sphere.

The final step, of course, is the loss of the elements Pd(II) and propionate from 2 to give exchange.



Probably the most unexpected result of this study was the finding that monomeric  $\pi$  complexes (see eq 5), similar to those postulated as intermediates in the aqueous ethylene oxidation, are formed but are unreactive within experimental error. The reason for this lack of reactivity may be trans effects<sup>10</sup> which are present in 1 because of the complexing of the chloride trans to the olefin by the second Pd(II). However, it seems more reasonable to the author that such dramatic differences in reactivity would more likely result from electrostatic effects. Thus the negative charge in 1 is spread over two Pd(II)'s and most likely concentrated on the Pd(II) which is not complexed to the olefin, while in the monomeric  $\pi$  complex there would be much more concentration of charge on the Pd(II) complexed to the allylic ester. This line of reasoning would apply only if acetate were attacking from outside the coordination sphere or from a fifth coordination position. Electrostatic effects would cancel out in an equilibrium such as represented by eq 11 because the



same charge types are on both sides of the equation. Thus the evidence points to attack of the acetate from

react at 0.001 of the rate of allyl propionate? This result is, however, consistent with the acetoxy-palladation mechanism.

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

(10) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

**Table V.** Values of  $k_{\text{obsd}}$  under Various Reaction Conditions for Allyl Trifluoroacetate and Two Substituted Allylic Propionates<sup>a</sup>

[Pd(II)] <sub>0</sub> , M	[Cl] <sub>0</sub> , M	[Li <sub>2</sub> Pd <sub>2</sub> Cl <sub>6</sub> ], M	[LiCl], M	[LiOAc], M	[Allyl ester], M	$k_{\text{obsd}}^b$ , sec <sup>-1</sup> × 10 <sup>5</sup>
Allyl Trifluoroacetate						
0.02052	0.1388	0.0939	0.0573	0.01	0.2	2.6
0.02052	0.1388	0.0939	0.0573	1.0	0.02	95
0.02052	0.1388	0.0939	0.0573	1.0	0.5	43
3-Penten-2-ol Propionate						
0.02668	0.1428	0.0125	0.0488	1.0	0.02	0.74
0.02668	0.1428	0.0125	0.0488	1.0	0.1	0.71
0.02668	0.1428	0.0125	0.0488	1.0	0.5	0.41
0.0224	0.1368	0.01034	0.0533	0.1	0.1	0.096
Methallyl Propionate						
0.02668	0.1428	0.0125	0.0488	1.0	0.02	1.1 × 10 <sup>-2</sup>
0.02668	0.1428	0.0125	0.0488	1.0	0.5	4.9 × 10 <sup>-3</sup>
0.0224	0.1368	0.01034	0.0533	0.1	0.1	8.2 × 10 <sup>-4</sup>
0.0224	0.1368	0.01034	0.0533	1.0	0.02	8.4 × 10 <sup>-3</sup>
0.0224	0.1368	0.01034	0.0533	1.0	0.1	7.1 × 10 <sup>-3</sup>

<sup>a</sup> Values of [Li<sub>2</sub>PdCl<sub>4</sub>] and [Li<sub>2</sub>Cl<sub>2</sub>] can readily be calculated from quantities given in the table. <sup>b</sup> Observed first-order rate constant assuming that the reaction is first order in allylic ester.

outside the coordination sphere of the Pd(II). This conclusion suggests that acetoxy-palladation would have trans stereochemistry. Since stereochemical results on exchange of vinyl chlorides with acetate indicate that acetoxy-palladation and dechloropalladation have opposite stereochemistries,<sup>3,11</sup> dechloropalladation (and chloropalladation, because of the principle of microscopic reversibility) would have cis stereochemistries. This reasoning is in keeping with the relative affinities of chloride and acetate for Pd(II) as well as recent stereochemical results<sup>12</sup> which suggest that acetoxy-palladation is trans. In the presence of chloride, Pd(II) is not complexed to any extent by acetate.<sup>6,13</sup> Thus, chloride would most likely attack cis since it is in the coordination sphere, while acetate would be required to attack trans since it is not.

The effect of structure on rate, which is qualitatively the same as that found earlier for vinyl ester exchange,<sup>1</sup> indicates that steric factors are very important in the acetoxy-palladation reaction. Quantitatively the effect is greater for vinyl ester exchange. This is reasonable, since the vinyl ester double bond has the acetate group in addition to the methyl group and is thus more crowded. Comparison of the rate constants for methallyl propionate and 3-penten-2-ol propionate indicates that disubstitution on the carbon to which the Pd(II) adds retards the reaction more than monosubstitution on each carbon of the double bonds. This result is in keeping with a large steric requirement for the Pd(II) dimer, which is quite reasonable. It is interesting that steric effects on  $K_2$  are much less than on rates. The magnitude of the effects is similar to that found for the aqueous olefin oxidation.<sup>14</sup>

The higher rate constant for allyl trifluoroacetate gives some insight into the electronic effects on acetoxy-palladation. However, the acceleration could occur from any of several factors. Thus the electron-withdrawing CF<sub>3</sub> group could result in the  $\pi$ -complex formation in the first step being more favorable (eq 8).

- (11) E. W. Stern, *Catal. Rev.*, **1**, 73 (1967) (see comment on p 125).  
 (12) P. M. Henry and G. W. Ward, *J. Amer. Chem. Soc.*, **93**, 1494 (1971).  
 (13) P. M. Henry, *Prepr., Amer. Chem. Soc., Div. Petrol. Chem.*, **14** (4), F3 (1969).  
 (14) P. M. Henry, *J. Amer. Chem. Soc.*, **88**, 1595 (1966).

However, this does not seem probable, since the value of  $K_2$  is actually lower than for allyl propionate. Since inductive effects for  $\pi$ -complex formation *via* eq 5 and 8 would be expected to be in the same direction, this does not seem to be a likely possibility.

A second possibility is elimination of trifluoroacetate from the intermediate **2**. However, since the tendencies of propionate and acetate to be eliminated from **2** would be equal, the largest rate acceleration expected would be a factor of only **2**, while the acceleration is a factor of over 5.

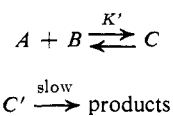
Thus it appears that the rate acceleration must occur in the acetoxy-palladation step. This conclusion is reasonable since electron-withdrawing groups would make the olefin more positive and thus more susceptible to nucleophilic attack.

## Experimental Section

**Materials.** Sources of most chemicals and preparation of stock solutions have been described previously.<sup>1</sup> The allylic esters were prepared by esterification of the commercially available alcohols with propionic anhydride using pyridine as catalyst. When trifluoroacetic anhydride was used, no catalyst was required.

**Kinetic Runs.** Reaction mixtures were prepared by mixing known amounts of Li<sub>2</sub>Pd<sub>2</sub>Cl<sub>6</sub>, LiCl, and LiOAc stock solutions of known composition and diluting to a given volume (usually either 1.0 or 5.0 ml). The reaction mixture was placed in a 25° bath for about an hour and the run started by adding a given amount of allyl ester. Samples were analyzed by gas chromatography using a 6-ft 20% Carbowax 20 M on ABS (70-80 mesh) column programmed from 80 to 200° at 7.5°/min. Helium flow rate was 60 ml/min. Samples were injected usually without work-up, although in some cases, the organic products were extracted into methylene chloride before injection to demonstrate that both procedures gave the same rates.

The kinetic scheme for inhibition *via* eq 8 is readily derived as follows. Let  $A = [\text{Li}_2\text{Pd}_2\text{Cl}_6]$ ,  $A_0 = [\text{Li}_2\text{Pd}_2\text{Cl}_6]$  before alkyl ester addition,  $B =$  total allyl ester, exchanged and unexchanged,  $B' =$  propionate ester,  $C = [\text{I}] + [\text{3}]$ , and  $C' = [\text{I}]/C$ .



where  $K'$  is the same for propionate and acetate esters.

$$K' = C/AB = C/(A_0 - C)B$$

Rearranging

$$C = KA_0B/(1 + K'B)$$

but since

$$C'/C = B'/B$$

$$dB'/dt = KC' = kK'A_0B'/(1 + K'B)$$

Since  $A_0$  is constant, this rate expression integrates to a first-order expression, where

$$k_{\text{obsd}} = kK'A_0/(1 + K'B)$$

Inverting we have

$$1/k_{\text{obsd}} = 1/kK'A_0 + B/kA_0$$

Thus a plot of  $1/k_{\text{obsd}}$  vs.  $B$  should be a straight line with  $1/kK'A_0$  as intercept and  $1/kA_0$  as slope. This treatment is an approximation in that it does not consider the equilibrium represented by eq 2. However, this approximation is not serious, since under the reaction conditions of Figure 2, 95% of the Pd(II) is in the form of dimer. In any case, this equilibrium would cause the plot to curve downward.

Rate data for the allylic esters other than allyl propionate from which the values of  $K_2$ ,  $k'$ , and  $k''$  in Table IV were calculated are listed in Table V.

**Ultraviolet Spectra Study.** The procedure was the same as described previously.<sup>6</sup> The computer program which treated the earlier data was altered to simultaneously include equilibria such as that represented by eq 5 and 8.

Absorbancies were determined at wavelengths of 245, 255, 269, 280, and 340 nm for 34 solutions in which  $[\text{Pd(II)}]_t$  was varied from 0.00112 to 0.012 M,  $[\text{Cl}]_t$  from 0.029 to 0.4 M, and allyl propionate from 0.05 to 2.0 M. Absorbancies at all five wavelengths were used in the nonlinear regression program simultaneously. The value of  $K$  for eq 5 was calculated to be  $0.26 \cdot M^{-1}$  with correlation coefficients of 0.02 to 0.08, while the  $K$  for eq 8 was found to give a very poor fit to the data. If the data are calculated assuming that both eq 5 and 8 are occurring simultaneously, a value of  $0.11 M^{-1}$  is obtained for  $K_2$ , while the value for  $K_3$  is about 0.08. However, the nature of the equilibria is such that the monomeric  $\pi$  complex is in at least fivefold excess over **1** under all experimental conditions. In any case, little reliance can be placed on these results. A much more detailed study would be required to determine if  $K_3$  is large enough to be calculated, and even then, the reliability of the data in such a complicated system would be doubtful.

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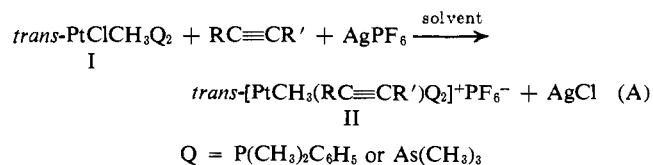
## Cationic Acetylenic Platinum(II) Compounds and Their Derivatives. III. Reactions of Platinum(II) Stabilized Carbonium Ions

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**Abstract:** Cationic acetylenic platinum complexes show reactivity characteristic of carbonium ions and are the reactive intermediates in the formation of acetylide, acyl, alkoxy-carbene, vinyl, vinyl ether, and cyclobutadiene complexes. The carbonium ion reactivity of the coordinated acetylene is dependent on (i) the substituents on the acetylene, (ii) the ligands on the platinum cation, and (iii) the availability of a nucleophile. Similar mechanisms involving transition metal induced carbonium ions may provide a general explanation for many transition metal catalyzed reactions of acetylenes and olefins.

Our interest in both acetylenic<sup>1-3</sup> and cationic<sup>4</sup> complexes of platinum(II) initiated a study of reaction A, which might lead to cationic acetylenic complexes II.



Although such complexes of platinum(II) are not unknown [e.g.,  $\{\text{PtX(en)(ac)}\}_n^+$  where  $n = 1$  or  $2$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{ or } \text{I}$ ,  $\text{ac} = (\text{CH}_3)_2\text{OHCC}\equiv\text{CC}(\text{CH}_3)_2\text{OH}$  and  $\text{en} = \text{ethylenediamine}^5$ ], the complexes II are

ideally suited for spectroscopic studies valuable in the elucidation of both the trans influence of the acetylene and the nature of the platinum-acetylene bond. However, it soon became apparent that the products obtained from (A) were dependent on the nature of the acetylene, the ligands Q, the solvent, and the reaction conditions.

The reaction of dialkyl or diaryl acetylenes in methanol or acetone solvent did in many instances yield II,<sup>6,7</sup> while monoalkyl acetylenes,  $\text{RC}\equiv\text{CH}$ , in methanol gave<sup>6,8</sup> cationic alkoxy-carbene complexes III according to (B).

Similarly, phenylacetylene gave a benzyl alkoxy-carbene complex, III, when  $\text{Q} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ , but

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