# Equilibrium Studies of α-Diimine Displacement in Cationic Allylpalladium(II) Complexes by Monodentate N-Donors and the Mechanism of Allyl Amination by Triethylamine and Pyridine

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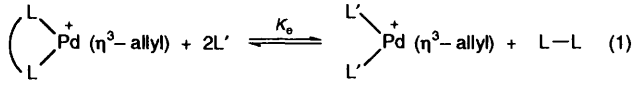
In the cationic complexes $[Pd(\eta^3\text{-allyl})(L\text{–}L)]ClO_4$ [L–L = 1,2-bis(imino)ethanes or 2-(iminomethyl)-pyridines] the chelated α-diimine was rapidly and reversibly displaced by secondary amines (*N*-methylaniline, morpholine or piperidine), triethylamine and 4-substituted pyridines. The observed equilibrium constants $K_e$ increased with increasing basicity and decreasing steric requirements of the entering N-donor. They strongly depend on the α-diimine and decrease in the order RN=CHCH=NR ≫ RN=C(Me)C(Me)=NR ≈ $NC_5H_4(CH{=}NR)$-2 (R = $C_6H_4OMe$-4). The cationic complex $[Pd(\eta^3\text{-}C_3H_5)\{NC_5H_4(CH{=}NC_6H_4OMe\text{-}4)\text{-}2\}]^+$ underwent a slow allyl amination by triethylamine or pyridine (L') in the presence of fumaronitrile (fn), yielding $[Pd(\eta^2\text{-fn})\{NC_5H_4(CH{=}NC_6H_4OMe\text{-}4)\text{-}2\}]$ and $Et_3\overset{+}{N}CH_2CH{=}CH_2$ or $C_5H_5\overset{+}{N}CH_2CH{=}CH_2$. Kinetic studies showed that the pseudo-first-order rate constants for amination ($k_{obs}$) are given by $k_{obs} = k_2[L']$, suggesting a direct bimolecular attack of L' on the $\eta^3$-allyl ligand. Amination hardly proceeds in the presence of the less-activated olefin dimethyl fumarate (dmf). The π-accepting properties of the olefinic ligands play an important role also in the reaction of $Et_3\overset{+}{N}CH_2CH{=}CH_2$ or $C_5H_5\overset{+}{N}CH_2CH{=}CH_2$ with $[Pd(\eta^2\text{-olefin})\{NC_5H_4(CH{=}NC_6H_4OMe\text{-}4)\text{-}2\}]$ (olefin = fn or dmf), *i.e.* the reverse of the amination reaction.

In the cationic complexes $[Pd(\eta^3\text{-}C_3H_5)(L\text{–}L)]ClO_4$ **1** [L–L = $NC_5H_4(CH{=}NCMe_3)$-2 or $NC_5H_4(CH{=}NC_6H_4OMe\text{-}4)$-2] the chelated α-diimine ligand L–L appears to be weakly bound to the metal centre and can be displaced even by acetonitrile.[1] Consistently, the reaction of **1** with an excess of diethylamine involves a rapid and reversible displacement of L–L followed by slow nucleophilic attack of $NHEt_2$ at the allyl moiety, which yields the palladium(0) derivative $[Pd(\eta^2\text{-dmf})(L\text{–}L)]$ and allyldiethylamine, in the presence of dimethyl fumarate (dmf) (Scheme 1).[2]

A mechanistic investigation has shown that when the α-diimine concentration is held constant (by using an excess) the overall reaction rate takes the form $-d[\mathbf{1}]/dt = k_{obs}[\mathbf{1}]$, with $k_{obs} = k/(1 + K_e[NHEt_2]^2/[L\text{–}L])$ and $k = k_2[NHEt_2] + k_2'[NHEt_2]^2$.[2] It thus appears that the equilibrium constant $K_e$ affects the reaction rates to such an extent that an independent assessment of its value is of prime importance for a better understanding of the amination mechanism. To this purpose, we have measured $K_e$ for a variety of cationic substrates **1** with a series of 4-substituted pyridines and also with secondary and tertiary amines. A kinetic study of the amination of the allyl group in **1** [L–L = $NC_5H_4(CH{=}NC_6H_4OMe\text{-}4)$-2] by triethylamine or pyridine in the presence of fumaronitrile was also carried out.

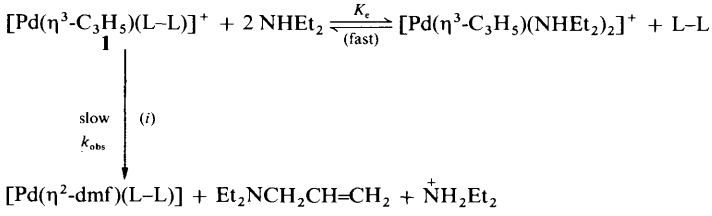
## Results and Discussion

*Equilibria of α-Diimine Displacement.*—When the cationic complex **1** is treated with secondary amines, triethylamine and pyridines (L') in chloroform, rapid reversible substitution of the chelated α-diimine ligand takes place according to equation (1)




**1** **2**

[L–L = RN=C($R^1$)C($R^1$)=NR (R = $C_6H_4OMe$-4, $R^1$ = H or Me), $NC_5H_4(CH{=}NR^2)$-2 ($R^2$ = $C_6H_4OMe$-4); allyl = $C_3H_5$ or 2-$MeC_3H_4$; L' = *N*-methylaniline, morpholine, piperidine, triethylamine, or 4-$R^3C_5H_4N$ ($R^3$ = MeCO, Cl, H, Et or $NMe_2$)]. Equilibrium (1) was studied by both $^1H$ NMR and UV/VIS spectrophotometry. In each case, spectral data for the systems **1** (allyl = $C_3H_5$)–secondary amine were recorded immediately after mixing the reactants to avoid changes caused by the subsequent slow amination reaction.[2] Abstract factor analysis of the observed UV/VIS spectral changes indicated that only two independently absorbing species were present in the




**Scheme 1** $CHCl_3$, 25 °C; L–L = $NC_5H_4(CH{=}NCMe_3)$-2 or $NC_5H_4(CH{=}NC_6H_4OMe\text{-}4)$-2. (*i*) dmf, excess of $NHEt_2$

**Table 1** Equilibrium constants ($K_e$/dm$^3$ mol$^{-1}$) for reaction (1) with 4-substituted pyridines at 25 °C in chloroform

| Complex $[Pd(\eta^3\text{-allyl})(L\text{–}L)]ClO_4$ | | | Pyridines, 4-$R^3C_5H_4N$ ($pK_a$)* | | | | |
|---|---|---|---|---|---|---|---|
| L–L = $RN{=}C(R^1)C(R^1){=}NR$ | | | $R^3$ = MeCO (3.51) | Cl (3.84) | H (5.25) | Et (5.87) | $NMe_2$ (9.72) |
| R | $R^1$ | allyl | | | | | |
| $C_6H_4OMe$-4 | H | 2-$MeC_3H_4$ | 0.81 ± 0.07 | 0.79 ± 0.07 | 12.2 ± 0.5 | 101 ± 4 | 94 900 ± 3000 |
| $C_6H_4OMe$-4 | Me | 2-$MeC_3H_4$ | | | (4.05 ± 0.09) × $10^{-2}$ | | |
| L–L = $NC_5H_4(CH{=}NR^2)$-2 | | | | | | | |
| $R^2$ | | allyl | | | | | |
| $C_6H_4OMe$-4 | | $C_3H_5$ | | | (2.29 ± 0.06) × $10^{-2}$ | | |
| $C_6H_4OMe$-4 | | 2-$MeC_3H_4$ | | | (1.51 ± 0.05) × $10^{-2}$ | | |

* $pK_a$ data from ref. 6.

**Table 2** Equilibrium constants ($K_e$/dm$^3$ mol$^{-1}$) for reaction (1) with secondary amines at 25 °C in chloroform

| Complex $[Pd(\eta^3\text{-allyl})(L\text{–}L)]ClO_4$ | | | Amine ($pK_a$)[a] | | | |
|---|---|---|---|---|---|---|
| L–L = $RN{=}C(R^1)C(R^1){=}NR$ | | | *N*-Methylaniline (4.85) | Morpholine (8.50) | $NHEt_2$[b] (11.04) | Piperidine (11.12) |
| R | $R^1$ | allyl | | | | |
| $C_6H_4OMe$-4 | H | $C_3H_5$[c] | | | 1390 ± 145 | |
| $C_6H_4OMe$-4 | H | 2-$MeC_3H_4$ | (1.20 ± 0.07) × $10^{-4}$ | 99 ± 3 | 1079 ± 33 | 3790 ± 450 |
| $C_6H_4OMe$-4 | Me | 2-$MeC_3H_4$ | | 0.36 ± 0.01 | 1.9 ± 0.1 | 14.3 ± 0.4 |
| L–L = $NC_5H_4(CH{=}NR^2)$-2 | | | | | | |
| $R^2$ | | allyl | | | | |
| $C_6H_4OMe$-4 | | $C_3H_5$[c] | | 0.16 ± 0.02 | 4.1 ± 0.3 | 7.2 ± 0.9 |
| $C_6H_4OMe$-4 | | 2-$MeC_3H_4$ | | 0.112 ± 0.009 | 1.33 ± 0.15 | 6.0 ± 0.2 |
| $CMe_3$ | | $C_3H_5$[c] | | | 0.19 ± 0.01 | |
| $CMe_3$ | | 2-$MeC_3H_4$ | | | 0.038 ± 0.005 | |

[a] $pK_a$ data from ref. 6. [b] Data from ref. 2. [c] From spectral data recorded immediately after mixing.

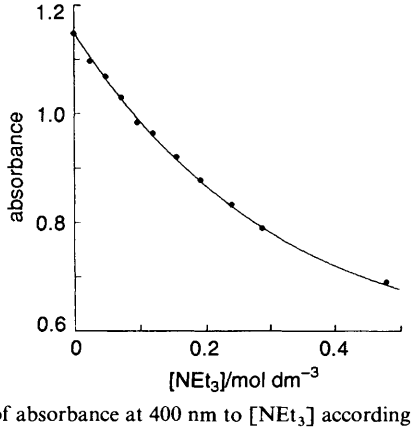



**Fig. 1** Fit of absorbance at 400 nm to $[NEt_3]$ according to equation (1) for allyl = $C_3H_5$ and L–L = $NC_5H_4(CH{=}NC_6H_4OMe$-4)-2 in $CHCl_3$ at 25 °C

range 250–600 nm, *i.e.* complex **1** and the free α-diimine L–L.[3] No five-co-ordinated intermediates with one amine and a *N*,*N*′-chelated α-diimine[4] nor four-co-ordinated species bearing one amine and a dangling *N*-monodentate α-diimine[5] were detected. This is also true according to $^1H$ NMR spectra ($CD_2Cl_2$) in the temperature range −80 to 25 °C.

Non-linear regression analysis of absorbance *vs.* [L′] data according to the model described in the Experimental section gave the $K_e$ values listed in Tables 1 and 2. For the reaction of L′ = $NEt_3$ with $[Pd(\eta^3\text{-}C_3H_5)\{NC_5H_4(CH{=}NC_6H_4OMe$-4)-2$\}]ClO_4$, $K_e$ was (1.0 ± 0.2) × $10^{-3}$ dm$^3$ mol$^{-1}$. A typical representation of spectral changes along with the least-squares fit is shown in Fig. 1.

The displacement of the chelated α-diimine appears to be markedly affected by the steric and electronic properties of the entering amine L′, by the structure and substituents of the L–L ligand, and to a lesser extent by the nature of the allyl group. As can be seen in Table 1, the $K_e$ values for the substrate $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(RN{=}CHCH{=}NR)]ClO_4$ (R = $C_6H_4OMe$-4) increase with increasing basicity of the 4-substituted pyridine, as measured by the $pK_a$ value in water. A linear free-energy relationship of log $K_e$ to $pK_a$[6] is apparent in Fig. 2. In this series of pyridines, which have comparable steric requirements, the value of $K_e$ is essentially governed by the electron density at the pyridine nitrogen. Similar trends are observed for the equilibria involving $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)\{RN{=}C(R^1)C(R^1){=}NR\}]ClO_4$ (R = $C_6H_4OMe$-4, $R^1$ = H or Me) and $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)\{NC_5H_4(CH{=}NC_6H_4OMe$-4)-2$\}]ClO_4$ and secondary amines (Table 2, Fig. 3). Here, however, the different steric requirements of the amines also play an important role. Thus, the lower basicity of *N*-methylaniline, compounded with the greater bulkiness at the co-ordinating nitrogen, results in the lowest $K_e$ value. The adverse role of steric effects stands out in the equilibria between $[Pd(\eta^3\text{-}C_3H_5)\{NC_5H_4(CH{=}NC_6H_4OMe$-4)-2$\}]ClO_4$ and $NEt_3$ *vs.* $NHEt_2$: since the amines have comparable $pK_a$ values,[6] the much lower ability of $NEt_3$ to displace the α-diimine is essentially related to the increased steric demand of the three N-bound ethyl groups.

A comparison of the equilibrium constants for L′ = $NHEt_2$[2] with those involving L′ = morpholine, piperidine and pyridine relating to complexes with various α-diimines (Table 2) shows that they are strongly dependent on the substrate α-diimine ligand and decrease in the order: $RN{=}CHCH{=}NR \gg RN{=}C(Me)C(Me){=}NR \approx NC_5H_4(CH{=}NR^2)$-2 > $NC_5H_4(CH{=}NCMe_3)$-2[2] where R = $R^2$ = $C_6H_4OMe$-4, in agreement with

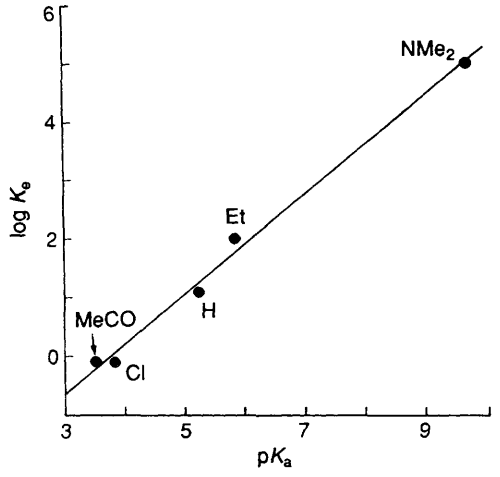



**Fig. 2** Correlation of log $K_e$ to p$K_a$ of 4-substituted pyridines for reaction (1) (allyl = 2-$MeC_3H_4$, L–L = RN=CHCH=NR, R = $C_6H_4$-OMe-4)

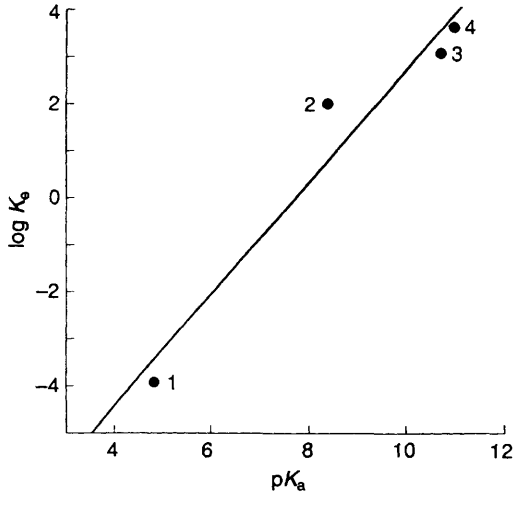



**Fig. 3** Correlation of log $K_e$ to p$K_a$ of secondary amines for reaction (1) (allyl = 2-$MeC_3H_4$, L–L = RN=CHCH=NR, R = $C_6H_4OMe$-4): 1, *N*-methylaniline; 2, morpholine; 3, $NHEt_2$; 4, piperidine

the order of increasing stability of the five-membered metallacycle in the cationic complexes **1** towards α-diimine dissociation in acetonitrile.[1] In particular, the large $K_e$ values for the 4-$MeOC_6H_4N$=CHCH=$NC_6H_4OMe$-4 complexes are outstanding and indicate a high substitution lability for this ligand. The ease of displacement of L–L decreases markedly on replacing the hydrogen by a methyl group on the imino-carbons [4-$MeOC_6H_4N$=C(Me)C(Me)=$NC_6H_4OMe$-4], on introducing a 2-pyridyl group into the α-diimine skeleton [$NC_5H_4$(CH=$NC_6H_4OMe$-4)-2], and on replacing the aryl $C_6H_4OMe$-4 by the better electron-donor group $CMe_3$ [$NC_5H_4$(CH=$NCMe_3$)-2]. The equilibrium constants also decrease appreciably on going from allyl = $C_3H_5$ to 2-$MeC_3H_4$, other things being equal, probably owing to an interplay of steric and inductive effects of the 2-Me substituent, resulting in a better stabilization of the substrate **1**.

The UV/VIS equilibrium results are in line with the findings of $^1$H NMR experiments carried out on reaction (1) in $CDCl_3$ at 25 °C. The initial $^1$H NMR spectra of the equilibrium mixtures [Pd($\eta^3$-2-$MeC_3H_4$){$NC_5H_4$(CH=$NR^2$)-2}]$ClO_4$–$NHEt_2$ ($R^2$ = $C_6H_4OMe$-4 or $CMe_3$), **1**:$NHEt_2$ molar ratio 1:2, provide the following pieces of information: (*i*) the free α-diimine $NC_5H_4$(CH=$NR^2$)-2 exchanges rapidly with the chelated one for $R^2$ = $C_6H_4OMe$-4 and slowly for $R^2$ = $CMe_3$; on cooling to −40 °C the rate of exchange is drastically reduced and the typical sharp signals of the free and co-ordinated imine are observed [*e.g.* δ(N=CH) as a singlet at 8.59 and 8.73 for free and co-ordinated $NC_5H_4$(CH=$NC_6H_4OMe$-4)-2 respectively]; (*ii*) for the system [Pd($\eta^3$-2-$MeC_3H_4$){$NC_5H_4$(CH=$NC_6H_4OMe$-4)-2}]$ClO_4$–$NHEt_2$ (1:2), a fast *syn-syn,anti-anti* exchange of the allyl protons occurs both at 25 and −40 °C,[1] whereas for [Pd($\eta^3$-2-$MeC_3H_4$)-{$NC_5H_4$(CH=$NCMe_3$)-2}]$ClO_4$–$NHEt_2$ (1:2) the exchange is fast at 25 °C but slows down at −40 °C (on the NMR time-scale), as shown by the observation of separate *syn*- and *anti*-proton resonances [$\delta(H)_{syn}$ 4.15 (s) and $\delta(H)_{anti}$ 3.35 (s, br) at 25 °C, 4.08 (s) and 4.03 (s) and 3.38 (s) and 3.09 (s) at −40 °C]; (*iii*) the interaction of the cationic substrate [Pd($\eta^3$-allyl)(L–L)]$^+$ with L′ and/or L–L brings about a fast *syn-syn,anti-anti* exchange of the allyl protons at 25 °C; under the same experimental conditions, however, no fast $\eta^3 \rightleftharpoons \sigma$ dynamic process is observed.

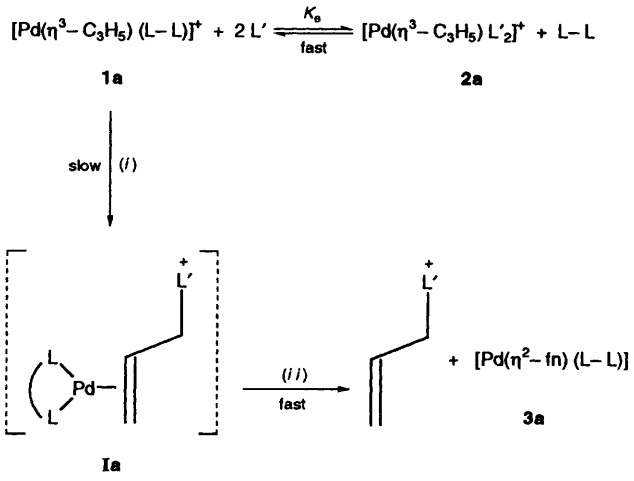
The cationic complexes **2** are easily identified by comparing the $^1$H NMR spectra of the equilibrium mixtures with those of authentic samples, independently prepared as their $BF_4^-$ salts (see Experimental section). At variance with the behaviour of [Pd($\eta^3$-allyl)$(NHEt_2)_2$]$^+$,[2] for the complexes [Pd($\eta^3$-allyl)$L'_2$]$^+$ **2** (L′ = morpholine, piperidine, or pyridine) a fast exchange between free and co-ordinated L′ is observed at 25 °C. For instance, in the system [Pd($\eta^3$-2-$MeC_3H_4$){$NC_5H_4$-(CH=$NC_6H_4OMe$-4)-2}]$ClO_4$–morpholine (1:5 molar ratio), the initial $^1$H NMR spectra in $CDCl_3$ show only two broad singlets centred at δ 3.7 and 2.9 for the methylene protons of the amine, whereas the allyl proton signals of species **1** and **2** appear as sharp and distinct singlets at δ 3.95 and 3.53 ($H_{syn}$), 3.38 and 2.84 ($H_{anti}$), 2.22 and 2.15 (2-Me), respectively. Furthermore, in the system [Pd($\eta^3$-2-$MeC_3H_4$){$NC_5H_4$(CH=$NC_6H_4OMe$-4)-2}]$ClO_4$–pyridine (1:40 molar ratio) in $CDCl_3$ a rapid exchange between the co-ordinated pyridine of **2** and the free α-diimine L–L of equilibrium (1) also takes place, as inferred from the detection of time-averaged broad resonances for the allyl protons of species **1** and **2** at δ 3.9 ($H_{syn}$), 3.3 ($H_{anti}$) and 2.2 (2-Me) at 25 °C. However, on cooling to −30 °C this exchange is frozen out and two sets of sharp allyl signals are observed for **1** and **2**, respectively [**1**, δ 3.95 (s, $H_{syn}$), 3.38 (s, $H_{anti}$) and 2.21 (s, 2-Me); **2**, δ 3.85 ($H_{syn}$, partially overlapping with the OMe signal), 3.22 (s, $H_{anti}$) and 2.25 (s, 2-Me)].

*Kinetics of Allyl Amination by Triethylamine and Pyridine.*—As in the case of $NHEt_2$,[2] the secondary amines piperidine and morpholine react further with the cationic complex [Pd($\eta^3$-$C_3H_5$){$NC_5H_4$(CH=$NC_6H_4OMe$-4)-2}]$^+$ **1a** *via* nucleophilic attack at the terminal carbon of the $\eta^3$-bound allyl group, in the presence of activated olefins such as dimethyl fumarate (dmf) and fumaronitrile (fn), according to Scheme 1.* An analogous allyl amination of **1a** also occurs with triethylamine or pyridine (L′) but only in the presence of the more π-accepting fumaronitrile [equation (2)]

$$[Pd(\eta^3\text{-}C_3H_5)(L\text{–}L)]^+ + L' \xrightarrow{fn} {}^+L'CH_2CH{=}CH_2 + [Pd(\eta^2\text{-fn})(L\text{–}L)] \quad (2)$$
**1a** **3a**

[L–L = $NC_5H_4$(CH=$NC_6H_4OMe$-4)-2; $^+L'CH_2CH{=}CH_2$ = $Et_3\overset{+}{N}CH_2CH{=}CH_2$ or $C_5H_5\overset{+}{N}CH_2CH{=}CH_2$]. The progress of reaction (2) was monitored by $^1$H NMR spectroscopy in $CDCl_3$ at 25 °C by using molar ratios **1a**:$NEt_3$:fn of 1:7:1.2 and **1a**:pyridine:fn of 1:40:1.2, with $[\mathbf{1a}]_0 = 2.5 \times 10^{-2}$ mol $dm^{-3}$. After 24 h the yields of the allyl cation $^+L'CH_2CH{=}CH_2$ were in the range 90–95 (L′ = $NEt_3$) and 65–70% (L′ = pyridine), based on dichloromethane or toluene as internal

* The kinetic data relating to piperidine and morpholine will be discussed in a forthcoming paper devoted to equilibrium thermodynamic parameters, activation parameters, and solvent effects in this class of reactions.




**Scheme 2** (*i*) Excess of L'; (*ii*) fn

**Table 3** Rate data for the reaction of $[Pd(\eta^3\text{-}C_3H_5)\{NC_5H_4(CH{=}N\text{-}C_6H_4OMe\text{-}4)\text{-}2\}]ClO_4$ with triethylamine or pyridine at 25 °C in chloroform. $[Pd]_{tot} = 1 \times 10^{-4}$ mol dm$^{-3}$

| $10^2$[L']/mol dm$^{-3}$ | $10^4$[fn]/mol dm$^{-3}$ | $10^4k^a$/s$^{-1}$ |
|---|---|---|
| L' = $NEt_3$[b] | | |
| 3.82 | 10 | 9.61 |
| 7.65 | 10 | 18.1 |
| 9.56 | 10 | 22.5 |
| 11.50 | 10 | 28.2 |
| L' = $C_5H_5N$[c] | | |
| 12.12 | 1.23 | 0.294 |
| 16.27 | 1.23 | 0.364 |
| 20.06 | 1.23 | 0.454 |
| 30.16 | 1.23 | 0.664 |
| 35.65 | 1.23 | 0.780 |
| 12.12 | 5.0 | 0.290 |
| 12.12 | 20.0 | 0.297 |

[a] Values calculated from equation (4). [b] $[NC_5H_4(CH{=}NC_6H_4OMe\text{-}4)\text{-}2]$, added in excess $1 \times 10^{-3}$ mol dm$^{-3}$. [c] $[NC_5H_4(CH{=}N\text{-}C_6H_4OMe\text{-}4)\text{-}2]$ $1.03 \times 10^{-3}$ mol dm$^{-3}$

standards. When dmf was used under the same experimental conditions the yield was as low as 2–5%, even after longer reaction times (24–48 h). The palladium(0) complex **3a** has been isolated and characterized from its IR and $^1$H NMR spectra,[7] whereas the products $^+L'CH_2CH{=}CH_2$ were identified in the reaction mixtures by their typical $^1$H NMR signals (see Experimental section).

In order to elucidate the observed role of the activated olefin in reaction (2), we have studied the reverse reaction between the quaternary allyl cations $^+L'CH_2CH{=}CH_2$ and [Pd(η²-olefin)(L–L)] in a 1:1 molar ratio. The $^1$H NMR data for the mixtures in $CDCl_3$ show that for olefin = dmf the reaction proceeds rapidly and almost quantitatively to **1a** and L', whereas for olefin = fn such a reaction has proceeded to *ca.* 20% with $Et_3\overset{+}{N}CH_2CH{=}CH_2$ and to *ca.* 40% with $C_5H_5\overset{+}{N}CH_2CH{=}CH_2$, after 4 h (see Experimental section).

Very recently,[8] the reaction of 1-allylpyridinium tetrafluoroborates with palladium(0) substrates was exploited for the preparation of the cationic complexes $[Pd(\eta^3\text{-allyl})L'_2]BF_4$ (L' = tertiary phosphine).

The kinetics of reaction (2) were also studied by UV/VIS spectrophotometry using an excess of amine L' over the substrate **1a** to ensure the constancy of its concentration in the presence of fn. A 10-fold excess of L–L was employed to govern the position of the displacement equilibrium (1). The kinetic Scheme 2 was assumed. The rapid-exchange equilibrium ($K_e$) was assumed to hold throughout the kinetics. Under these conditions the experimental rate law takes on the pseudo-first-order form (3) where $k_{obs}$ is given by expression (4). The term

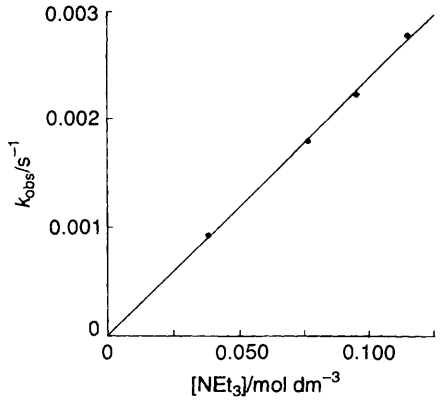



**Fig. 4** Fit of $k_{obs}$ to $[NEt_3]$ for the reaction of $[Pd(\eta^3\text{-}C_3H_5)\{NC_5H_4(CH{=}NC_6H_4OMe\text{-}4)\text{-}2\}]ClO_4$ in $CHCl_3$ at 25 °C (conditions as in Table 3)

$$-d[\mathbf{1a}]/dt = k_{obs}[\mathbf{1a}] \quad (3)$$

$$k_{obs} = k/\{1 + (K_e[L']^2/[L\text{–}L])\} \quad (4)$$

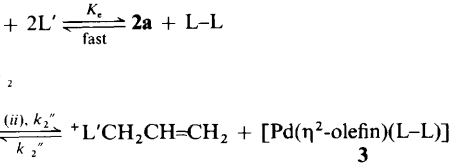
$1/\{1 + (K_e[L']^2/[L\text{–}L])\}$ simply represents the fraction of unreacted palladium that is present as the substrate **1a**. Equation (3) can be integrated to the monoexponential expression $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$, in terms of absorbance $D$ *vs.* time $t$ data.

With L' = $NEt_3$ the equilibrium ($K_e$) is shifted almost completely to the left under the prevailing conditions: therefore $1 \gg K_e[L']^2/[L\text{–}L]$ and thus $k_{obs} = k$. A plot of $k_{obs}$ *vs.* $[NEt_3]$ gives a straight line with statistically insignificant intercept and a slope $k_2 = (2.4 \pm 0.1) \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ (Table 3 and Fig. 4), according to the rate equation $k_{obs} = k_2[NEt_3]$.

With L' = pyridine the equilibrium was not driven completely to the left due to the larger $K_e$ value, so that the bis(pyridine) complex **2a** was also present in appreciable concentration throughout. In this case, $k$ values were calculated by equation (4) from the experimental $k_{obs}$ data, the appropriate $[NC_5H_5]$ and [L–L] values, and the $K_e$ value of Table 1. The resulting $k$ was again found to depend linearly on the amine concentration, according to the rate law $k = k_2[NC_5H_5]$, with $k_2 = (2.17 \pm 0.04) \times 10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ (Table 3).

The reaction rates appear to be independent of the fn concentration in the range $1.23 \times 10^{-4}$–$2 \times 10^{-3}$ mol dm$^{-3}$, in agreement with the kinetic Scheme 2. In a separate experiment the cationic species **2a** (isolated as its $BF_4^-$ salt in the same way as its 2-methylallyl analogue, see Experimental section) proved to be unreactive towards nucleophilic attack at the allyl group by a large excess of pyridine (Pd : $NC_5H_5$ 1 : 40).

The rate-determining step involves a second-order $k_2$ path which can be related to a direct bimolecular attack of L' on the allyl group of complex **1a**. The higher $k_2$ value of $NEt_3$ compared to pyridine is clearly a consequence of the much higher nucleophilic power of the former, as related to its greater basicity, despite the larger steric hindrance at the attacking nitrogen. For the corresponding reaction of **1a** with diethylamine a higher $k_2$ value of $(4.43 \pm 0.01) \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ was obtained,[2] in line with the lower steric requirements of $NHEt_2$ relative to $NEt_3$, these amines having comparable basicity.[6] With diethylamine a two-term rate equation of the type $k = k_2[NHEt_2] + k_2'[NHEt_2]^2$ was observed. The absence of a corresponding third-order quadratic $k_2'$ contribution in the kinetics with $NEt_3$ and pyridine lends support to the mechanism proposed for the $k_2'$ term, which was interpreted as a parallel nucleophilic attack by a hydrogen-bonded




**Scheme 3** (*i*) L'; (*ii*) olefin

$Et_2N–H\cdots NHEt_2$ dimer in rapid associative equilibrium with the monomer.[2]

The above kinetic results combined with the previously discussed reactivity trends, involving reaction (2) and its reverse, suggest that the mechanism in Scheme 2 is a particular case of a more general pattern in which the slow amination step **1a** ⟶ **Ia** and the subsequent $\eta^2$-olefin substitution step **Ia** ⟶ $^+L'CH_2CH{=}CH_2$ + **3a** can be made reversible under appropriate conditions (Scheme 3). The observed reactivity can be rationalized in terms of $k_{-2} \gg k_2$ and rapid $k_2''$ and $k_{-2}''$ substitution steps, depending on the different π-accepting abilities of the olefins involved (olefin and $^+L'CH_2CH{=}CH_2$). Thus, with the better π-acceptor fumaronitrile, the olefin-displacement equilibrium is shifted well over to the right and Scheme 2 becomes operative. On the contrary, the $\eta^2$-bound quaternary allyl cation in **Ia** can hardly be displaced by the less-activated dimethyl fumarate, so that the amination reaction (2) proceeds only to a small extent in the presence of dmf. The postulated intermediate **Ia** is probably a transient in the stepwise mechanism, since it escaped detection by spectroscopic techniques. In line with this mechanistic picture, the almost quantitative reaction of $^+L'CH_2CH{=}CH_2$ with [Pd($\eta^2$-olefin)(L–L)] [*i.e.* the reverse of reaction (2)] for olefin = dmf is related to the easier displacement of dimethyl fumarate by the quaternary allyl cation. The reversibility of allyl amination was described previously for the reaction of $\eta^3$-geranyl-, $\eta^3$-neryl-,[9] and $\eta^3$-1,1-dimethylallyl-palladium(II)[10] complexes.

On the other hand, prior co-ordination of the C=C double bond of the allyl substrate to the metal appears to be a prerequisite of oxidative addition of allylic electrophiles to low-valent metal complexes.[11] The fact that the amination of **1a** with $NHEt_2$ occurs in the presence of either fn or dmf may be ascribed to a rapid deprotonation of the $\eta^2$-co-ordinated $Et_2\overset{+}{N}HCH_2CH{=}CH_2$ moiety in a labile intermediate of type **Ia** by the excess of diethylamime, yielding a *neutral* [Pd($\eta^2$-$CH_2{=}CH{-}CH_2NEt_2$)(L–L)] species, from which the less-activated diethylaminopropene is easily displaced even by dmf. Such a species would also be the direct product of the proposed[2] allyl amination by the hydrogen-bonded diethylamine dimer.

## Experimental

The complexes [Pd($\eta^3$-allyl)(L–L)]$ClO_4$ (allyl = $C_3H_5$ or 2-$MeC_3H_4$) and [Pd($\eta^2$-olefin)(L–L)] (olefin = fn or dmf) were prepared by published procedures.[1,7] Morpholine and piperidine were distilled over anhydrous $K_2CO_3$ under nitrogen, while the liquid pyridines, 4-$R^3C_5H_4N$ ($R^3$ = MeCO, H or Et), were distilled over KOH pellets under nitrogen. 4-Chloropyridine hydrochloride was dissolved in water and treated dropwise with a slight excess of aqueous NaOH. The free pyridine was extracted with dichloromethane. The $CH_2Cl_2$ solution was taken to dryness on a rotary evaporator and the resulting oily product distilled over KOH pellets under reduced pressure. All other chemicals were reagent grade used without further purification. The solvents were evaporated to small volume or to dryness at reduced pressure on a rotary evaporator.

*Preparation of Complexes.* [Pd($\eta^3$-2-$MeC_3H_4$)$L'_2$]$BF_4$ **2**.—The complexes **2** (L' = morpholine or pyridine) were prepared from the reaction of [{PdCl($\eta^3$-2-$MeC_3H_4$)}$_2$] with the appropriate ligand and $AgBF_4$ in the molar ratio 0.5:3:1, as described for the analogue [Pd($\eta^3$-2-$MeC_3H_4$)($NHEt_2$)$_2$]$BF_4$.[2] The compounds must be stored at −20 °C to prevent rapid decomposition. The morpholine complex was obtained in 68.6% yield (based on the theoretical amount) and was characterized by molar conductivity (96.1 S cm$^2$ mol$^{-1}$ for a $10^{-3}$ mol dm$^{-3}$ MeOH solution at 25 °C), elemental analysis (Found: C, 34.3; H, 6.0; N, 6.5. $C_{12}H_{25}BF_4N_2O_2Pd$ requires C, 34.10; H, 5.95; N, 6.65%), and the $^1H$ NMR spectrum in $CDCl_3$ [allyl protons, δ 3.53 (2 H, s, $H_{syn}$), 2.84 (2 H, s, $H_{anti}$), and 2.15 (3 H, s, $CH_3$); morpholine protons, δ 4.15 (2 H, br s, NH), 4.0–3.6 (8 H, m, $OCH_2$) and 3.4–3.0 (8 H, m, $NCH_2$)]. The pyridine complex was isolated in 73.0% yield and identified similarly: $\Lambda_M$ 103.4 S cm$^2$ mol$^{-1}$ (Found: C, 41.1; H, 4.1; N, 6.8. $C_{14}H_{17}BF_4N_2Pd$ requires C, 41.35; H, 4.20; N, 6.90%); $^1H$ NMR spectrum [allyl protons, δ 3.83 (2 H, s, $H_{syn}$), 3.26 (2 H, s, $H_{anti}$) and 2.26 (3 H, s, $CH_3$); pyridine protons, δ 8.60–8.55 (4 H, m, $H^2$ and $H^6$), 7.90–7.80 (2 H, m, $H^4$) and 7.50–7.40 (4 H, m, $H^3$ and $H^5$)].

In an attempt to prepare the analogous complex with piperidine (pip) an oily product was obtained the $^1H$ NMR spectrum ($CDCl_3$) of which suggests the presence of the cationic species [Pd($\eta^3$-2-$MeC_3H_4$)(pip)$_2$]$^+$, which undergoes a rapid ligand exchange with trace amounts of un-co-ordinated piperidine [allyl protons, δ 3.55 (2 H, s, $H_{syn}$), 2.71 (2 H, s, $H_{anti}$), and 2.07 (3 H, s, $CH_3$); piperidine protons, δ 3.0 (8 H, br s, $NCH_2$) and 1.6 (12 H, br s, $CH_2$)].

*Reactions of* [Pd($\eta^3$-$C_3H_5$){$NC_5H_4$(CH=N$C_6H_4$OMe-4)-2}]$ClO_4$ *with* $NEt_3$ *or Pyridine.*—Fumaronitrile (0.06 mmol) and triethylamine (0.35 mmol) or pyridine (2.0 mmol) were added to a stirred suspension of the cationic complex (0.05 mmol) in $CDCl_3$ (2 cm$^3$), containing known amounts of dichloromethane or toluene as internal standards. In the course of the reaction the allyl substrate dissolved progressively while some [Pd($\eta^2$-fn){$NC_5H_4$(CH=N$C_6H_4$OMe-4)-2}] **3a** precipitated. The $^1H$ NMR measurements were carried out on clear portions of the supernatant solution. When the reaction was complete (24 h for triethylamine, 48 h for pyridine), the solid product **3a** was filtered off, purified, and identified by spectral data as previously reported for an independently prepared sample.[7] In the reaction mixtures the amination products [triethyl(prop-2-enyl)ammonium or 1-(prop-2-enyl)pyridinium cations] were identified by comparison of their $^1H$ NMR spectra with those of authentic samples (see below).

The corresponding reactions in the presence of dimethyl fumarate were carried out under the same experimental conditions and monitored by $^1H$ NMR measurements of the changes in concentration of $^+L'CH_2CH{=}CH_2$ with time.

*Preparation of* $Et_3\overset{+}{N}CH_2CH{=}CH_2$ *and* $C_5H_5\overset{+}{N}CH_2CH{=}CH_2$ *as Perchlorate Salts.*—A two-fold excess of allyl bromide (3.63 g, 30.0 mmol) was added to a methanol solution of $NEt_3$ (1.52 g, 15.0 mmol in 50 cm$^3$). After 24 h at ambient temperature $NaClO_4{\cdot}H_2O$ (4.21 g, 30.0 mmol) was added. The solvent was evaporated to dryness and the solid residue taken up in $CH_2Cl_2$ (*ca.* 100 cm$^3$). After filtration of the insoluble salts the solution was concentrated to *ca.* 10 cm$^3$ and diluted by slow addition of diethyl ether to precipitate the white product [$Et_3NCH_2$-$CH{=}CH_2$]$ClO_4$ (3.48 g, 96.0%). It was characterized by molar conductivity (106.3 S cm$^2$ mol$^{-1}$ for a $10^{-3}$ mol dm$^{-3}$ MeOH solution at 25 °C), by the Nujol mull IR spectrum [ν(Cl–O) 1094, δ(Cl–O) 623 cm$^{-1}$], and by the $^1H$ NMR spectrum in $CDCl_3$ [allyl protons, δ 6.0–5.85 (1 H, m, $CH_2{=}CH$), 5.8–5.7 (2 H, m, $CH_2{=}CH$) and 3.87 (2 H, d, *J* 7.6, $CHCH_2$); ethyl protons, δ 3.33 (6 H, q, *J* 7.3 Hz, $CH_2$) and 1.36 (9 H, t, $CH_3$)].

1-(Prop-2-enyl)pyridinium bromide was prepared according to the literature[12] and was converted into the perchlorate by treatment with an excess of $NaClO_4{\cdot}H_2O$, as described above: [$\Lambda_M$ = 111.5 S cm$^2$ mol$^{-1}$ for a $10^{-3}$ mol dm$^{-3}$ MeOH solution at 25 °C; IR spectrum (Nujol mull), ν(Cl–O) 1087, δ(Cl–O) 627 cm$^{-1}$; $^1H$ NMR spectrum in $CDCl_3$, allyl protons, δ 6.2–6.05 (1 H, m, $CH_2{=}CH$), 5.65–5.55 (2 H, m, $CH_2{=}CH$), 5.32 (2 H, d, *J* 7.0 Hz, $CHCH_2$); pyridinium protons, δ 8.9–8.8 (2 H, m, $H^2$ and $H^6$), 8.5–8.4 (1 H, m, $H^4$) and 8.1–8.0 (2 H, m, $H^3$ and $H^5$)].

*Reactions of* $Et_3\overset{+}{N}CH_2CH{=}CH_2$ *and* $C_5H_5\overset{+}{N}CH_2CH{=}CH_2$ *with* [Pd(η²-olefin){$NC_5H_4$(CH=$NC_6H_4$OMe-4)-2}] (*olefin = dmf or fn*).—The compound [$Et_3NCH_2CH{=}CH_2$]$ClO_4$ (60.4 mg, 0.25 mmol) was added to a stirred solution of [Pd(η²-dmf){$NC_5H_4$(CH=$NC_6H_4$OMe-4)-2}] (0.116 mg, 0.25 mmol) in $CHCl_3$ (5 $cm^3$). The sparingly soluble product [Pd(η³-$C_3H_5$){$NC_5H_4$(CH=$NC_6H_4$OMe-4)-2}]$ClO_4$ immediately precipitated. Upon stirring for 6 h at ambient temperature the solution changed from red-orange to yellow. Addition of $Et_2O$ (5 $cm^3$) completed the precipitation of the product (0.101 g, 89.0%), which was identified by comparison of its IR and $^1H$ NMR spectra with those of an independently prepared sample[1] [$^1H$ NMR in $(CD_3)_2SO$: allyl protons, δ 6.03 (1 H, m, $CH_2CHCH_2$), 4.29 (2 H, d, *J* 6.3, $H_{syn}$) and 3.62 (2 H, d, *J* 12.2 Hz, $H_{anti}$); pyridine protons, δ 9.00 (1 H, m, $H^6$), 8.39 (1 H, m, $H^4$), 8.25 (1 H, m, $H^3$) and 7.91 (1 H, m, $H^5$); imino protons, δ 9.07 (1 H, s); methoxy protons, δ 3.85 (3 H, s)].

The reaction of [$C_5H_5NCH_2CH{=}CH_2$]$ClO_4$ (55.0 mg, 0.25 mmol) with [Pd(η²-dmf){$NC_5H_4$(CH=$NC_6H_4$OMe-4)-2}] (0.116 mg, 0.25 mmol) was carried out in the same way to yield the complex [Pd(η³-$C_3H_5$){$NC_5H_4$(CH=$NC_6H_4$OMe-4)-2}]$ClO_4$ (0.105 g, 91.5%).

The progress of the reaction was also monitored by $^1H$ NMR spectroscopy at 25 °C. The allyl cation $^+L'CH_2CH{=}CH_2$ (0.04 mmol) was added to a solution or suspension of [Pd(η²-olefin){$NC_5H_4$(CH=$NC_6H_4$OMe-4)-2}] (0.04 mmol) in $CDCl_3$ (4 $cm^3$), containing known amounts of dichloromethane or toluene as internal standards. In the course of the reaction some [Pd(η³-$C_3H_5$){$NC_5H_4$(CH=$NC_6H_4$OMe-4)-2}]$ClO_4$ precipitated. The $^1H$ NMR spectra were recorded at different times on clear portions of the supernatant solution. For olefin = dmf the reaction was almost complete (90–95%) in *ca.* 4 h; for fn, the reaction with [$Et_3NCH_2CH{=}CH_2$]$ClO_4$ had proceeded to *ca.* 20% after 4 h from mixing of the reactants and that with [$C_5H_5NCH_2CH{=}CH_2$]$ClO_4$ to *ca.* 40%.

*Physical Measurements and Instrumentation.*—The conductivity was measured with a CDM83 conductivity meter. The $^1H$ NMR spectra were run on Bruker AM400 and WP80SY spectrometers at 25 °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 on a Perkin-Elmer 983G instrument, using CsI windows, in the range 4000–200 $cm^{-1}$.

*Determination of Equilibrium Constants.*—Equilibrium constants in equation (2) were determined spectrophotometrically by adding known amounts of $CHCl_3$ solutions of L′ of known concentration to a solution of complex **1** in the thermostatted cell compartment of the spectrophotometer and by recording the absorption spectra of the reaction solution in the wavelength range 300–600 nm. The analytical concentrations of the palladium substrate and L′ were in the range $5 \times 10^{-5}$–$2 \times 10^{-4}$ and $9 \times 10^{-6}$–1.5 mol $dm^{-3}$, respectively.

The absorbance data were fitted by non-linear least squares[13] using the mathematical model in equations (1) and (5)–(9)

$$\mathbf{1} + 2L' \overset{K_e}{\rightleftharpoons} \mathbf{2} + L\text{–}L \quad (1)$$

$$K_e = [\mathbf{2}][L\text{–}L]/[\mathbf{1}][L']^2 \quad (5)$$

$$[\mathbf{1}]_0 = [\mathbf{1}] + [\mathbf{2}] \quad (6)$$

$$[\mathbf{2}] = [L\text{–}L] \quad (7)$$

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

$$D_\lambda = \varepsilon_1[\mathbf{1}] + (\varepsilon_2 + \varepsilon_{L\text{–}L})[\mathbf{2}] \quad (9)$$

($D_\lambda$ = absorbance at wavelength λ). The function minimized was $\varphi = \Sigma(D_{obs} - D_{calc})^2$. The optimized parameters were $K_e$ and the absorption 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 at the current parameter values by means of a Newton system solver based on an LU (lower–upper) decomposition/back substitution scheme.[14] The uncertainties quoted in Tables 1 and 2 are one standard error of estimate.

*Spectrophotometric Kinetic Measurements.*—The kinetics of reaction (2) was studied by adding known aliquots of solutions of L′ to freshly prepared solutions of complex **1a** in the presence of fumaronitrile and recording the absorbance readings at 470 nm. An excess of L′ over the palladium substrate was used throughout all runs to ensure the constancy of [L′]. Since the α-diimine concentration was held constant by adding an excess, the kinetic model was as in equations (10)–(13).

$$[\mathbf{1a}]_{tot} = [\mathbf{1a}] + [\mathbf{2a}] + [\mathbf{3a}] \quad (10)$$

$$K_e = [\mathbf{2a}][L\text{–}L]/[\mathbf{1a}][L']^2 \quad (11)$$

$$[L'] = \text{constant} \quad (12)$$

$$[L\text{–}L] = \text{constant} \quad (13)$$

Thus, $d[\mathbf{3a}]/dt = k[\mathbf{1a}] = -\{1 + (K_e[L']^2/[L\text{–}L])\}d[\mathbf{1a}]/dt$, whence $-d[\mathbf{1a}]/dt = k[\mathbf{1a}]/\{1 + (K_e[L']^2/[L\text{–}L])\} = k_{obs} \times [\mathbf{1a}]$, *cf.* equations (3) and (4). The model corresponds therefore to the customary first-order monoexponential rate expression $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$, from which $k_{obs}$ can be obtained by non-linear regression[13] of $D_t$ *vs.* time data.

*Data Reduction and Analysis.*—Mathematical and statistical analyses of equilibrium and kinetic data were carried out on a personal computer equipped with an INTEL 486 66 MHz central processing unit by the use of a locally adapted version of Marquardt's non-linear regression algorithm[13] written in TURBOBASIC™ (Borland). The plots were obtained with the SIGMAPLOT™ (Jandel) graphic package.

## Acknowledgements

Financial support by the Italian Ministero per l'Università e la Ricerca Scientifica e Tecnologica (Research Funds 40 and 60%) is gratefully acknowledged.

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*Received* 11*th May* 1994; *Paper* 4/02804J