

Mechanistic Aspects of the Carbonylation of Allyl Chloride Catalysed by π -Allylic Palladium Complexes

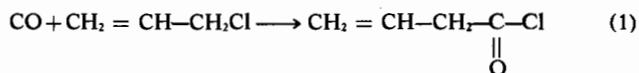
H. C. Volger, K. Vrieze, J. W. F. M. Lemmers, A. P. Praat,
and P. W. N. M. van Leeuwen

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The mechanism of the carbonylation of allyl chloride to vinyl acetyl chloride catalysed by π -allylic palladium complexes has been investigated in some detail. An earlier observation that on addition of group V donor ligands (L) the reaction rate is a maximum for L/Pd = 0.5 (ref. 2) has been confirmed. It has been found that the value of the rate depends on the nature of L. The present results combined with those of an NMR investigation of the catalytic system induce us to propose a trinuclear palladium species as the catalytically active species.

Introduction

The carbonylation of allyl chloride to vinyl acetyl chloride



catalysed by π -allylic palladium complexes has been reported independently by Tsuji and coworkers¹ and by Medema, Kohll, and van Helden of our laboratory.² The reaction is not restricted to allyl chloride; substituted allyl chlorides and bromides, alcohols and ethers react in a similar fashion. The reaction conditions reported by both groups are about the same: carbon monoxide pressure 90 atm; temperature 80-90°C; benzene or chloroform as solvent. The yields are nearly quantitative (80-100%).

Medema, Kohll and van Helden also presented some kinetic data on this insertion reaction. They reported that the rate of carbon monoxide consumption is first order in both allyl chloride and bis(π -allylpalladium chloride) concentrations and second order in the carbon monoxide pressure. They mentioned a very interesting effect of the addition of triphenylphosphine on the rate of the reaction; a maximum rate (1.7 times the rate in the absence of triphenylphosphine) was observed for L/Pd = 0.5. Clearly, this observation has important consequences for the mechanism of the carbonylation reaction.

In order to shed more light on the mechanism we have studied the effect of various phosphines and arsines on the rate of consumption of carbon monoxide. In addition and as part of our extensive NMR investigation of π -allylic palladium complexes in the presence of phosphines and arsines⁴ we investigated these systems in combination with carbon monoxide* and with olefins (e.g. allyl chloride).

As a result the previously suggested mechanism has been refined. The insertion of carbon monoxide is proposed to be rate determining and assumed to occur via a σ -allyl intermediate complex. Factors which promote the required π - σ allyl rearrangement will be discussed. The maximum rate observed for L/Pd = 0.5 can be satisfactorily explained via the formation of a trinuclear complex in which the required π - σ -allyl rearrangement is facilitated.

Experimental Section

The π -allylpalladium complexes were prepared by reported standard methods^{1,2} and recrystallized from chloroform. The carbonylation experiments were carried out in a mechanically stirred, double-walled autoclave of 500 ml connected with a thermostat and equipped with baffles, a thermocouple well and a precision manometer. A solution of 30 ml of allyl chloride (0.4 mole), 1.8 g of bis(π -allylpalladium chloride) (4.86 mmole) and varying amounts of a group V donor ligand (0-10 mmole) in benzene or chloroform (150 ml) was heated at 87°. Then, carbon monoxide was rapidly introduced without stirring the homogeneous solution until the required pressure was reached. By stirring the reaction was started; the pressure drop was measured against time.

In some experiments the yield of vinyl acetyl chloride was determined by GLC after treatment with methanol; it was found to be equal within experimental error (5%) to the amount of carbon monoxide consumed.

The NMR spectra were recorded on a Varian spectrometer (HA 100 or DP 60) using CDCl_3 as solvent

(1) J. Tsuji, J. Kiji, S. Imamura, and M. Morikawa, *J. Amer. Chem. Soc.*, **86**, 4350 (1964).

(2) D. Medema, R. van Helden, and C. F. Kohll, *Inorg. Chim. Acta*, **3**, 255 (1969).

(3) J. Powell and B. L. Shaw, *J. Chem. Soc.*, (A), 1850 (1967).

* Powell and Shaw recently reported some qualitative results of an NMR investigation of solutions of carbon monoxide and bis(π -methallylpalladium chloride).³

(4) K. Vrieze, H. C. Volger, and P.W.N.M. van Leeuwen, *Inorg. Chim. Acta Rev.*, **3**, 109 (1969).

and TMS as internal reference. The reaction mixtures of the π -allylic complexes and carbon monoxide were prepared by saturation of a solution of the appropriate complex at -75° with carbon monoxide of one atmosphere.

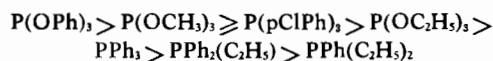
The rates of the π - σ reaction were calculated by the slow-exchange-limit approximation.⁵ The infrared spectra of solutions of the π -allylic complexes and carbon monoxide in CDCl_3 were measured in a thermostatted cell in the range -80° to $+25^\circ$ on a Beckman IR 7.

Results

Kinetic study of the insertion of CO. The kinetics of the carbonylation of allyl chloride to vinyl acetyl chloride under the reaction conditions previously reported (87°C ; 90 atm CO; catalytic amounts of bis(π -allylpalladium chloride); benzene as solvent)² were reinvestigated. We obtained confirmation of the earlier findings² that in the absence of triphenylphosphine the rate is first order in both the allyl chloride and catalyst concentrations. The reported second-order dependence on the pressure of carbon monoxide could roughly be confirmed. In consequence, the rate expression can be written as

$$-\left[\frac{d[\text{CO}]}{dt}\right]_{t=0} = k_1 [\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}] [(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}_2] [\text{pco}]^2 \quad (2)^*$$

Next we investigated the effect of a series of group V donor ligands on the initial rate at a constant concentration of bis(π -allylpalladium chloride). Identical results were obtained, no matter whether the catalyst solution was prepared from the ligand and bis(π -allylpalladium chloride) or from the appropriate amounts of $(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}(\text{L})$ and bis(π -allylpalladium chloride). The effect of L on the rate depended on its nature and its concentration. For most of the ligands L investigated, the rate was a maximum at a ratio $\text{L}/\text{Pd} = 0.5$, just as was found for triphenylphosphine.² The value of this maximum depended on the structure of L, as is illustrated in Figure 1. The following sequence of decreasing order in reactivity was observed for the phosphorus-containing ligands:



The first and the last member of the series differ in reactivity by a factor of four (Figure 1).

Triphenylarsine and tris(*p*-dimethylaminophenyl)arsine show roughly the same activity as tris(*p*-chlorophenyl)phosphine and diphenylethylphosphine, respectively. Tris(dimethylamino)phosphine — a ligand with very poor coordinating ability — did not display any activity; PCl_3 , SnCl_2 and SbPh_3 act as inhibitors rather than as catalysts.

* It should be emphasized that eq. (2) is only valid for the carbonylation in the absence of a group V donor ligand.
(5) A. Allerhand, H. S. Gutowski, J. Jonas, and R. A. Meisner, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).

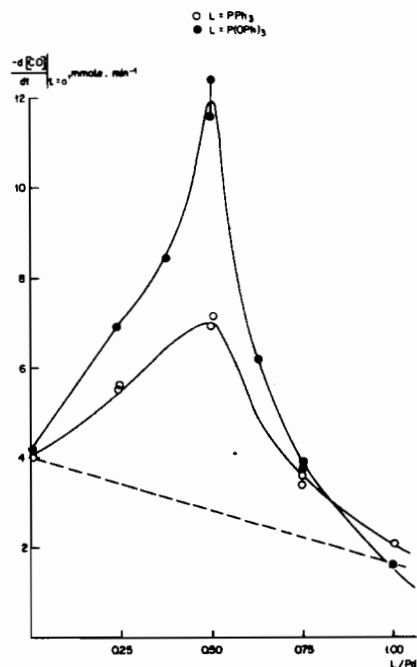
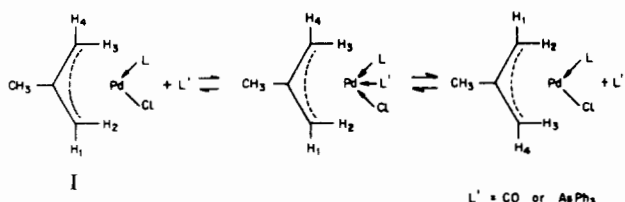


Figure 1. Dependence of the initial rate of carbon monoxide consumption on the ratio of L/Pd. L = PPh_3 or P(OPh)_3 . Reaction conditions: 87° , 90 atm CO, 150 ml of benzene, 2.7 mole l^{-1} of allyl chloride, 4.86 mmole of $(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}_2$ or 9.72 meq palladium

NMR spectroscopic investigation. Triphenylphosphine π -methallylpalladium chloride (I, L = PPh_3), when dissolved in CDCl_3 , does not react with carbon monoxide (1 atm) in the temperature range of -70° to $+20^\circ$ according to the NMR spectra. In contrast, the analogous triphenylarsine complex (I, L = AsPh_3) reacts with carbon monoxide, as was inferred from the fact that the *anti* protons (2 and 3) and the *syn* protons (1 and 4) became mutually magnetically equivalent.



The interchange may occur via a five-coordinative associative complex, which is formed either by coordination of CO or by coordination of free triphenylarsine (formed from I by displacement by CO). In such a five-coordinative complex rotation of the allyl group in its own plane is allowed by virtue of pseudo trigonal symmetry. The intermediate was not detectable by NMR or IR. It may well be that for L = PPh_3 a similar interchange reaction occurs, although too slow relative to the NMR time scale to be noticeable.

Upon introduction of carbon monoxide (1 atm) at -77°C the originally yellow solution of bis(π -methallylpalladium chloride) in CDCl_3 turns red; the NMR spectrum (Figure 2) shows the presence of an

Table I. Chemical shifts of the Allylic Protons (in ppm from TMS) of $(\pi\text{-C}_3\text{H}_5)\text{PdCl}(\text{PPh}_3)$, $[(\pi\text{-C}_3\text{H}_5)\text{PdCl}]_2$ and its carbon-monoxide derivative (in CDCl_3)

Compound	°C	Proton 1	Proton 4	Proton 2	Proton 3	CH_3
$(\pi\text{-C}_3\text{H}_5)\text{PdCl}(\text{PPh}_3)$	-35	two doublets 4.50 $J_{\text{P-1}}=6.5$ c/s $J_{1-4}=2.9$ c/s	doublet 2.89 $J_{1-4}=2.9$ c/s	doublet 3.62 $J_{\text{P-2}}=9.8$ c/s	singlet 2.80	singlet 1.96
$[(\pi\text{-C}_3\text{H}_5)\text{PdCl}]_2$	+20	singlet 3.85	singlet 3.85	singlet 2.86	singlet 2.86	singlet 2.12
$[(\pi\text{-C}_3\text{H}_5)\text{PdCl}]_2 + \text{CO}$	-77	doublet 4.75 $J_{1-4}=2.9$ c/s	doublet 4.65 $J_{1-4}=2.9$ c/s	singlet 3.72	singlet 3.35	singlet 2.12
$(\pi\text{-C}_3\text{H}_5)\text{PdCl}(\text{PPh}_3)$	-50	triplet 4.78 $J_{\text{P-1}}=7.0$ c/s $J_{1-5}=7.0$ c/s	doublet 3.13 $J_{1-5}=6$ c/s	quartet 3.77 $J_{\text{P-2}}=10.0$ c/s $J_{2-5}=13.0$ c/s	doublet 2.88 $J_{3-5}=10$ c/s	
$[(\pi\text{-C}_3\text{H}_5)\text{PdCl}]_2$	+20	doublet 4.11 $J_{1-5}=6.5$ c/s	doublet 4.11 $J_{4-5}=6.5$ c/s	doublet 3.02 $J_{2-5}=12.5$ c/s	doublet 3.54 $J_{3-5}=12.5$ c/s	
$[(\pi\text{-C}_3\text{H}_5)\text{PdCl}]_2 + \text{CO}$	-78	doublet 4.82 $J_{1-5}=7$ c/s	doublet 4.82 $J_{4-5}=7$ c/s	doublet 3.87 $J_{2-5}=12$ c/s	doublet 3.54 $J_{3-5}=11$ c/s	

asymmetrically coordinated π -methylallyl group. The complex formed is supposed to be $[(\pi\text{-C}_4\text{H}_7)\text{PdCl}(\text{CO})]_n$ (III). For $n = 1$, the palladium is four-coordinated; in the case of a dimeric complex ($n = 2$), five coordination is required.

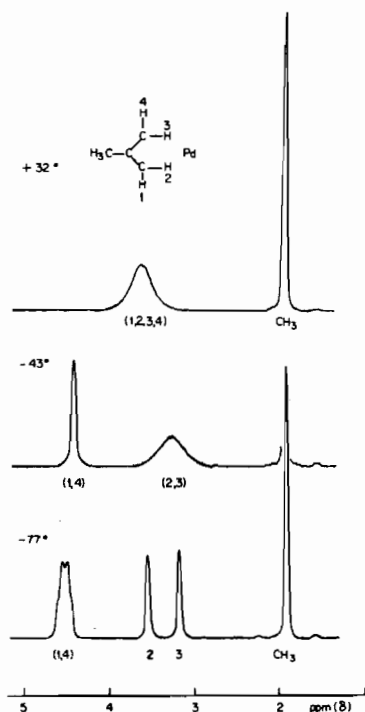
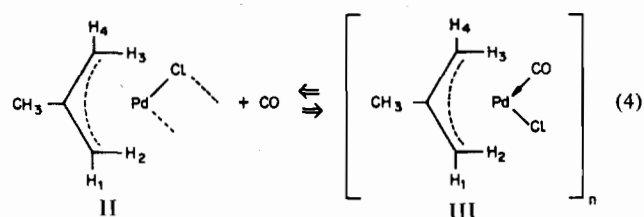


Figure 2. Temperature dependence of the NMR signals of protons 1, 2, 3 and 4 of $[(\pi\text{-C}_3\text{H}_5)\text{PdCl}(\text{CO})]_2$ in CDCl_3 .

The NMR data together with those of the original

π -methylallyl complexes are recorded in Table I.



The infrared spectrum of the reaction mixture showed an intense absorption at 2132 cm^{-1} ; a much less intense one at the same frequency fortuitously occurs for a solution of carbon monoxide in CDCl_3 . The observed frequency suggests that the carbonyl group must be very loosely coordinated.

Gradual increase in temperature gives rise to broadening and coalescence of the signals of the allylic protons to two signals (for the *syn* and *anti* protons, respectively) and finally to the appearance of one signal. The upfield shift of this signal compared with the calculated weighted mean of the four original signals is ascribed to the presence of bis(π -methylallylpalladium chloride) II, formed by decomposition of the carbonyl complex III. At still higher temperatures ($>32^\circ\text{C}$) a further upfield shift of the collapsed signal is observed to 3.35 ppm, which is the weighted mean of the signals of the allylic protons in II. Consequently the decomposition is virtually quantitative under these conditions.

The loss of carbon monoxide suggests that the NMR changes just mentioned arise from the occurrence of a carbon monoxide exchange process. Such interchange processes have been reported to be effected by ligands like triphenylphosphine and triphenylarsine and the mechanism involved has been interpreted as a bimolecular exchange process as is pic-

tured in eq. 4 ($n = 2$).⁴ It should be noted that the rate of interchange of *syn* and *anti* protons has to be considered a lower limit for the actual rate of exchange of carbon monoxide.

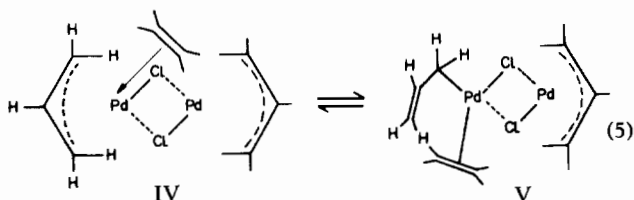
Another series of experiments to be mentioned is the NMR spectroscopic investigation of CDCl_3 solutions containing bis(π -allylpalladium chloride) and various olefins. The olefins studied (hexene-1, octene-2, cyclooctadiene-1,5 allyl chloride, styrene, allyl acetate and 2,3-dimethylbut-2-ene) do not form complexes in detectable amounts. However, addition of these olefins results in an interchange of the *syn* and *anti* protons of the allylic ligand at appreciably lower temperatures than in the absence of the olefins. This observation indicates the formation of a complex — albeit in a very low concentration — between bis(π -allylpalladium chloride) and the olefins.

The line broadening does not depend on the concentration of the dimeric complex and is proportional to the concentration of the olefin. Thus $1/\tau(\cdot)$ [olefin] or

$$\frac{-d[(\pi\text{-allyl PdCl})_2]}{dt} = k_2[(\pi\text{-allyl PdCl})_2][\text{olefin}]$$

The second-order rate constants at 40° are in the order of 1-2000 l.mole⁻¹ sec⁻¹. The rate of this intramolecular rearrangement increases in the order 2,3-dimethylbut-2-ene < styrene, allyl acetate, allyl chloride < n-hexene-1, n-octene-2 < cyclooctadiene-1,5, which roughly parallels the stability order of olefin complexes.

The structure of the intermediate complex is presumably IV:



which can undergo a π - σ allyl rearrangement, thereby giving rise to the magnetical equivalence of the allylic protons.

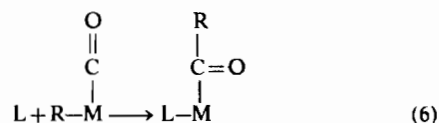
Again it should be mentioned that the coordination of the olefin has to be at least as fast as the rate of the proton interchange made observable by the NMR technique. More specifically the rate of the coordination of allyl chloride towards bis(π -allylpalladium chloride) is much faster than the overall rate of the carbonylation of allyl chloride. Medema, Kohl, and van Helden have previously considered the coordination of allyl chloride to be the rate-determining step in the carbonylation reaction. In view of our results, this seems rather unlikely, even if one bears in mind that under carbonylation conditions allyl chloride coordinates to a palladium species different from bis(π -allylpalladium chloride) as we used in our model system.

Discussion

The main emphasis in this discussion will be laid

on the function of bis(π -allylpalladium chloride) and the effect of the group V donor ligands on the rate.

One of the essential steps in the carbonylation of allyl chloride must be the insertion of carbon monoxide. Accumulated experimental data on a variety of alkyl/transition-metal systems have indicated that the insertion reaction involves an attack of a ligand L on a complex containing a σ -bonded alkyl group and a coordinated carbon monoxide molecule in mutual *cis* position, thereby effecting a migration of the alkyl group towards the carbonyl group.⁶

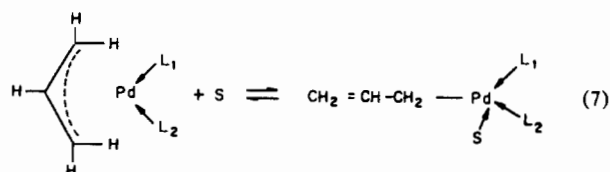


A theoretical analysis of the migration has been published by Cossee.⁷

The mechanistic picture makes it likely that in the carbonylation of allyl chloride the insertion involves a migration of a σ -allyl group towards the carbonyl group, effected either by carbon monoxide or by allyl chloride.

Only π -bonded allyl ligands have been encountered in crystalline palladium-allyl complexes. However, it is well established that in solution π - σ interconversions can occur.⁴ The stabilization of the allyl group, whether π - or σ -bonded, as governed by ligands is reasonably well understood.^{4,8}

The formation of the σ -allyl species is facilitated if the two ligands L_1 and L_2 coordinated to palladium differ most widely in their respective *trans* effect and if one of the ligands exhibits a good electron-donating capacity:



where S stands for solvent or another ligand.

The difference in *trans* effect between the ligands L_1 and L_2 can be enhanced by adding a second complex to the system, which is capable of coordinating with one of the ligands.⁸ An example is provided in the paper by Vrieze *et al.*⁹ on the system π -methallylpalladium triphenylphosphine chloride ($(\pi\text{-C}_4\text{H}_7)\text{Pd}(\text{PPh}_3)\text{Cl}$) and the parent dimer. The π -methallyl group in this complex did not undergo a $\pi \rightleftharpoons \sigma$ interconversion fast enough to be detectable by NMR line-broadening technique. On addition of bis(π -methallylpalladium chloride) a rapid $\pi \rightleftharpoons \sigma$ interconversion was observed at the terminal carbon of the allyl ligand *cis* with respect to the phosphine ligand. The

(6) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **86**, 3994, 5043 (1964).

— K. Noack and F. Calderazzo, *J. Organomet. Chem.*, **10**, 101 (1967).

(7) P. Cossee, *Rec. Trav. Chim.*, **85**, 1151 (1966).

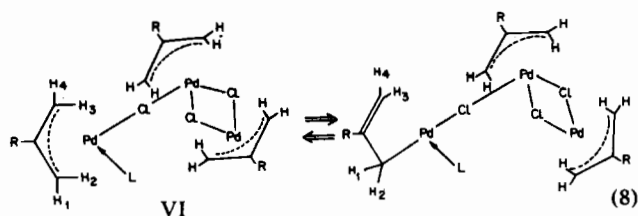
(8) K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, **7**, 345 (1968).

— K. Noack, *J. Organomet. Chem.*, **12**, 181 (1968).

(9) P. W. N. M. van Leeuwen and A. P. Praat, *J. Organometal. Chem.*, **21**, 501 (1970).

(9) K. Vrieze, P. Cossee, A. P. Praat, and C. W. Hilbers, *J. Organomet. Chem.*, **11**, 353 (1968).

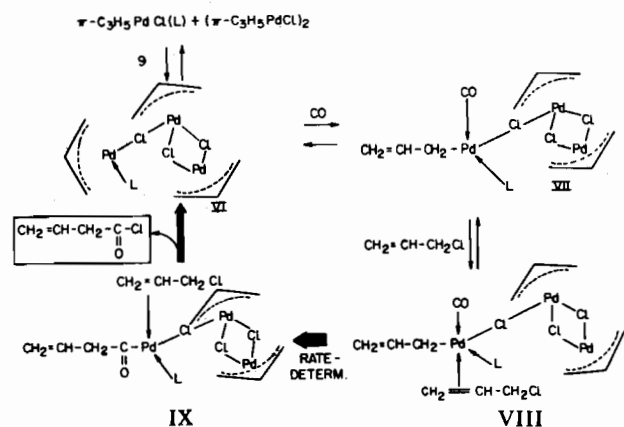
reaction was visualized as follows:



Coordination of the chloride of the monomeric complex by the palladium of the dimeric complex causes withdrawal of electrons from the palladium bearing the ligand L, thereby enhancing the difference in *trans* effect between L and Cl and facilitating the formation of a σ -allyl species (eq. 8). Rotation about the σ -carbon palladium bond interconverts protons 1 and 2.

The catalytic activity observed in the carbonylation of allyl chloride with the system bis(π -allylpalladium chloride)-group V donor ligand can be satisfactorily attributed to the same trinuclear complex. The concentration of this trinuclear species is greatest for a ratio of L/Pd = 0.5 as is outlined in the appendix. The only condition that had to be fulfilled in the derivation of the relationship between L and bis(π -allylpalladium chloride) is that the total concentration of $(\pi-C_3H_5)Pd(Cl)(L)$ and $[(\pi-C_3H_5)PdCl]_2$ has to account for virtually all of the palladium present in the system*. The general validity of the derivation does not depend on the actual value of the equilibrium constant (9).

Assuming that the insertion occurs at the palladium bearing the ligand L, we may visualize the insertion as follows:



Coordination of carbon monoxide gives rise to a (σ - or π -)allyl-palladium carbonyl species (VII), which subsequently coordinates allyl chloride to give a σ -allyl species (VIII). In a rate-determining step the σ -allyl group migrates to give an allylcarbonyl palladium complex, which decomposes into the original trinuclear complex (VI) and the final product vinyl acetyl chloride.

* Complexes like $(\pi-C_3H_5)_2Pd(Cl)(CO)$ or $[(\sigma-C_3H_5)_2Pd(Cl)(CO)]_n$ with $n=1$ or 2 , each having the required vacant coordination site for the formation of a chloride bridge with $(\pi-C_3H_5)_2Pd(Cl)(L)$ have to be ruled out since kinetic data for systems in the absence of L indicate that the major part of the $[(\pi-C_3H_5)_2PdCl]_2$ originally added is still present as such under carbonylation conditions (ref. 2).

The nature of the ligand has surprisingly little influence on the reaction rate. Moreover, the observed order of decreasing activity of the ligand $P(OPh)_3 > P(OCH_3)_3 \geq P(pClPh)_3 > P(OC_2H_5)_3 > PPh_3 > PPh_2(C_2H_5) > PPh(C_2H_5)_2 > PPh_2(pBrPh)$ does not parallel the order of decreasing σ -donor capacity as one would anticipate, considering the $\pi \rightleftharpoons \sigma$ -allyl conversion to be one of the key steps. The picture is apparently complicated by the fact that the overall result is composed of the effects of the ligand on three equilibrium constants and one rate constant rather than on one single equilibrium. Counteracting capabilities of the ligand are required to enhance every separate reaction step in this scheme. On the one hand the formation of a σ -allylpalladium species is facilitated by a strong donating ligand; on the other hand an increase of the effective positive charge on the palladium atom, favouring the extension of the coordination to the metal, is brought about by strong π -acceptor ligands such as phosphites.

According to the scheme, the overall rate of the carbonylation reaction should be first order in carbon monoxide. Experimental evidence for this suggestion is not yet available.

For carbonylation in the absence of L, the overall rate expression (eq. 2) shows that two molecules of carbon monoxide are involved in the pre-equilibria prior to or in the rate-determining step. The mechanism proposed by Medema, Kohll, and van Helden² indeed accounts for all the experimental details for this case.

Our interpretation of the carbonylation reaction in the system $(\pi-C_3H_5)_2Pd(Cl)$ group V ligand differs from the one proposed by Medema, Kohll, and van Helden. They propose a binuclear rather than a trinuclear complex as catalytically active species. In their mechanistic proposal they have ignored the formation of $(\pi-C_3H_5)_2Pd(Cl)(L)$. We feel that this is not justifiable even under carbonylation conditions. In this connexion it should be pointed out that bis(π -allylpalladium chloride) is assumed to be present as such even under carbonylation conditions² in the absence of L and furthermore that the coordination of L towards palladium is quantitative according to NMR observation.

We are well aware of the simplifications made in our mechanistic interpretation. A number of possible intermediate complexes have also been ignored on purpose. There is no theoretical or experimental evidence that the concentrations of these species are relatively large.

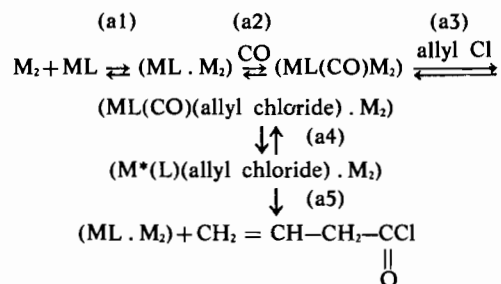
Summarizing, we have attempted to rationalize the experimental data available for the carbonylation of allyl chloride in terms of a trinuclear catalytically active species. Migration of a σ -allyl group to give a vinyl acetyl group is considered to be rate determining.

APPENDIX

Derivation of the Relationship between the Concentrations of the Active Catalyst(VI) and the Ligand.

Using the abbreviations M_2 for $(\pi-C_3H_5)_2Pd(Cl)_2$ and

ML for $\pi\text{-C}_3\text{H}_5\text{PdCl(L)}$, we may rewrite the scheme (p. 12) as follows:



The general starting conditions for these equilibria are

$$\begin{aligned}
 \text{(a6)} \quad [\text{M}_2]_0 &= [\text{M}_2] + \frac{1}{2} [\text{ML}] + \frac{3}{2} [\text{ML} \cdot \text{M}_2] + \\
 &\frac{3}{2} [\text{ML}(\text{CO}) \cdot \text{M}_2] + \frac{3}{2} [\text{ML}(\text{CO})(\text{allyl Cl}) \cdot \text{M}_2] + \\
 &\frac{3}{2} [\text{M}^*(\text{L})(\text{allyl Cl}) \cdot \text{M}_2]
 \end{aligned}$$

$$\text{(a7)} \quad \text{L}_0 = [\text{ML}] + [\text{ML} \cdot \text{M}_2] + [\text{ML}(\text{CO}) \cdot \text{M}_2] + [\text{ML}(\text{CO})(\text{allyl Cl}) \cdot \text{M}_2] + [\text{M}^*(\text{L})(\text{allyl Cl}) \cdot \text{M}_2]$$

The concentration of the key intermediate complex $[\text{ML} \cdot \text{M}_2]$ is given by

$$K = \frac{[\text{ML} \cdot \text{M}_2]}{[\text{M}_2][\text{ML}]} \quad \text{(a8)}$$

Assuming $[\text{ML}(\text{CO}) \cdot \text{M}_2] + [\text{ML}(\text{CO})(\text{allyl Cl}) \cdot \text{M}_2] + [\text{M}^*(\text{L})(\text{allyl Cl}) \cdot \text{M}_2] + [\text{ML} \cdot \text{M}_2] \ll [\text{M}_2] + \frac{1}{2}[\text{ML}]$, the starting conditions become

$$[\text{M}_2]_0 = [\text{M}_2] + \frac{1}{2}[\text{ML}] \quad \text{(a9)}$$

$$\text{L}_0 = \text{ML} \quad \text{(a10)}$$

Substitution of a9 and a10 in a8 leads to

$$K = \frac{[\text{ML} \cdot \text{M}_2]}{([\text{M}_2]_0 - \frac{1}{2}[\text{ML}][\text{ML}]})[\text{ML}]}$$

$$[\text{ML} \cdot \text{M}_2] = K([\text{M}_2]_0 - \frac{1}{2}\text{L}_0)(\text{L}_0)$$

Hence the relation between $[\text{ML} \cdot \text{M}_2]$ and $[\text{L}_0]$ is described by a parabola. Maximum value for $[\text{ML} \cdot \text{M}_2]$ is attained when $[\text{L}_0] = [\text{M}_2]_0$ or $\text{L}/\text{Pd} = 0.5$.