

## Mechanism of oxidative allyl transfer from allylic ammonium cations to palladium(0) $\alpha$ -diimine complexes

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### Abstract

The palladium(0) complex  $[\text{Pd}(\eta^2\text{-fn})(\text{N}-\text{N}')] (1, \text{fn} = \text{fumaronitrile}; \text{N}-\text{N}' = \text{C}_5\text{H}_4\text{N}-2\text{-CH}=\text{NC}_6\text{H}_4\text{OMe}-4)$  reacts slowly and reversibly with  $\overset{+}{\text{A}}-\text{CH}_2-\text{CH}=\text{CH}_2 (2\mathbf{a}, \text{A} = \text{NEt}_3; 2\mathbf{b}, \text{A} = \text{C}_5\text{H}_5\text{N})$  to yield the cationic  $\eta^3$ -allylpalladium(II) derivative  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{N}-\text{N}')^+] (3)$  the free amine A and fn. The equilibrium constant  $K_e$  is  $(2.6 \pm 0.1) \times 10^{-3}$  for  $2\mathbf{a}$  and  $1.0 \pm 0.4$  for  $2\mathbf{b}$ . Kinetic studies of these oxidative allyl-transfer reactions show that the rates increase with increasing concentration of  $2$  and with decreasing concentration of fn. A stepwise mechanism is proposed which involves slow and reversible displacement of fn by  $2$  to give a labile intermediate  $[\text{Pd}(\eta^2\text{-CH}_2=\text{CH}-\text{CH}_2-\overset{+}{\text{A}})(\text{N}-\text{N}')] (4)$ . This undergoes slow and reversible intramolecular allyl transfer through nucleophilic attack by the palladium(0) metal centre on the nitrogen-bound allyl carbon. The kinetic parameters evaluated by a steady-state treatment satisfactorily generate the observed equilibrium constant  $K_e$ . The rate of formation of the intermediate and the relative rate of its decay to the starting reactants and final products are virtually independent of the nature of the amine A.

**Keywords:** Palladium; Allyl transfer; Kinetic studies

### 1. Introduction

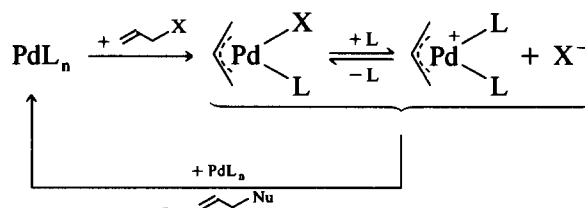
Oxidative addition of an electrophilic allyl halide, sulphide, carboxylate, sulphonate or carbonate to a palladium(0) substrate is a key step in the palladium-catalyzed nucleophilic substitution of allylic compounds (Scheme 1) [1].

The stereochemistry of these catalytic reactions is a subject of much current interest. In respect of the oxidative addition, special attention has been given to the elucidation of the factors that favour retention vs. inversion of configuration at the allylic carbon bearing the leaving group X [2]. In all cases, prior coordination of the C=C double bond of the allylic electrophile to the metal seems to be an essential feature of the mechanism, and evidence for it has been reported [2b].

When the ligating properties of L are better than those of the leaving group X, the reaction of  $\text{PdL}_n$  with

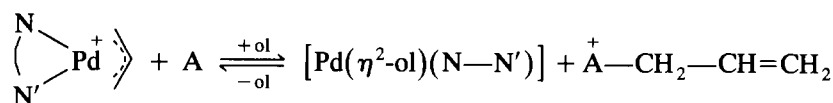
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{X}$ , leading to the cationic species  $[\text{Pd}(\eta^3\text{-all})\text{L}_2]^+$ , can be better viewed as an *oxidative transfer* of the allyl group to the metal. Such is the case for the reactions with (allyloxy)phosphonium, (allylthio)uronium and allylpyridinium salts [3]. A particular case of oxidative allyl transfer is also involved in the reactions of  $\eta^3$ -allylpalladium(II) complexes with palladium(0) [4] and platinum(0) [5] derivatives (*redox transmetallation*).

Following on recent study of the mechanism of nucleophilic attack by triethylamine or pyridine on  $[\text{Pd}(\eta^3\text{-all})(\text{N}-\text{N}')^+]^+$  substrates ( $\text{N}-\text{N}' = \alpha$ -diimine)



Scheme 1.

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$\text{N}-\text{N}' = \text{C}_5\text{H}_4\text{N}-2\text{-CH}=\text{NC}_6\text{H}_4\text{OMe}-4$ ;  $\text{A} = \text{NEt}_3$  or  $\text{C}_5\text{H}_5\text{N}$ ;  $\text{ol} = \text{fumarionitrile}$  or  $\text{dimethyl fumarate}$

Scheme 2.

in the presence of fumarionitrile or dimethyl fumarate (Scheme 2), we reported some preliminary data for the influence of the activated olefin on the reverse reaction, i.e. the oxidative transfer of the allyl group from the ammonium cation  $\overset{+}{\text{A}}-\text{CH}_2-\text{CH}=\text{CH}_2$  to the species  $[\text{Pd}(\eta^2\text{-ol})(\text{N}-\text{N}')]^+$  [6]. We now report the results of a novel equilibrium and kinetic investigation of the latter reaction in the presence of fumarionitrile (fn). One aim of this study was to provide further evidence for prior coordination of the C=C double bond of the allylic electrophile to palladium by oxidative transfer of an allylic substrate to palladium(0).

## 2. Results and discussion

### 2.1. Equilibria of oxidative allyl transfer

When the palladium(0) complex **1** is treated with (prop-2-enyl)triethylammonium (**2a**) or 1-(prop-2-enyl)pyridinium (**2b**) perchlorate in chloroform at 25°C, an equilibrium is slowly established involving the  $\eta^3$ -allylpalladium(II) complex **3**, the free amine A ( $\text{NEt}_3$  or  $\text{C}_5\text{H}_5\text{N}$ ) and fumarionitrile [Eq. (1)].

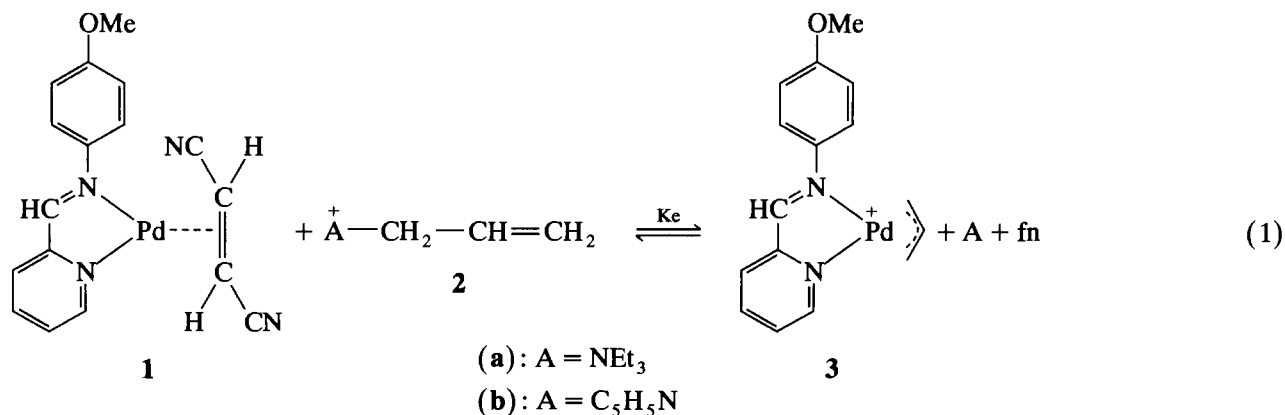
No reaction was observed when **1** was treated with (2-methylprop-2-enyl) triethylammonium perchlorate. Equilibrium (1) was studied by UV-vis spectrophotometry by recording the spectral changes in the presence of a known excess of both A and fn over the palladium substrate **1** after sufficient time had elapsed following mixing of the reactants to ensure the attainment of

equilibrium. Initial concentrations were:  $[\mathbf{1}]_0 = 1 \times 10^{-4} \text{ mol l}^{-1}$ ,  $[\mathbf{A}]_0 = 1 \times 10^{-3} \text{ mol l}^{-1}$ ,  $[\text{fn}]_0$  in the range  $1 \times 10^{-3}$  to  $5 \times 10^{-3} \text{ mol l}^{-1}$ ,  $[\mathbf{2}]_0$  in the range  $2 \times 10^{-5}$  to  $2 \times 10^{-3} \text{ mol l}^{-1}$ . The concentration of A was such that no appreciable  $\alpha$ -diimine displacement by A took place in **3**, the corresponding equilibrium  $\mathbf{3} + 2\mathbf{A} \rightleftharpoons [\text{Pd}(\text{C}_3\text{H}_5)(\text{A})_2]^+ + \text{N}-\text{N}'$  being shifted completely to the left under these conditions [6]. Abstract-factor analysis of the observed UV-vis spectral changes indicated that only two independently absorbing species were present in the range 300–540 nm, i.e. complexes **1** and **3** [7].

Non-linear regression analysis of the dependence of the absorbance on the concentration of **2**, in terms of the model described in Experimental details, gave the following  $K_e$  values:  $(2.6 \pm 0.1) \times 10^{-3}$  for **2a** and  $1.0 \pm 0.4$  for **2b**. These findings can be explained in terms of the much higher basicity of triethylamine than of pyridine in so far as this governs the stability of the  $\text{C}_{\text{allyl}}-\text{N}$  bond in **2**. An example of the spectral changes along with the least-squares fit is shown in Fig. 1.

### 2.2. Kinetics of oxidative allyl transfer

A kinetic study of reaction (1) was also carried out in chloroform at 25°C in the presence of an excess of **2**, A and fn relative to the palladium(0) substrate **1** in order to ensure effective constancy of their concentrations. The progress of the reaction with time was monitored by UV-vis spectroscopy in the range 280–540 nm. Under these conditions the extent of reaction, evaluated



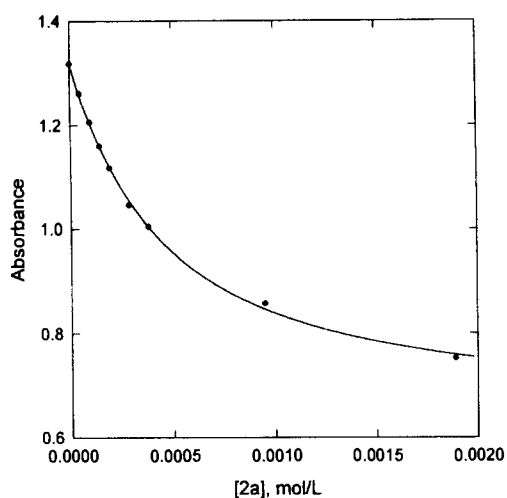


Fig. 1. Fit of the absorbance at 340 nm to  $[2a]$  for equilibrium (1) ( $[Pd]_0 = 1 \times 10^{-4} \text{ mol l}^{-1}$ ,  $[NEt_3] = 1 \times 10^{-3} \text{ mol l}^{-1}$ ,  $[fn] = 1 \times 10^{-3} \text{ mol l}^{-1}$ ).

from the above equilibrium constants, was  $> 60\%$ . In all cases the reactions were monitored for up to six to seven half-lives. Again, abstract-factor analysis showed the presence of only two absorbing species, i.e. **1** and **3**,

as confirmed by the observed two well-defined isosbestic points. The optical density changes were found to obey the mono-exponential law  $D_t = D_\infty + (D_0 - D_\infty) \exp(-k_{\text{obs}} t)$ , where  $k_{\text{obs}}$  is the pseudo-first order rate constant for the process.

The  $k_{\text{obs}}$  values are listed in Tables 1 and 2 for the reactions of **2a** and **2b**, respectively.

In general, the rates appear to increase with increasing concentrations of **2a** and with decreasing concentrations of **fn**, but are not affected by the concentration of **A**. For runs carried out at various concentrations of **2** but with a fixed amine **A** and fumaronitrile concentrations, the  $k_{\text{obs}}$  values increase linearly with  $[2]$  (Fig. 2), according to the relationship:

$$k_{\text{obs}} = In + Sl[2] \quad (2)$$

The slopes  $Sl$  of the straight lines generated by use of relationship [2] for a series of experiments at varying **fn** concentrations (Table 3) decrease with the concentration of **fn** according to Eq. (3) (Fig. 3):

$$Sl = \alpha / (1 + \beta [fn]) \quad (3)$$

Table 1  
Rate data for the reaction of **1** with **2a** in  $CHCl_3$  at  $25^\circ C$ <sup>a</sup>

$10^3 [Et_3N^+-CH_2-CH=CH_2] (2a)$ ( $\text{mol l}^{-1}$ )	$10^3 [fn]$ ( $\text{mol l}^{-1}$ )	$10^3 [NEt_3]$ ( $\text{mol l}^{-1}$ )	$10^4 k_{\text{obs}}$ ( $\text{s}^{-1}$ )
2.37	0.5	1.0	$2.56 \pm 0.05^b$
4.74	0.5	1.0	$5.11 \pm 0.01^b$
9.47	0.5	1.0	$9.81 \pm 0.03^b$
18.90	0.5	1.0	$19.42 \pm 0.05^b$
2.37	1.0	1.0	$1.81 \pm 0.02$
4.74	1.0	1.0	$3.20 \pm 0.03$
9.47	1.0	1.0	$6.21 \pm 0.04$
18.90	1.0	1.0	$12.01 \pm 0.02$
2.37	1.0	2.0	$1.90 \pm 0.02$
4.74	1.0	2.0	$3.25 \pm 0.03$
9.47	1.0	2.0	$6.28 \pm 0.08$
18.90	1.0	2.0	$12.20 \pm 0.02$
2.37	1.5	1.0	$1.40 \pm 0.02$
4.74	1.5	1.0	$2.45 \pm 0.03$
9.47	1.5	1.0	$4.70 \pm 0.05$
18.90	1.5	1.0	$9.41 \pm 0.08$
2.37	2.5	1.0	$0.99 \pm 0.02$
4.74	2.5	1.0	$1.73 \pm 0.03$
9.47	2.5	1.0	$3.41 \pm 0.05$
18.90	2.5	1.0	$6.71 \pm 0.07$
2.37	5.0	1.0	$0.61 \pm 0.08$
4.74	5.0	1.0	$1.15 \pm 0.02$
9.47	5.0	1.0	$1.91 \pm 0.03$
18.90	5.0	1.0	$3.45 \pm 0.07$

<sup>a</sup>  $[1]_0 = 1.0 \times 10^{-4} \text{ mol l}^{-1}$ , unless otherwise stated.

<sup>b</sup>  $[1]_0 = 5.0 \times 10^{-5} \text{ mol l}^{-1}$ .

Table 2  
Rate data for the reaction of **1** with **2b** in CHCl<sub>3</sub> at 25°C<sup>a</sup>

$10^3[\text{C}_5\text{H}_5\text{N}^+-\text{CH}_2-\text{CH}=\text{CH}_2]$ ( <b>2b</b> ) (mol l <sup>-1</sup> )	$10^3[\text{fn}]$ (mol l <sup>-1</sup> )	$10^3[\text{C}_5\text{H}_5\text{N}]$ (mol l <sup>-1</sup> )	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )
0.83	0.21	0.2	1.53 ± 0.01 <sup>b</sup>
1.67	0.21	0.2	2.90 ± 0.02 <sup>b</sup>
2.50	0.21	0.2	4.33 ± 0.02 <sup>b</sup>
3.34	0.21	0.2	5.73 ± 0.05 <sup>b</sup>
0.83	0.41	0.4	1.20 ± 0.01 <sup>b</sup>
1.67	0.41	0.4	2.41 ± 0.03 <sup>b</sup>
2.50	0.41	0.4	3.46 ± 0.03 <sup>b</sup>
3.34	0.41	0.4	4.85 ± 0.03 <sup>b</sup>
0.83	0.84	0.4	0.72 ± 0.01 <sup>b</sup>
1.67	0.84	0.4	1.42 ± 0.02 <sup>b</sup>
2.50	0.84	0.4	2.0 ± 0.1 <sup>b</sup>
3.34	0.84	0.4	2.6 ± 0.2 <sup>b</sup>
0.83	1.73	1.0	0.40 ± 0.01
1.67	1.73	1.0	0.75 ± 0.01
2.50	1.73	1.0	1.20 ± 0.01
3.34	1.73	1.0	1.59 ± 0.01
0.83	4.84	1.0	0.19 ± 0.01
1.67	4.84	1.0	0.35 ± 0.01
2.50	4.84	1.0	0.49 ± 0.01
3.34	4.84	1.0	0.69 ± 0.01

<sup>a</sup>  $[\mathbf{1}]_0 = 1.0 \times 10^{-4}$  mol l<sup>-1</sup>, unless otherwise stated.

<sup>b</sup>  $[\mathbf{1}]_0 = 2 \times 10^{-5}$  mol l<sup>-1</sup>.

with  $\alpha = 0.22 \pm 0.02$  (NEt<sub>3</sub>),  $0.27 \pm 0.04$  (C<sub>5</sub>H<sub>5</sub>N) mol<sup>-1</sup> l s<sup>-1</sup>, and  $\beta = 2420 \pm 400$  (NEt<sub>3</sub>),  $2600 \pm 750$  (C<sub>5</sub>H<sub>5</sub>N) mol<sup>-1</sup> l. The slopes *Sl* are virtually independent of the concentration of A in the ranges examined ( $5 \times 10^{-4}$  to  $2 \times 10^{-3}$  mol l<sup>-1</sup> for [NEt<sub>3</sub>] and  $2 \times 10^{-4}$  to  $1 \times 10^{-3}$  mol l<sup>-1</sup> for [C<sub>5</sub>H<sub>5</sub>N]).

These findings can be interpreted in terms of the following stepwise mechanism (Scheme 3):

The step  $k_1$  corresponds to substitution of the  $\eta^2$ -bound fumaronitrile in **1** by **2** to give the labile palla-

dium(0) intermediate **I** containing the  $\eta^2$ -coordinated allyl cation. This may either revert to the starting species **1** by re-entry of fn ( $k_{-1}$ ) or undergo intramolecular oxidative rearrangement to the  $\eta^3$ -allyl palladium(II) product **3** with release of the free amine A through heterolytic breaking of the carbon–quaternary nitrogen bond under nucleophilic attack by the palladium(0) metal centre ( $k_2$ ). The reverse step,  $k_{-2}$ , represents the first stage of the reductive amination of **3**, which was previously studied in detail [6,8]. Formation of the intermediate **I**, with accompanying reversible dissocia-

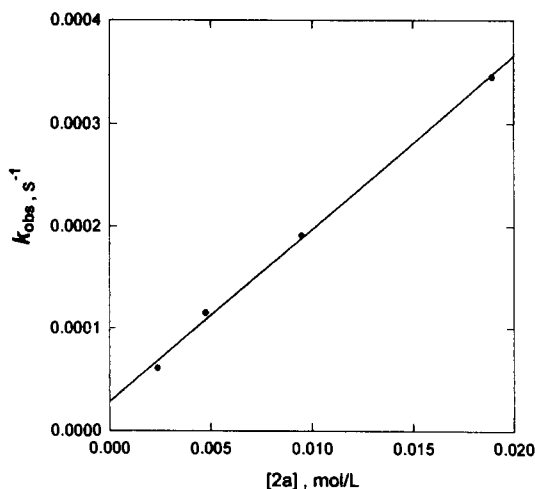


Fig. 2. Linear dependence of  $k_{\text{obs}}$  on  $[\mathbf{2a}]$  for reaction (1) ( $[\text{NEt}_3] = 1 \times 10^{-3}$  mol l<sup>-1</sup>,  $[\text{fn}] = 5 \times 10^{-3}$  mol l<sup>-1</sup>).

Table 3  
Slopes (*Sl*) of plots of  $k_{\text{obs}}$  versus  $[\mathbf{2}]$

<sup>+</sup> A-CH <sub>2</sub> -CH=CH <sub>2</sub> ( <b>2</b> )	$10^3[\text{A}]$ (mol l <sup>-1</sup> )	$10^3[\text{fn}]$ (mol l <sup>-1</sup> )	$10^2 Sl$ (mol <sup>-1</sup> l s <sup>-1</sup> )
<b>2a</b> : A = NEt <sub>3</sub>	1.0	0.5	10.16 ± 0.06
	1.0	1.0	6.18 ± 0.04
	2.0	1.0	6.20 ± 0.05
	1.0	1.5	4.86 ± 0.07
	1.0	2.5	3.48 ± 0.03
	1.0	5.0	1.69 ± 0.06
<b>2b</b> : A = C <sub>5</sub> H <sub>5</sub> N	0.2	0.21	16.8 ± 0.1
	0.4	0.41	14.3 ± 0.1
	0.4	0.84	7.4 ± 0.2
	1.0	1.73	4.8 ± 0.2
	1.0	4.84	1.9 ± 0.1

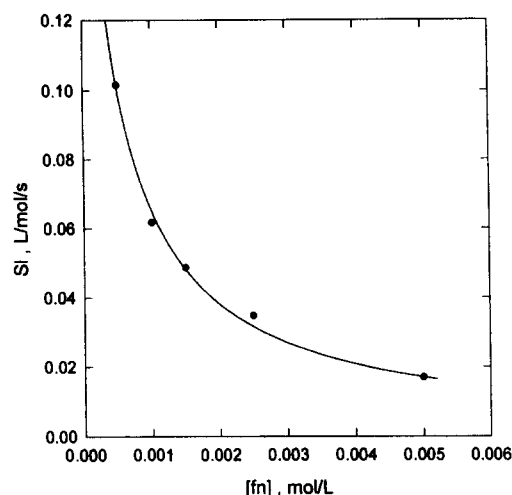
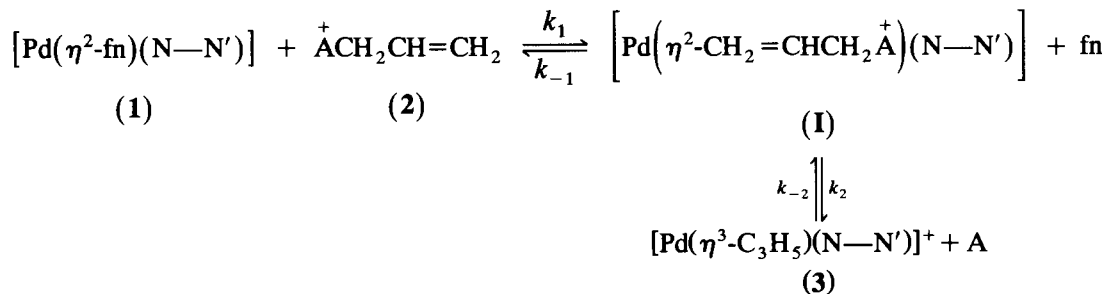


Fig. 3. Fit of slopes  $SI$  to  $[fn]$  [Eq. (3)] for reaction (1) ( $[NEt_3] = 1 \times 10^{-3} \text{ mol l}^{-1}$ ).

tion of  $fn$ , is reasonable in the light of the retarding effect of added  $fn$  on the rates [Eq. (3)] and in line with earlier reports on the mechanism of (i) olefin substitution in palladium(0) complexes with rigid  $\alpha$ -diimino ligands [9] and (ii) oxidative addition of allylic halides to palladium(0) olefin complexes [2b], for which prior coordination of the C=C part of the entering ligand was proposed. The intermediate I, although kinetically significant, must be present in only very low concentration since it escaped detection by UV-vis (vide infra) and  $^1\text{H}$  NMR spectroscopy ( $\text{CDCl}_3$  at  $25^\circ\text{C}$ ). In the NMR spectra, only the typical proton resonances of the reactants 1 and 2, and of the products 3,  $fn$ , and A, were observed throughout the reaction (Experimental details) [6]. On the other hand, for the unreactive system 1/(2-methylprop-2-enyl)triethylammonium perchlorate (1:5 molar ratio) in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ , only a slight broadening of the AB pattern at  $\delta$  2.98 ppm for the coordinated  $fn$  protons was observed, possibly due to a fast olefin exchange between 1 and trace amounts of a type I species. Therefore, by applying the steady-state approximation on [I] to Scheme 3, it can be shown (Experimental details) that, with the assumption  $k_1[2] \ll k_2 + k_{-1}[fn]$ , the decay of 1 and formation of 3 follow a simple first-order differential law of the type  $-d[1]/dt =$



Scheme 3.

$d[3]/dt = \varphi - k_{\text{obs}}[3]$ , where  $\varphi$  is a constant and  $k_{\text{obs}}$  is given by Eq. (4):

$$k_{\text{obs}} = \frac{k_{-2}[A][fn]}{k_2/k_{-1} + [fn]} + \frac{k_1[2]}{1 + (k_{-1}/k_2)[fn]} \quad (4)$$

To the extent that the above approximation is valid, Eq. (4) is equivalent to the experimental rate law (2), where

$$In = \frac{k_{-2}[A][fn]}{k_2/k_{-1} + [fn]} \quad \text{and} \quad SI = \frac{k_1}{1 + (k_{-1}/k_2)[fn]}$$

Moreover, comparison of the expression for  $SI$  with the experimental rate law (3) yields  $\alpha = k_1$  and  $\beta = k_{-1}/k_2$ .

The assumption  $k_1[2] \ll k_2 + k_{-1}[fn]$  ( $k_1[2\text{a}]$  in the range  $(0.5\text{--}4.2) \times 10^{-3}$ ;  $k_1[2\text{b}]$  in the range  $(2.2\text{--}9.0) \times 10^{-4} \text{ s}^{-1}$ ) is reasonable in the light of a steady-state approximation, for which the overall rate of decay of the intermediate I should be much higher than the rate of its formation. This is also in agreement with our failure to detect intermediate I.

The slopes  $SI$  of Eq. (2) can be measured with good accuracy (Table 3) from plots of the type shown in Fig. 2, and exhibit the inverse dependence on  $[fn]$  shown in Eq. (3) (Fig. 3). In contrast, the extrapolated intercept values  $In$  are very uncertain, and show erratic features that preclude any correlation with  $[A]$  and/or  $[fn]$  data, thereby preventing any independent evaluation of the parameters  $k_{-2}$  and  $k_2/k_{-1}$  according to the relationship  $In = k_{-2}[A][fn]/(k_2/k_{-1} + [fn])$ .

The equilibrium constants  $K_e$  for reaction (1) can also be calculated from the rate constants for the mechanism in Scheme 3 as  $K_e = k_1 k_2 / k_{-1} k_{-2}$ . The resulting values based on the appropriate  $k_{-2}$  values from Ref. [6] [ $K_e = (3.8 \pm 2) \times 10^{-3}$  for  $A = \text{NEt}_3$ ;  $0.5 \pm 0.3$  for  $A = \text{C}_3\text{H}_5\text{N}$ ] are in satisfactory agreement with those obtained from direct equilibrium measurements [ $(2.6 \pm 0.1) \times 10^{-3}$  and  $1.0 \pm 0.4$ , respectively]. This lends further support to the proposed mechanism and shows the internal consistency of the independently determined parameters.

The  $k_1$  and  $k_{-1}/k_2$  terms for  $A = \text{NEt}_3$  are very close to those for  $A = \text{C}_3\text{H}_5\text{N}$ , indicating that the rate

of formation of **1** and the relative rates of the reactions by which it disappears are virtually independent of the nature of the amine A. Therefore, the large differences in the equilibrium constants  $K_e$  observed for reaction (1) are essentially due to the large difference in the  $k_{-2}$  terms for the reverse amination reaction [6]. Whereas the reactivities of the two allylammonium cations **2** are rather similar, a large fall occurs upon replacement of the 2-allyl proton by a methyl group. The unreactivity of the (2-methylprop-2-enyl)triethylammonium cation may arise either from lack of formation of a type **I** intermediate or from its inertness toward oxidative allyl transfer caused by unfavourable electronic and steric properties of the methyl group. This is in line with the adverse role played by methyl substituents at the C=C carbons on the rates of oxidative addition of allyl halides to low-valent metal complexes.

### 3. Experimental details

The complexes  $[\text{Pd}(\eta^2\text{-fn})(\text{N}-\text{N}')] [10\text{a}]$ ,  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{N}-\text{N}')]\text{ClO}_4 [10\text{b}]$  and the allyl ammonium salts  $[\text{Et}_3\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{ClO}_4$  and  $[\text{C}_5\text{H}_5\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{ClO}_4 [6]$  were prepared by published methods. Triethylamine and pyridine were distilled under nitrogen from anhydrous  $\text{K}_2\text{CO}_3$  and KOH, respectively. Freshly distilled  $\text{CHCl}_3$  was used for all kinetic runs. All other chemicals and solvents were reagent grade and were used without purification.

#### 3.1. Preparation of $\text{Et}_3\text{N}^+-\text{CH}_2-\text{C}(\text{Me})=\text{CH}_2$ as the perchlorate salt

A two-fold excess of freshly distilled 2-methylprop-2-enyl chloride (5.43 g, 60.0 mmol) was added to a methanol solution of  $\text{NEt}_3$  (3.04 g, 30.0 mmol in 100 ml). The mixture was heated under reflux for 24 h. After addition of  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (8.41 g, 60.0 mmol), the mixture was worked-up as previously described for the preparation of  $[\text{Et}_3\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{ClO}_4 [6]$  to give the white product  $[\text{Et}_3\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{ClO}_4$  (7.30 g, 95.1%).

Molar conductivity:  $110.9 \text{ S cm}^2 \text{ mol}^{-1}$  for a  $10^{-3} \text{ mol l}^{-1}$  MeOH solution at  $25^\circ\text{C}$ ; IR spectrum (KBr pellet) ( $\text{cm}^{-1}$ ):  $\nu(\text{Cl}-\text{O})$  1091,  $\delta(\text{Cl}-\text{O})$  631;  $^1\text{H}$  NMR spectrum (in  $\text{CDCl}_3$ ): allyl protons:  $\delta$  5.54 (1H, s,  $\text{C}=\text{CH}_2$ ); 5.37 (1H, s,  $\text{C}=\text{CH}_2$ ); 3.84 [2H, s,  $\text{C}(\text{CH}_3)-\text{CH}_2$ ]; 2.00 [3H,  $\text{C}(\text{CH}_3)-\text{CH}_2$ ] ppm; ethyl protons:  $\delta$  3.35 (6H, q,  $J = 7.3 \text{ Hz}$ ,  $\text{CH}_2$ ); 1.40 (9H, t,  $\text{CH}_3$ ) ppm.

#### 3.2. Reactions of **1** with a 1:6 molar excess of allyl ammonium cations

##### Method a

The salt  $[\text{Et}_3\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{ClO}_4$  (0.09 mmol, 21.8 mg) was added to 3 ml of a  $5 \times 10^{-3} \text{ mol l}^{-1}$   $\text{CDCl}_3$  solution of **1**. The progress of the reaction was monitored by  $^1\text{H}$  NMR spectroscopy at  $25^\circ\text{C}$ . The initial spectrum showed the typical signals of **1** at virtually the same chemical shifts as those for the complex alone (with the amino proton as a singlet at  $\delta$  8.70 ppm and the  $\text{H}^6$  pyridine proton as a multiplet at  $\delta$  8.90 ppm). The only significant difference was in the change of the  $\eta^2$ -coordinated fn proton signal from an AB system to a broad singlet at ca.  $\delta$  3.0 ppm. The signals of **1** decreased progressively with time with concomitant increase in those of **3** [imino proton as a singlet at  $\delta$  8.86 ppm, the  $\text{H}^6$  pyridine proton as a multiplet at  $\delta$  8.80 ppm, the *syn*-allyl protons as a doublet at  $\delta$  4.20 ppm ( $J = 7.0 \text{ Hz}$ ) and the *anti*-allyl protons as a doublet at  $\delta$  3.55 ppm ( $J = 12.2 \text{ Hz}$ )] and of  $\text{NEt}_3$  ( $\text{CH}_2$  protons as a quartet at  $\delta$  2.70 ppm and  $\text{CH}_3$  protons as a triplet at  $\delta$  1.10 ppm). The olefin proton signal of free fumaronitrile could not be detected because of the fast exchange (on the NMR time scale) with the  $\eta^2$ -bound olefin in **1**. No other species was observed in the mixture. In the course of the reaction, some precipitation of product **3** took place.

Similar results were obtained for the reaction of **1** with  $[\text{C}_5\text{H}_5\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{ClO}_4$  under the same conditions.

##### Method b

The salt  $[\text{Et}_3\text{N}-\text{CH}_2-\text{C}(\text{Me})=\text{CH}_2]\text{ClO}_4$  (0.09 mmol, 23.0 mg) was added to 3 ml of a  $5 \times 10^{-3} \text{ mol l}^{-1}$   $\text{CDCl}_3$  solution of **1**. The  $^1\text{H}$  NMR spectra showed that no reaction took place at  $25^\circ\text{C}$  even after prolonged time and further addition of the allyl cation.

#### 3.3. Physical measurements and instrumentation

The conductivity was measured with a CDM83 conductivity meter. The  $^1\text{H}$  NMR spectra were run on Bruker AM-400 and AC-200 spectrometers at  $25^\circ\text{C}$  using tetramethylsilane as internal standard. Equilibrium and kinetic measurements were carried out on a Perkin-Elmer Lambda 5 spectrophotometer using 1-cm quartz cells. The IR spectra were recorded in the range 4000–200  $\text{cm}^{-1}$  on a Perkin-Elmer 983G instrument fitted with CsI windows.

#### 3.4. Determination of equilibrium constants

Equilibrium constants in Eq. (1) were determined spectrophotometrically by adding known amounts of

chloroform solutions of **2** of known concentration to a solution of substrate **1** containing a known excess of fumaronitrile and base A over palladium in the thermostatted cell compartment of the spectrophotometer. Sufficient time was allowed for the establishment of the slow equilibrium. Spectral changes upon addition of **2** were monitored in the range 300–600 nm, in which only **1** and **3** show appreciable absorptions. The optical density data  $D_\lambda$  were fitted by non-linear least-squares [11] using the following model:



$$K_e = [\mathbf{3}][\text{A}][\text{fn}]/[\mathbf{1}][\mathbf{2}] \quad (6)$$

$$[\text{Pd}]_0 = [\mathbf{1}] + [\mathbf{3}] \quad (7)$$

$$[\mathbf{2}]_0 = [\mathbf{2}] + [\mathbf{3}] \quad (8)$$

$$[\text{fn}], [\text{A}] \text{ constant (excess)} \quad (9)$$

$$D_\lambda = \epsilon_1[\mathbf{1}] + \epsilon_3[\mathbf{3}] \quad (10)$$

The function minimized was  $\psi = \sum(D_{\text{obs}} - D_{\text{calc}})^2$ . The optimized parameters were  $K_e$  and the extinction coefficients. During each iterative cycle of the refining process the concentrations of all species involved were determined by solving the equilibrium and mass-balance equation system analytically (it reduces to a quadratic equation in  $[\mathbf{3}]$ ). The uncertainties quoted refer to the standard deviation.

### 3.5. Spectrophotometric kinetic measurements

The kinetics of reaction (1) were studied by adding known aliquots of chloroform solutions of **2** to freshly prepared solutions of **1** in the presence of an excess of both fn and A relative to the metal. The concentration of **2** was also much higher than that of palladium (Tables 1 and 2). Spectral changes at 25°C were monitored in the range 280–540 nm. The kinetic system in Scheme 3 can be described by the following system of equations ( $[\mathbf{2}]$ ,  $[\text{fn}]$ ,  $[\text{A}]$  are constant):

$$d[\mathbf{3}]/dt = k_2[\mathbf{I}] - k_{-2}[\mathbf{3}][\text{A}] \quad (11)$$

$$[\text{Pd}]_0 = [\mathbf{1}] + [\mathbf{I}] + [\mathbf{3}] \quad (12)$$

$$d[\mathbf{I}]/dt = k_1[\mathbf{1}][\mathbf{2}] + k_{-2}[\mathbf{3}][\text{A}] - k_{-1}[\mathbf{I}][\text{fn}] - k_2[\mathbf{I}] \quad (13)$$

Under the hypothesis of steady-state for  $[\mathbf{I}]$  ( $d[\mathbf{I}]/dt \sim 0$ ,  $[\mathbf{I}] \sim 0$ ) and using the approximation  $k_1[\mathbf{2}] \ll k_2 + k_{-1}[\text{fn}]$ , combination of these equations will yield:

$$d[\mathbf{3}]/dt = \varphi - k_{\text{obs}}[\mathbf{3}] \quad (14)$$

where

$$\varphi = \frac{k_1[\text{Pd}]_0[\mathbf{2}]}{1 + (k_{-1}/k_2)[\text{fn}]}$$

$$k_{\text{obs}} = \frac{k_{-2}[\text{A}][\text{fn}]}{k_2/k_{-1} + [\text{fn}]} + \frac{k_1[\mathbf{2}]}{1 + (k_{-1}/k_2)[\text{fn}]}$$

The first-order differential equation (14) can be integrated to give the customary mono-exponential rate law as the dependence of optical density  $D_t$  on  $t$ , i.e.  $D_t = D_\infty + (D_0 - D_\infty) \exp(-k_{\text{obs}}t)$ , since  $[\mathbf{3}] = (\varphi/k_{\text{obs}})[1 - \exp(-k_{\text{obs}}t)]$  (by integration),  $[\mathbf{1}] \sim [\text{Pd}]_0 - [\mathbf{3}]$  [from Eq. (12) and the hypothesis  $[\mathbf{I}] \sim 0$ ],  $D_0 = \epsilon_1[\text{Pd}]_0$ ,  $D_t = \epsilon_1[\mathbf{1}] + \epsilon_3[\mathbf{3}] = D_0 + (\epsilon_3 - \epsilon_1)[\mathbf{3}]$  and  $D_\infty = D_0 + (\varphi/k_{\text{obs}})(\epsilon_3 - \epsilon_1)$ . Values of  $k_{\text{obs}}$  were obtained by non-linear regression [11] of the  $D_t$  versus time data.

### 3.6. Data reduction and analysis

Mathematical and statistical analysis of equilibrium and kinetic data was carried out on a personal computer equipped with an INTEL 486 66 MHz central processor by the use of a locally adapted version of Marquardt's algorithm written in TURBOBASIC™ (Borland). Abstract factor analysis was carried out in the MATLAB™ (Mathworks) environment.

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