Dinuclear Intermediates in the Oxidation of Pendant Olefinic Groups of Palladium(II)-co-ordinated Schiff-base Ligands

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The palladium(II) complexes $[PdL^1Cl][ClO_4]$, $[PdL^2(ClO_4)][ClO_4]$, and $[PdL^3(ClO_4)][ClO_4]$ of the Schiff-base ligands L^1, L^2, and L^3 derived from the condensation of 2,6-diacetylpyridine with 2 mol respectively, of 4-aminobut-1-ene, allylamine, and 1-aminopropane have been prepared. Infrared and ^1H and ^{13}C n.m.r. spectra show that in each complex the trimethine ' N_3 ' donor group is co-ordinated to the palladium(II) ion together with one anionic ligand, but that the olefinic groups of the ligand side arms in L^1 and L^2 are not. However, treatment of the L^1 and L^2 complexes in solution with $\geqslant 2$ equivalents of $[Pd(MeCN)_2Cl_2]$ in the presence of water leads to complexes of the new ligands L^4 and L^5 in which the pendant olefinic groups of L^1 and L^2 have been oxidized to keto-groups. Evidence is presented for a Wacker-type mechanism wherein a key step is the formation of dinuclear intermediates in which the olefinic group of the reactant complexes are co-ordinated to a second palladium(II) ion {from $[Pd(MeCN)_2Cl_2]$} with concomitant activation to nucleophilic attack by water.

Nucleophilic attack at palladium(II)-co-ordinated olefin has been extensively studied and is the basis of the industrially important Wacker process for the conversion of ethylene into acetaldehyde.[1] In the course of studies on metal complexes of macrocyclic ligands[2] derived from the condensation of 2,6-diacetylpyridine with diprimary amines we have had occasion to prepare complexes of related acyclic Schiff-base ligands[3,4] formed by reaction of the diketone with monoprimary amines. These include the ligands L^1—L^3, two of which contain terminal olefinic groups in the side arms. Since the planar conjugated trimethine ' N_3 ' donor set is well suited to co-ordinate at three corners of an approximate square plane, we were interested to see whether L^1 and L^2 might complex with Pd^{II} in such a way that one of the terminal olefinic groups would occupy the fourth co-ordination site. If this proved to be the case there would then be the possibility of activation of the olefinic group to attack by nucleophiles as in Wacker-type reactions.

This paper describes the results of an investigation of the reaction of $[Pd(MeCN)_2Cl_2]$ with the ligands L^1—L^3. It will be shown that in the mononuclear palladium(II) complexes of L^1 and L^2 the (pendant) olefinic groups are *not* co-ordinated but that they do interact intermolecularly with other palladium(II) ions present in solution with accompanying activation to nucleophilic attack by water.

Experimental

2,6-Diacetylpyridine, allylamine, and 1-aminopropane were used as supplied commercially.

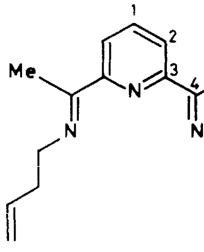
4-Aminobut-1-ene was prepared by a modification of the method described by Roberts and Mazur.[5] To potassium phthalimide (56 g) and 4-bromobut-1-ene (37.8 g) in dimethylformamide (200 cm^3) in a 500-cm^3 flask equipped with stirrer, condenser, and N_2-gas inlet, KI (0.4 g) was added. The mixture was heated to 120 °C with stirring for 30 min and then at 160 °C for a further 30 min. The hot suspension was poured onto ice (220 g) to form a creamy white solid and then extracted with chloroform (4×65 cm^3). The combined extracts were shaken with, successively, 1 mol dm^{-3} KOH, water, and 0.5 mol dm^{-3} HCl and dried over $MgSO_4$. Removal of chloroform by rotary evaporation afforded a light yellow oily liquid which solidified on standing. The white solid was refluxed with hydrazine hydrate (20 g, 99%) in ethanol (200 cm^3) for 1 h and, after cooling in an ice-bath, treated slowly with 10 mol dm^{-3} HCl (37 cm^3). The white solid so formed was removed by filtration and the filtrate concentrated to yield a syrup which solidified on standing at room temperature. This was treated with a cold solution of KOH (26 g) in water (50 cm^3). The precipitated KCl was filtered off and the remaining yellow aqueous solution extracted with diethyl ether (4×20 cm^3). The combined ether extracts were dried over KOH and then concentrated to give a light yellow oil. This was distilled [78 °C, 760 mmHg (*ca.* 10^5 Pa)] to afford the product as a colourless liquid in 55% yield.

The ligands L^1—L^3 were prepared in >90% yield by the same general method. This consisted of the reaction of 2,6-diacetylpyridine (0.01 mol) with the appropriate amine (0.023 mol) in dry benzene (80 cm^3) over 3 Å molecular sieves at room temperature for up to 10 d. The molecular sieves were changed from time to time. The products were isolated as yellow oils by rotary evaporation of the benzene and excess of amine at reduced pressure. The products were characterized by chemical analysis, mass spectra, and ^1H n.m.r. spectra (see later).

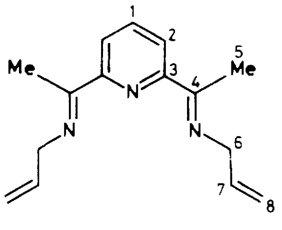
Preparation of the Complexes.—$[PdL^1Cl][ClO_4]$. A solution of $[Pd(MeCN)_2Cl_2]$ (9.5×10^{-4} mol) in warm dry MeCN (30 cm^3) was added with stirring to a solution of L^1 (10^{-3} mol) and $NaClO_4$ (2×10^{-3} mol) in dry ethanol (40 cm^3) at *ca.* 35 °C. Stirring at room temperature was continued for several hours during which time a white solid (NaCl) was seen to form. This was removed by filtration. The filtrate was concentrated to about half-volume and on standing the yellow microcrystalline product separated in 70% yield.

$[PdL^2(ClO_4)][ClO_4]$ and $[PdL^3(ClO_4)][ClO_4]$. These complexes were prepared in 48 and 80% yields, respectively, in a dry 2 : 1 EtOH–MeCN solvent mixture at room temperature as described above for $[PdL^1Cl][ClO_4]$.

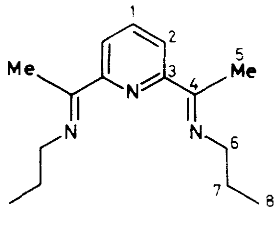
$[PdL^4Cl][ClO_4]$. In a typical experiment $[PdL^1Cl][ClO_4]$ (5×10^{-4} mol) was dissolved in undried ethanol (60 cm^3) to which two drops of water (*ca.* 0.5 g) had been added. A separate solution of $[Pd(MeCN)_2Cl_2]$ (1.25×10^{-3} mol) in undried MeCN (30 cm^3) was prepared. The two solutions were mixed and stirred at room temperature for varying periods of time (up to 10 d). During the course of reaction Pd metal precipitated out of the orange-yellow solution. It was filtered off and the filtrate concentrated to 20—30 cm^3 to give a yellow microcrystalline solid. The yield of product was dependent on the reaction conditions, *viz.* reaction time, temperature, relative concentration of reactants, and solvent



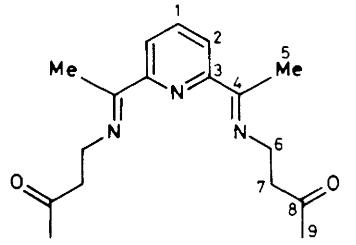
L^1



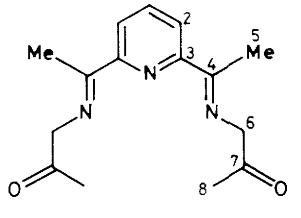
L^2



L^3



L^4



L^5

composition. Maximum yields (*ca.* 75%) of recovered product were obtained only when at least a 2 : 1 excess of [Pd(MeCN)$_2$Cl$_2$] over [PdL^{1}Cl][ClO$_4$] was used. Smaller reactant ratios gave products contaminated with [PdL^{1}Cl][ClO$_4$] as judged by i.r. and ^{1}H n.m.r. spectra. No reaction occurred when either [Pd(MeCN)$_2$Cl$_2$] or water was absent. Similarly, reaction times shorter than *ca.* 2 d (at room temperature) also gave products contaminated with [PdL^{1}Cl][ClO$_4$]. Rates of conversion were increased by the use of higher reaction temperatures but yields were lower. Rates of reaction appeared somewhat lower when the solvent was MeCN only.

[PdL^{5}Cl]Cl. This complex was prepared by oxidation of [PdL^2(ClO$_4$)][ClO$_4$] as described for the preparation of [PdL^{4}Cl][ClO$_4$] from [PdL^{1}Cl][ClO$_4$]. As before, maximum yields were obtained only where at least a 2 : 1 excess of [Pd(MeCN)$_2$Cl$_2$] over [PdL^2(ClO$_4$)][ClO$_4$] was used and when water was present. However, maximum yields (*ca.* 50%) were lower and longer reaction times (up to 5 d at room temperature) were required.

Physical Measurements.—Infrared spectra were measured on KBr discs and Nujol mulls using a Perkin-Elmer 598 spectrophotometer. Proton and ^{13}C n.m.r. spectra were recorded at 250 and 62.9 MHz using a Bruker WM 250 instrument.

Results and Discussion

Analytical, i.r., and electrical conductance data for the palladium(II) complexes are given in Table 1 together with relevant data for the free ligands L^1—L^3. The formulation of the complexes as perchlorate salts of the singly charged square-planar [PdLX]$^+$ (X = Cl or ClO$_4$) cations is based on the following evidence. All three complexes have electrical conductances in MeCN in the range expected for 1 : 1 electrolytes. For [PdL^{1}Cl][ClO$_4$] the O–Cl–O asymmetric stretching and bending vibrations, ν_3 and ν_4, of the ClO$_4^-$ ion at 1 090 and 625 cm^{-1}, respectively, are unsplit and characteristic of 'ionic' ClO$_4^-$. This complex exhibits a medium-intensity band at 330 cm^{-1}, not present in the spectra of [PdL^2(ClO$_4$)][ClO$_4$] or [PdL^3(ClO$_4$)][ClO$_4$], which may be assigned to ν(Pd–Cl) of a terminally bound Cl$^-$ ion.[6] The ν_4 vibration of the ClO$_4^-$ group in the two diperchlorates is split (620 and 625 cm^{-1}) while the ν_3 vibration, although without resolved splitting, is significantly broader than in the spectrum of [PdL^{1}Cl][ClO$_4$]. These observations are consistent with the occurrence of both co-ordinated and unco-ordinated ClO$_4^-$ groups in the diperchlorates.

The i.r. spectra of the free ligands L^1 and L^2 showed one strong absorption at *ca.* 1 640 cm^{-1}, which is assigned to overlapping ν(C=N) and ν(C=C) vibrations.[7] This assignment is supported by the observation that L^3, which lacks a C=C chromophore, also absorbs (less intensely) at 1 640 cm^{-1}, while in the spectra of the amino-olefin precursors, allylamine and 4-aminobut-1-ene, which lack a C=N chromophore the ν(C=C) vibration occurs at 1 640 cm^{-1}. In the spectra of the complexes [PdL^{1}Cl][ClO$_4$] and [PdL^2(ClO$_4$)][ClO$_4$] only a single band (of reduced intensity) is apparent between 1 600 and 1 650 cm^{-1}, while for [PdL^3(ClO$_4$)][ClO$_4$] no absorption occurs in this region. These, at first sight surprising, results indicate that the ν(C=N) vibration is inactive in the palladium(II) complexes. Similar effects have been observed previously [3] in low-spin (S = 0) iron(II) and cobalt(III) complexes of ligands containing the trimethine pyridyl di-imine moiety, and have been explained in terms of extensive $d_\pi \rightarrow p_\pi{}^*$ overlap leading to strong coupling between vibration modes within the five-membered chelate rings. In such cases the group-frequency approach is inadequate and characteristic C=N modes cannot be identified. It follows, then, that the single absorption occurring at *ca.* 1 640 cm^{-1} in the spectra of the palladium(II) complexes of L^1 and L^2 is due to the ν(C=C) vibration. This is the same frequency observed for ν(C=C) in the spectra of the uncomplexed ligands L^1 and L^2 and in those of the precursor aminoalkenes from which they were prepared. Since ν(C=C) vibrations are known to undergo a shift to lower wavenumbers on co-ordination,[7] we conclude that the terminal olefin groups in the palladium(II) complexes of L^1 and L^2 are unco-ordinated. A copper(I) complex of L^1 shown [8] by an *X*-ray crystal-structure determination to contain both co-ordinated and unco-ordinated olefinic groups exhibits two ν(C=C) vibrations, at 1 567 and 1 636 cm^{-1}.

The structural conclusions based on the i.r. data are reinforced by the ^{1}H n.m.r. spectra of the ligands and complexes. Assignments are in Table 2. Comparison of the spectra of the L^1—L^3 ligands with those of the corresponding palladium(II) complexes shows that there are appreciable (downfield) co-ordination shifts for protons adjacent to the trimethine nitrogen atoms. In contrast, the chemical shift

Table 1. Analytical, i.r., and electrical conductance data for the ligands and complexes

Compound	Analysis (%) Found C	H	N	Calc. C	H	N	Λ/ S cm^2 mol^{-1}	I.r. bands/cm^{-1} ν(C=N)	ν(C=C)	ν(C=O)
L^1	75.4	8.6	15.2	75.8	8.6	15.6		1 636[a]	1 636[a]	
$L^2 \cdot H_2O$	69.9	7.9	15.6	69.5	8.2	16.2		1 638[a]	1 638[a]	
L^3	73.0	9.1	16.3	73.4	9.4	17.1		1 640		
$[PdL^1Cl][ClO_4]$	40.2	4.6	8.5	40.0	4.5	8.2	156	*b*	1 642	
$[PdL^2(ClO_4)][ClO_4]$	32.7	3.5	7.5	32.9	3.5	7.7	190	*b*	1 640	
$[PdL^3(ClO_4)][ClO_4]$	32.4	4.2	7.8	32.7	4.2	7.6	166	*b*		
$[PdL^4Cl][ClO_4]$	37.5	4.4	7.7	37.6	4.3	7.7	110	*b*		1 710, 1 718
$[PdL^5Cl]Cl$	39.6	4.2	9.1	40.0	4.2	9.3	120	*b*		1 695

[a] Overlapping ν(C=N) and ν(C=C) vibrations. [b] Not observed (see text).

Table 2. Proton n.m.r. spectral data for the ligands and complexes in CD_3CN

Compound	δ/p.p.m. H^1	H^2	H^5	H^6	H^7	H^8	H^9
L^1	7.6 (t)	8.02 (d)	2.32 (s)	3.50 (t)	2.46 (q)	5.96 (m)	5.09 (m)
L^2	7.55 (m)	8.10 (d)	2.30 (s)	4.11 (t)	5.99 (m)	5.18 (m)	
L^3	7.12 (m)	7.63 (d)	1.83 (s)	2.92 (t)	1.3 (m)	0.52 (t)	
$[PdL^1Cl][ClO_4]$	8.55 (t)	8.29 (d)	2.61 (s)	3.78 (t)	2.51 (q)	5.96 (m)	5.15 (m)
$[PdL^2(ClO_4)][ClO_4]$	8.30 (m)	8.0 (d)	2.52 (s)	4.42 (t)	5.90 (m)	5.90 (m)	
$[PdL^3(ClO_4)][ClO_4]$	8.39 (t)	7.96 (d)	2.52 (s)	3.70 (t)	1.76 (m)	0.99 (t)	
$[PdL^4Cl][ClO_4]$	8.4 (t)	8.00 (d)	2.58 (s)	3.89 (t)	3.02 (t)		2.2 (s)
$[PdL^5Cl]Cl$	8.2 (m)	8.0 (m)	3.89 (s)	4.20 (t)		2.26 (s)	

s = Singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

Table 3. Carbon-13 n.m.r. spectra data (with broad-band decoupling) for free and co-ordinated L^1 and L^3 in CD_3CN

Compound	δ/p.p.m. C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9
L^1	121.0	137.3	156.6	166.4	13.5	52.4	35.7	137.0	115.7
$[PdL^1Cl][ClO_4]$	128.7	143.0	155.8	182.4	16.6	53.5	32.7	134.4	117.9
L^3	120.9	136.3	156.4	166.1	13.5	54.3	24.2	12.2	
$[PdL^3(ClO_4)][ClO_4]$	128.5	142.9	155.8	181.9	16.5	56.0	22.2	11.1	

changes of the olefinic protons on co-ordination are substantially less. Thus, the olefinic protons H^8 (of L^1) and H^7 (of L^2) are shifted (upfield) by less than 0.10 p.p.m. while the terminal olefinic protons H^9 (of L^1) and H^8 (of L^2) move (downfield) by less than 0.2 p.p.m. (see Figure). Since there is abundant evidence[9] that all olefinic protons undergo substantial upfield shifts on co-ordination, the conclusion to be drawn from the ^1H n.m.r., as well as the i.r., spectra, is that the olefinic functions of the ligands L^1 and L^2 are not bound to the palladium(II) ions.

Similar conclusions follow from a consideration of the ^{13}C n.m.r. spectra. Assignments (Table 3) were made on the basis of the off-resonance $^1H-^{13}C$ coupling patterns and by reference to the spectra of related compounds.[10] Comparison of the spectra of L^1 with $[PdL^1Cl][ClO_4]$ and of L^3 with $[PdL^3(ClO_4)][ClO_4]$ shows that the imino-group carbon nuclei are deshielded (by *ca.* 16 p.p.m.) in the complexes compared to the free ligands. Similar, although smaller, effects are seen also for two of the pyridine-carbon nuclei and for the imino-methyl groups. Much smaller shifts are apparent for other carbon nuclei outside the trimethine moiety. Of particular significance is the observation that the resonances due to the olefinic carbons in $[PdL^1Cl][ClO_4]$ are shifted only by ±2—3 p.p.m. This contrasts with the much larger upfield shifts generally observed[11] for co-ordinated olefinic carbon atoms. For example, in a series of substituted ethene complexes of the type $[Pt(olefin)(4\text{-}MeC_5H_4N)Cl_2]$ the upfield co-ordination shifts for the $-CH=$ and $=CH_2$ carbon nuclei fall in the ranges 30—37 and 43—47 p.p.m., respectively.[11]

Oxidation of the Pendant Olefinic Groups in $[PdL^1Cl]^+$ *and* $[PdL^2(ClO_4)]^+$.—It was found that, when $[PdL^1Cl][ClO_4]$ and $[PdL^2(ClO_4)][ClO_4]$ were treated with at least 2 equivalents of $[Pd(MeCN)_2Cl_2]$ in 'wet' EtOH–MeCN solvent mixtures, oxidation of the alkene groups in the side arms of L^1 and L^2 occurred affording the complexes $[PdL^4Cl][ClO_4]$ and $[PdL^5Cl]Cl$ together with precipitated palladium metal. These complexes were characterized by chemical analysis, i.r., and ^1H n.m.r. data (Tables 1 and 2). Distinctive features of the i.r. spectra were strong absorption at *ca.* 1 700 cm^{-1} characteristic of unco-ordinated ν(C=O). The absorption occurring at *ca.* 1 640 cm^{-1} in the spectra of reactant L^1 and L^2 complexes and attributed to ν(C=C) was absent in those of the product L^4 and L^5 complexes. Both complexes were 1 : 1 electrolytes in MeCN (Table 1) and both showed a medium-intensity ν(Pd–Cl) band at 330 cm^{-1}. In $[PdL^4Cl][ClO_4]$ the ν_3 and ν_4 modes of the ClO_4^- ion are unsplit indicative of the occurrence of this group as an unco-ordinated counter ion.

The ^1H n.m.r. spectra (Table 2) of $[PdL^4Cl][ClO_4]$ and $[PdL^5Cl]Cl$ are similarly consistent with their proposed

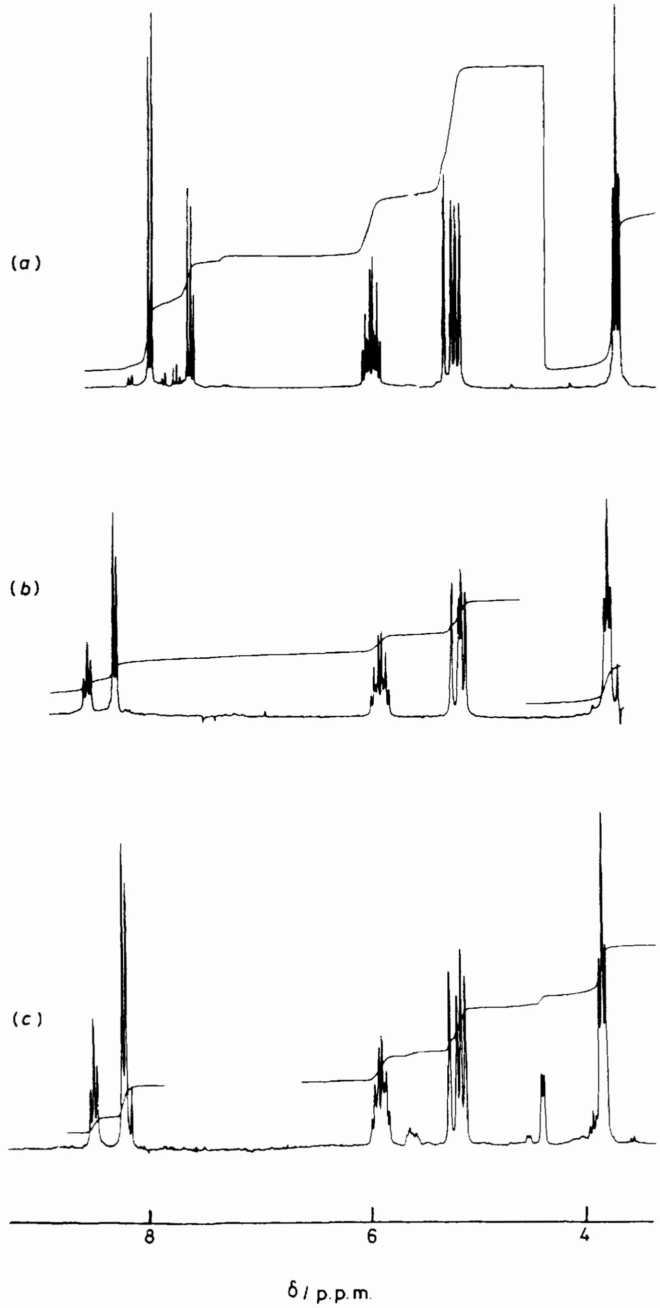


Figure. The 250-MHz ^{1}H n.m.r. spectra (δ 4—8 region) in [^{2}H$_3$]acetonitrile of (*a*) L^1, (*b*) [PdL^{1}Cl][ClO$_4$], and (*c*) [PdL^{1}Cl][ClO$_4$] with 1 equivalent of [Pd(MeCN)$_2$Cl$_2$]

constitution. Significant features of the spectra are the absence of resonances between δ 5.0 and 6.0 attributable to olefinic protons and the presence of a singlet (3 H) attributable to a methyl group adjacent to C=O.

Mechanism of the Oxidation of Olefin to Ketone.—The following observations are relevant to a consideration of the mechanism of the oxidation of [PdL^{1}Cl][ClO$_4$] to [PdL^{4}Cl][ClO$_4$] and of [PdL^2(ClO$_4$)][ClO$_4$] to [PdL^{5}Cl]Cl: (*i*) no oxidation occurred under anhydrous conditions; (*ii*) the reactions were unaffected by carrying them out under anaerobic (N$_2$) conditions instead of in air; (*iii*) no reaction occurred in the absence of added [Pd(MeCN)$_2$Cl$_2$] even in the presence of water; (*iv*) a ratio of [Pd(MeCN)$_2$Cl$_2$] to reactant complex of at least 2 : 1 was necessary for maximum product yield uncontaminated by reactant; (*v*) no oxidation of allylamine or 4-aminobut-1-ene on treatment with [Pd(MeCN)$_2$Cl$_2$] (various mol ratios) in ' wet ' EtOH–MeCN mixed solvents was observed; and (*vi*) the rate of oxidation of L^1 in [PdL^{1}Cl][ClO$_4$] was substantially greater than that of L^2 in [PdL^2(ClO$_4$)][ClO$_4$].

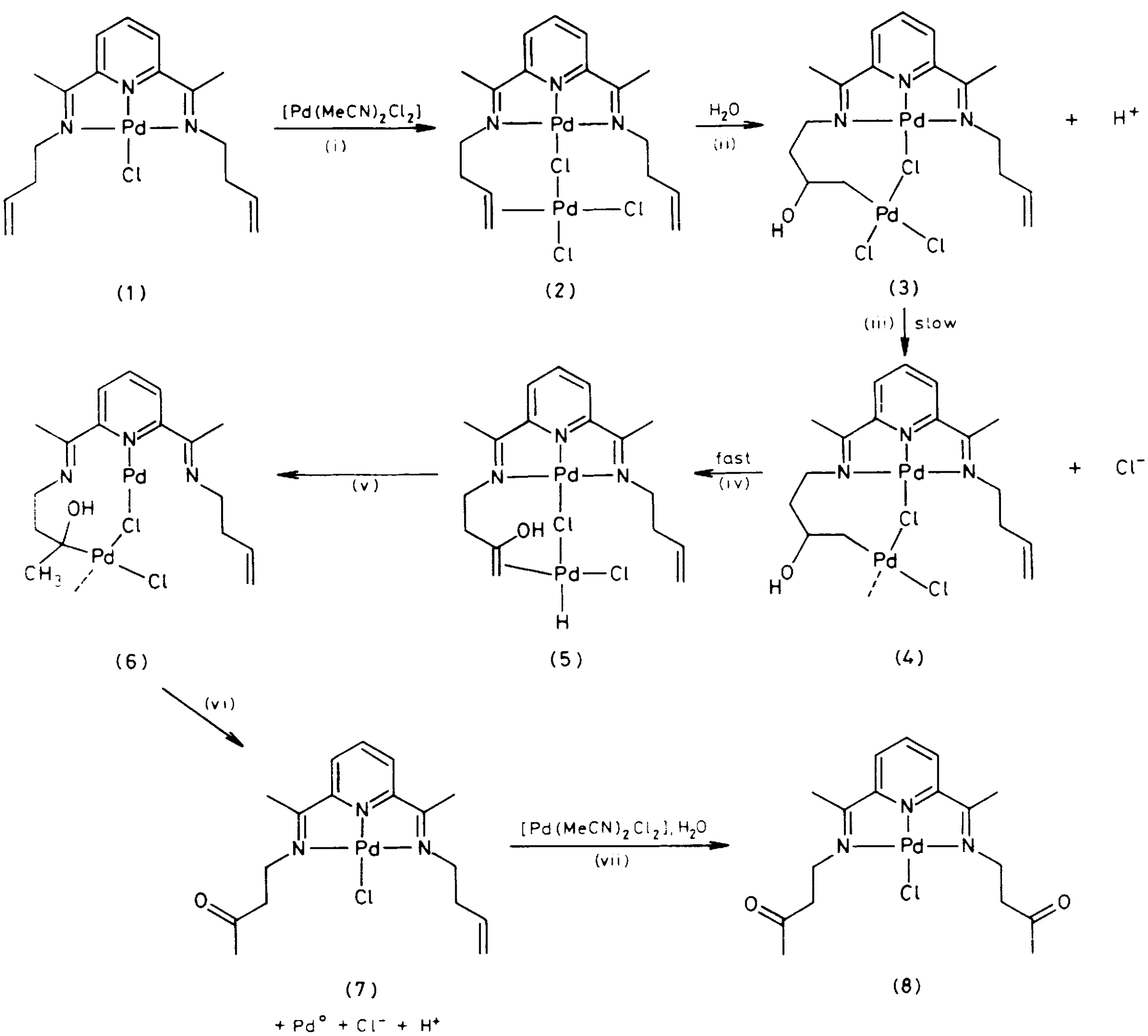
These observations suggest the stoicheiometry (i) for the overall oxidation reaction (for the L^1 ⟶ L^4 case). The fact

$$[\mathrm{PdL^1Cl}]^+ + 2[\mathrm{Pd(MeCN)_2Cl_2}] + 2\mathrm{H_2O} \longrightarrow [\mathrm{PdL^4Cl}]^+ + 2\mathrm{Pd^0} + 2\mathrm{MeCN} + 4\mathrm{H^+} + 4\mathrm{Cl^-} \quad \text{(i)}$$

that the pendant olefinic groups of L^1 or L^2 are not co-ordinated in the reactant complexes together with the necessity for an added source of Pd^{II} is strong evidence for the occurrence of intermediates in which pendant olefinic groups of [PdL^{1}Cl]$^+$ become attached to a palladium(II) centre of a dinuclear species formed by the union of [PdL^{1}Cl]$^+$ and [Pd(MeCN)$_2$Cl$_2$].

Support for the participation of dinuclear species in the reactions under consideration comes from two sources. First, there is precedent for the formation of dinuclear complexes of L^1. It has been shown [8] by *X*-ray analysis that the copper(I) complex of empirical formula CuL^1(BPh$_4$) has a dinuclear structure in the solid state in which each four-co-ordinate Cu^I is bonded to two nitrogen donors of one L^1 molecule and to one imine nitrogen and one olefinic group of a second L^1 molecule, leaving two olefinic groups of the dinuclear unit unco-ordinated. Secondly, direct evidence for olefinic co-ordination in solutions of [PdL^{1}Cl][ClO$_4$] in dry CD$_3$CN in the presence of added [Pd(MeCN)$_2$Cl$_2$] has been obtained. As shown in the Figure the ^{1}H n.m.r. spectra of such solutions show signals at δ 5.58 (H^8) and 4.37 (H^9) and at δ 5.88 (H^8) and 5.16 (H^9) corresponding to the presence of, respectively, co-ordinated and unco-ordinated $-$CH=CH$_2$ protons. The observed upfield shift on co-ordination is as expected.[9] The observation of separate sharp resonances also demonstrates that exchange of free and co-ordinated alkene groups is slow on the n.m.r. time-scale. This contrasts with the situation in the complex [Cu$_2$(L^1)$_2$][BPh$_4$]$_2$ where single time-averaged resonances corresponding to a dynamic equilibrium of free and unco-ordinated olefinic groups were observed. Under the conditions of the experiment {1 : 1 molar proportions of [Pd(MeCN)$_2$Cl$_2$] and [PdL^{1}Cl][ClO$_4$]} only a rather small increase in the relative intensity of the resonances due to the co-ordinated olefinic group was apparent on lowering the temperature to -30 °C.

It is not possible on the available evidence to define precisely the nature of the dinuclear intermediate formed between *e.g.* [PdL^{1}Cl]$^+$ and [Pd(MeCN)$_2$Cl$_2$]. Two structural possibilities come to mind. In one, a pendant olefinic group of [PdL^{1}Cl]$^+$ simply co-ordinates to a second palladium(II) ion by replacement of one MeCN molecule from [Pd(MeCN)$_2$Cl$_2$]. In this case there is no connection between the two palladium(II) centres other than that provided by the side arm of L^1. In the second possibility [structure (2) of the Scheme] the palladium(II) ions are also linked *via* a bridging chloride ligand. We strongly favour the second structural model for the following reasons. First, no oxidation of the aminoalkene precursors on treatment with [Pd(MeCN)$_2$Cl$_2$] in ' wet ' solvents was observed. Secondly, the rate of oxidation of complexed L^1 was much greater than that of complexed L^2. If the oxidation occurred simply as a result of an intermolecular interaction of the pendant olefinic group with [Pd(MeCN)$_2$Cl$_2$] we would not expect it to be so critically dependent on the chemical nature of the other (nitrogen) end



Scheme. Proposed mechanism for the oxidation of [PdL^{1}Cl]$^+$ (1) to [PdL^{4}Cl]$^+$ (8); charges are omitted for clarity

of the saturated side arm nor on the side arm chain length. However, if the intermediate is truly dinuclear, as in structure (2), in that the metal centres are held in proximity (*via* a bridging chloride) independently of the olefinic functions, then geometrical effects relating to the structure of the dinuclear unit also come into play. The lower reaction rate observed for the oxidation of complexed L^2 may thus be associated with the shorter chain length of the side arms in this case. It is difficult to draw definite conclusions on this question merely from an inspection of molecular models since the facility of olefinic side-arm co-ordination to the ' outer ' palladium(II) ion in the two cases depends on the detailed geometry, particularly the Cl–Pd–Cl bond angle, assumed for the dinuclear intermediate. However, the longer side arm (in L^1) does appear to have some advantage in achieving a conformation in which the C=C axis is parallel or perpendicular to the co-ordination square plane, as required for optimum d_π–p_π overlap. It may be significant in this regard that the i.r. spectrum of the complex of empirical formula CuL^2(BPh$_4$) shows no evidence for olefin co-ordination, whereas in the corresponding (dimeric) complex of L^1 olefin co-ordination does occur (both i.r. and *X*-ray evidence) as pointed out above.

The proposed mechanism for the overall oxidation of [PdL^{1}Cl]$^+$ to [PdL^{4}Cl]$^+$ is summarized in the Scheme. The co-ordinated olefinic group in the initially formed binuclear species (2) undergoes *trans* nucleophilic attack by water present in the solvent [step (ii)] to form the hydroxylated species (3). The subsequent steps involving, successively, Cl$^-$ dissociation [step (iii)], β elimination [step (iv)], hydride addition [step (v)], and a second β elimination [step (vi)] to yield the mono-olefin–monoketo-intermediate (7) are based on the mechanism of Bäckvall *et al.*[12] for the palladium(II)-catalysed oxidation of ethene. Repetition of the cycle then converts (7) into the final product (8).

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Received 4th July 1983; *Paper* 3/1142