Mechanism of Nucleophilic Attack by Diethylamine on Cationic Palladium(II) Allyl Complexes containing α-Diimine Ligands

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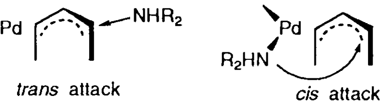
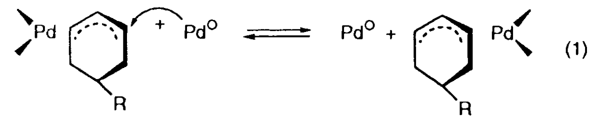
The reactions of the cationic complexes [Pd(η^3-allyl)(N–N′)]ClO_4 (allyl = 4-methoxycyclohexenyl, allyl or 2-methylallyl; N–N′ = 1,2-bis(imino)ethanes or pyridine-2-carbaldimines) with diethylamine, in the presence of an activated olefin, in chloroform at 25 °C have been studied. They involve a fast equilibrium displacement of the co-ordinated α-diimine to yield [Pd(η^3-allyl)($NHEt_2$)$_2$]$^+$, accompanied by slow nucleophilic attack at the allyl ligand of the [Pd(η^3-allyl)(N–N′)]$^+$ substrate producing [Pd(η^2-olefin)(N–N′)] (olefin = dimethyl fumarate or fumaronitrile) and allyldiethylamine. As shown by the stereochemical course of the reaction with [Pd(1–3-η^3-C_6H_8OMe)(C_5H_4N-2-CH=NC_6H_4OMe-4)]ClO_4, the nucleophilic attack takes place on the allyl face opposite the metal. The equilibrium constants for α-diimine displacement have been determined. They are strongly affected by the structure of the N–N′ ligand and decrease in the order RN=CH–CH=NR ≫ RN=C(Me)–C(Me)=NR ≈ C_5H_4N-2-CH=NR > C_5H_4N-2-CH=NCMe_3 (R = C_6H_4OMe-4). Kinetic studies showed that the pseudo-first-order rate constants (k_{obs}) for the slow amination path display both a first- and second-order dependence on the $NHEt_2$ concentration of type $k_{obs} = k_2[NHEt_2] + k_2'[NHEt_2]^2$. The k_2 term is related to direct bimolecular attack of $NHEt_2$ on the terminal allyl carbon, whereas the k_2' term is ascribed to a parallel nucleophilic attack by a hydrogen-bonded diethylamine dimer arising from amine self-association.

In recent years the nucleophilic attack of amines at the allyl ligand of palladium(II) complexes has been extensively studied because of its implication in the palladium-catalysed amination of allyl substrates.[1,2] The reaction has been also applied to the preparation of heterocyclic compounds.[3] In general, the attack occurs at a terminal carbon on the allylic face opposite the metal (*trans*), as was established by the stereochemistry of stoichiometric reactions between dialkylamines and cyclic allyl palladium complexes,[4,5] and of catalysed reactions between morpholine and sterically hindered allyl acetates.[6] The catalytic amination of *cis*- or *trans*-3-acetoxy-5-methoxycarbonylcyclohexenes, however, leads in each case to a *cis*/*trans* mixture of 3-dialkylamino-5-methoxycarbonylcyclohexenes,[7] in contrast to the retention of configuration observed in the catalytic alkylation of the same compounds with stabilized carbanions.[8] The loss of stereospecificity in the amination reactions was earlier ascribed to an internal transfer of the initially co-ordinated amine from palladium to the allyl carbon (*cis* attack), competing with the intermolecular *trans* attack (Scheme 1).[7]

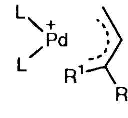


Scheme 1

As was later suggested, the loss of stereospecificity may also arise from isomerization of the starting products,[8] and from isomerization of the η^3-allyl intermediate through nucleophilic displacement by palladium(0) [equation (1)].[9]



The regiochemistry of the reactions with amines appears to be dictated by both steric and electronic factors. Increasing steric requirements of the allyl ligand and/or the incoming nucleophile will direct the attack at the less substituted allyl carbon,[10] whereas for the cationic complexes **I**, containing π-accepting L ligands such as tertiary phosphines or phosphites, the attack occurs preferentially at the more substituted terminus.[10b,11]



I

In comparison with the large body of evidence gathered for the stereo- and regio-chemistry of these reactions, only one preliminary kinetic study has appeared so far, concerning the attack of $NHMe_2$ on the complexes [PdCl(η^3-$C_3H_3Me_2$-1,1)(PPh_3)] and [PdL(η^3-$C_3H_3Me_2$-1,1)(PPh_3)]$^+$ (L = monodentate N-donor ligand).[12] On the basis of ^1H NMR data, the observed second-order dependence on the amine concentration was explained by a mechanism involving fast addition of the nucleophile to the allyl moiety followed by slow deprotonation of the ensuing intermediate.

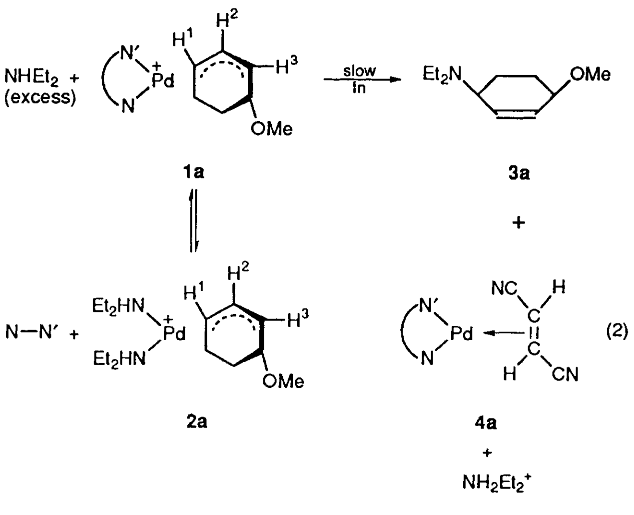
In the overwhelming majority of these studies phosphorus ligands bound to palladium-(II) and -(0) substrates were employed, except for some nitrogen-donor ligands, *i.e.* *N,N,N′,N′*-tetramethylethylenediamine (tmen), pyridine (py), 2,2′-bipyridine (bipy) and 2,9-dimethyl-1,10-phenanthroline.[10b,13] For cationic complexes of type **I**, with tmen, a purely σ-donor ligand, no amination was observed, whereas with bipy the nucleophilic attack by amines does occur, albeit at lower rates than with L = PPh_3. The cationic substrates with the sterically demanding dmphen were used to control the *syn–anti* configuration of the allyl group and also the *E/Z* isomeric ratio of the olefinic products.

In the course of our studies on η^3-allyl palladium(II) and platinum(II) complexes with α-diimine ligands, such as 1,2-bis(imino)ethanes, pyridine-2-carbaldimines, bipy and 1,10-phenanthroline, we observed a facile phenylation of the allyl group by the BPh_4^- anion.[14] A detailed kinetic study of this reaction indicated that the phenyl transfer to the palladium centre is the rate-determining step, followed by fast reductive elimination of allylbenzenes.[15] These investigations were made possible by stabilization of the resulting α-diimine palladium(0) fragment through η^2-co-ordination of activated olefins (fumaronitrile, dimethyl fumarate or maleic anhydride).

We have exploited the peculiar properties of these α-diimines (N–N′) in promoting the nucleophilic attack on complexes $[Pd(\eta^3\text{-allyl})(N\text{–}N')]^+$ **1** and of activated olefins in stabilizing the $[Pd(\eta^2\text{-olefin})(N\text{–}N')]$ **4** products in order to carry out a kinetic investigation of the mechanism of allyl amination of the cationic derivatives **1** by secondary amines, as will be reported herein.

Results and Discussion

Stereochemistry of Amination.—In order to determine the stereochemistry of amination, we have examined the products of the reaction of $[Pd(\eta^3\text{-}C_6H_8OMe)(N\text{–}N')]ClO_4$ **1a** (η^3-C_6H_8-OMe = 4-methoxy-1–3-η^3-cyclohexenyl, N–N′ = C_5H_4N-2-$CH{=}NC_6H_4OMe$-4) with an excess of diethylamine in the presence of fumaronitrile (fn) (molar ratio **1a**:$NHEt_2$:fn = 1:7:1.2) [equation (2)].



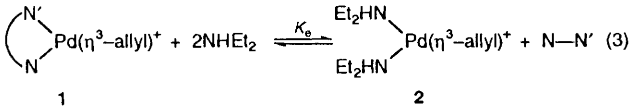
(2)

The course of reaction (2) in $CDCl_3$ was monitored by ^1H NMR spectroscopy. The initial spectra show the immediate establishment of an equilibrium between the α-diimine substrate **1a** and the bis(diethylamine) derivative **2a**, the latter being characterized by allyl proton resonances as multiplets centred at δ 5.62 (H^2), 4.67 (H^1) and 4.48 (H^3), and the former by the corresponding signals at δ 5.84 (H^2), 5.33 (H^1) and 5.07 (H^3). For an initial **1a** concentration of 2.5×10^{-2} mol dm^{-3} integration gives a **2a**:**1a** molar ratio of *ca.* 0.63:1, which remains virtually constant throughout the reaction. The signals of **1a** and **2a** progressively decrease with concomitant increase of those of the product **3a**, while the sparingly soluble $[Pd(\eta^2\text{-fn})(N\text{–}N')]$ complex separates as a yellow precipitate.[15a] After 24 h, the ^1H NMR spectrum shows the presence of **3a** (the only amination product within instrumental detection limits) along with trace amounts of the palladium(0) derivative and excess $NHEt_2$.

In a separate experiment the bis(amine) complex **2a** was prepared *in situ* from the reaction of $[\{PdCl(\eta^3\text{-}C_6H_8OMe)\}_2]$ with $AgBF_4$ (Pd:Ag = 1:1) in the presence of $NHEt_2$ (Pd:$NHEt_2$ = 1:2) in $CDCl_3$. After filtration of the solid AgCl the ^1H NMR spectrum shows the allyl proton resonances of **2a** virtually at the same chemical shifts as in the above reaction mixture, in addition to those of the co-ordinated amine (see Experimental section). Upon addition of $NHEt_2$ (5 equivalents) and fumaronitrile (1.2 equivalents), **2a** does not undergo amination to **3a**, even after prolonged time (24 h). *cis*-3-Diethylamino-6-methoxycyclohexene **3a** was isolated from reaction (2) carried out under preparative conditions in tetrahydrofuran (see Experimental section) and its ^1H NMR spectrum ($CDCl_3$) matches well that reported in the literature.[5]

Thus, it appears that reaction (2) is highly stereo- and regio-selective, since formation of **3a** indicates that attack of the amine takes place on the allyl face opposite the metal on **1a**, the C^1 allyl carbon being the site of amination.

Equilibria of α-Diimine Displacement by Diethylamine.—The rapid and reversible displacement of the N–N′ chelated α-diimine in complex **1a** by $NHEt_2$ is a general feature of cationic substrates of type **1**. In this context, we have carried out a UV/VIS spectrophotometric study of equilibrium (3) in $CHCl_3$



(3)

1 **2**

[N–N′ = $RN{=}C(R^1){-}C(R^1){=}NR$, R = C_6H_4OMe-4, R^1 = H or Me; C_5H_4N-2-$CH{=}NR^2$, R^2 = C_6H_4OMe-4 or CMe_3; allyl = C_3H_5, C_3H_4Me-2 or C_6H_8OMe].

For all substrates **1**, and particularly for those containing the C_3H_5 allyl ligand, absorbance readings were taken immediately after mixing of the reactants to avoid changes due to the onset of the subsequent slow allyl amination (see below). Abstract factor analysis of the observed spectral changes indicated the presence of only two independently absorbing species in the wavelength range 250–600 nm, namely the complex **1** and the free α-diimine N–N′.[16] One or more isosbestic points were observed in all cases under study. These findings rule out the presence of detectable amounts of intermediates bearing both one amine and an *N*-monodentate dangling α-diimine ligand.[17] This is confirmed by the failure to detect such a mixed species in the ^1H NMR spectra of reaction mixtures even at temperatures as low as −80 °C (CD_2Cl_2). The K_e values obtained by non-linear regression of absorbance *vs.* $[NHEt_2]$ data are listed in Table 1.

A typical three-dimensional representation of spectral changes is shown in Fig. 1 and a sample of the fit in Fig. 2.

The bis(amine) derivatives **2** were isolated and characterized as tetrafluoroborate salts for allyl = C_3H_5 or C_3H_4Me-2. Moreover, the equilibrium constants for the reverse of reaction (3), starting from $[Pd(\eta^3\text{-}C_3H_4Me\text{-}2)(NHEt_2)_2]BF_4$ and N–N′ = $RN{=}CH{-}CH{=}NR$ or C_5H_4N-2-$CH{=}NR^2$ (R = R^2 = C_6H_4OMe-4) were measured and found to be virtually identical to the inverse values for the direct reaction (3).

The displacement of the chelated α-diimine appears to be markedly affected by the structure and substituents of the N–N′ ligands and, to a lesser extent, by the nature of the allyl group. As can be seen, the K_e values decrease in the order $RN{=}CH{-}CH{=}NR \gg RN{=}C(Me){-}C(Me){=}NR \approx C_5H_4N\text{-}2\text{-}CH{=}NR^2 > C_5H_4N\text{-}2\text{-}CH{=}NCMe_3$ (R = R^2 = C_6H_4OMe-4), in agreement with the order of increasing stability of the five-membered metallacycle in the cationic complexes **1** towards α-diimine dissociation in acetonitrile.[14] In particular, the large K_e values for the 4-$MeOC_6H_4N{=}CH{-}CH{=}NC_6H_4OMe$-4 complexes are outstanding and indicate a high lability for this ligand.

The UV/VIS equilibrium results are in line with the findings of ^1H NMR experiments carried out for reaction (3) in $CDCl_3$

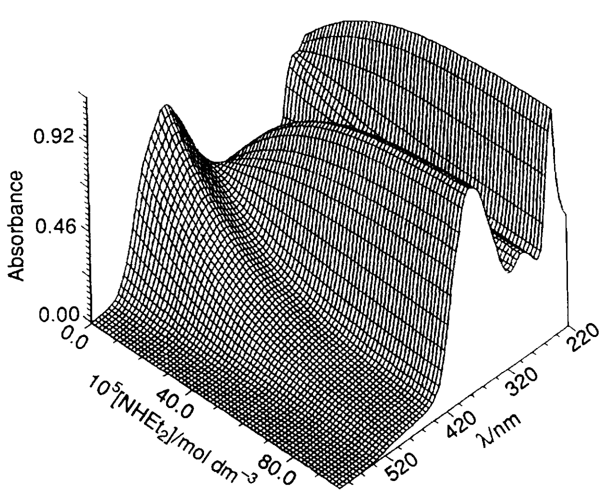


Fig. 1 Three-dimensional representation of spectral changes relating to equilibrium in equation (3) for allyl = C_3H_4Me-2, N-N' = RN=CH-CH=NR (R = C_6H_4OMe-4) in $CHCl_3$ at 25 °C

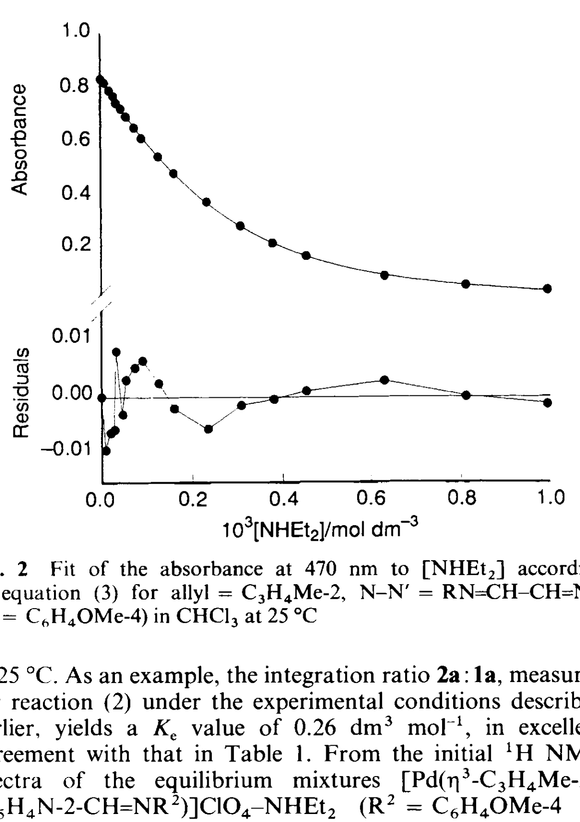


Fig. 2 Fit of the absorbance at 470 nm to [NHEt$_2$] according to equation (3) for allyl = C_3H_4Me-2, N-N' = RN=CH-CH=NR (R = C_6H_4OMe-4) in $CHCl_3$ at 25 °C

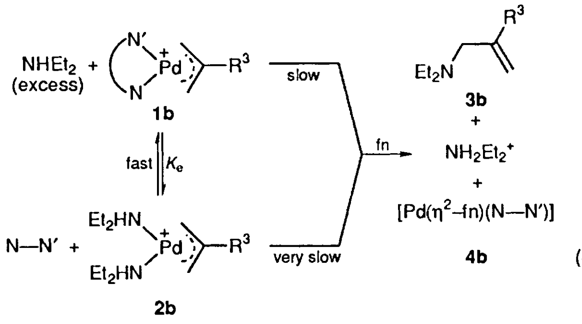
at 25 °C. As an example, the integration ratio **2a**:**1a**, measured for reaction (2) under the experimental conditions described earlier, yields a K_e value of 0.26 dm^3 mol^{-1}, in excellent agreement with that in Table 1. From the initial ^1H NMR spectra of the equilibrium mixtures [Pd(η^3-C_3H_4Me-2)-(C_5H_4N-2-CH=NR^2)]ClO$_4$-NHEt$_2$ (R^2 = C_6H_4OMe-4 or CMe$_3$; **1**:NHEt$_2$ molar ratio = 1:2) it appears that the free α-diimine C_5H_4N-2-CH=NR^2 exchanges rapidly with the chelated one for R^2 = C_6H_4OMe-4 but slowly for R^2 = CMe$_3$, whereas for the cationic complex [Pd(η^3-C_3H_4Me-2)-(NHEt$_2$)$_2$]$^+$, no fast exchange between free and co-ordinated NHEt$_2$ takes place at 25 °C. In this compound, the allyl ligand is η^3-bound to palladium [$\delta_{H_{syn}}$ 3.42 (s), $\delta_{H_{anti}}$ 2.71 (s)], while the methyl and methylene protons of the two ethyl groups on the same NHEt$_2$ molecule are non-equivalent due to the lack of a plane of symmetry passing through the Pd and N atoms [δ(CH$_2$) 3.2–2.5, δ(CH$_3$) 1.40 (t) and 1.25 (t)]. This also holds true for the related complexes [Pd(η^3-allyl)(NHEt$_2$)$_2$]$^+$ (allyl = C_3H_5 or C_6H_8OMe). Furthermore, interaction of the cationic substrate [Pd(η^3-allyl)(N-N)']$^+$ with NHEt$_2$ and/or N-N' 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.

Table 1 Equilibrium constants (K_e) for reaction (3) at 25 °C in chloroform

Compound [Pd(η^3-allyl)(RN=C(R^1)-C(R^1)=NR)]ClO$_4$ R	R^1	allyl	K_e/dm^3 mol^{-1}
C_6H_4OMe-4	H	C_3H_5^{a}	1390 ± 140
C_6H_4OMe-4	H	C_3H_4Me-2	1079 ± 33
C_6H_4OMe-4	Me	C_3H_4Me-2	1.90 ± 0.16
[Pd(η^3-allyl)(C_5H_4N-2-CH=NR^2)]ClO$_4$ R^2			
C_6H_4OMe-4		C_3H_5^{a}	4.1 ± 0.3
C_6H_4OMe-4		C_3H_4Me-2	1.3 ± 0.2
C_6H_4OMe-4		C_6H_8OMe^{b}	0.27 ± 0.01
CMe$_3$		C_3H_5^{a}	0.19 ± 0.01
CMe$_3$		C_3H_4Me-2	0.038 ± 0.005

^{a} From spectral data recorded immediately after mixing of the reactants. ^{b} C_6H_8OMe = 4-methoxycyclohexenyl.

Kinetics of Amination.—In order to gather qualitative reactivity data preliminary to a quantitative UV/VIS kinetic study, the amination reaction (4) [N-N' = RN=CH-CH=NR,



(4)

R = C_6H_4OMe-4; C_5H_4N-2-CH=NR^2, R^2 = C_6H_4OMe-4 or CMe$_3$; R^3 = H or Me] was examined by ^1H NMR spectroscopy in CDCl$_3$ at 25 °C.

Molar ratios **1b**:NHEt$_2$:fn of 1:7:1.2 with [**1b**]$_0$ = 2.5 × 10^{-2} mol dm^{-3} were used throughout. After 24 h the yields of allylamine **3b** were in the range 75–80 (R^3 = Me) and 90–95% (R^3 = H), based on CH$_2$Cl$_2$ or toluene as internal standards. The products **3b** were identified in the reaction mixture by their characteristic signals (see Experimental section). For the slower reactions (R^3 = Me), trace amounts of unidentified side-products were observed, presumably arising from decomposition of the free α-diimine.

In separate experiments, the reactivity of the cationic complexes **2b**, independently isolated as BF$_4^-$ salts, was also studied (**2b**:NHEt$_2$:fn = 1:5:1.2; [**2b**]$_0$ = 2.5 × 10^{-2} mol dm^{-3}). The bis(amine) complexes **2b** also undergo amination, but at a drastically reduced rate [*e.g.*, for R^3 = Me, reaction (4) proceeds to only 8% conversion after 24 h].

On the basis of spectral changes with time, combined with the results of reaction (2), the rates appear to depend on the α-diimine and on the allyl ligand in the order: C_5H_4N-2-CH=NR^2 ≫ RN=CH-CH=NR and C_3H_5 > C_6H_8OMe > C_3H_4Me-2.

The much lower reactivity of substrates **1b** with N-N' = RN=CH-CH=NR is due to the almost quantitative conversion to the much less reactive species **2b**, under the prevailing experimental conditions (*cf.* the large K_e values in Table 1). In fact, the ^1H NMR spectrum of a mixture of [Pd(η^3-C_3H_4Me-2)(RN=CH-CH=NR)]ClO$_4$-NHEt$_2$ (R = C_6H_4OMe-4) in CDCl$_3$ shows the presence of only the displaced α-diimine [δ(N=C-H) at 8.37] and of the bis(amine) derivative **2b**. The higher rates displayed by complexes **1b** with N-N' = C_5H_4N-

Table 2 Selected ^{13}C NMR spectral data

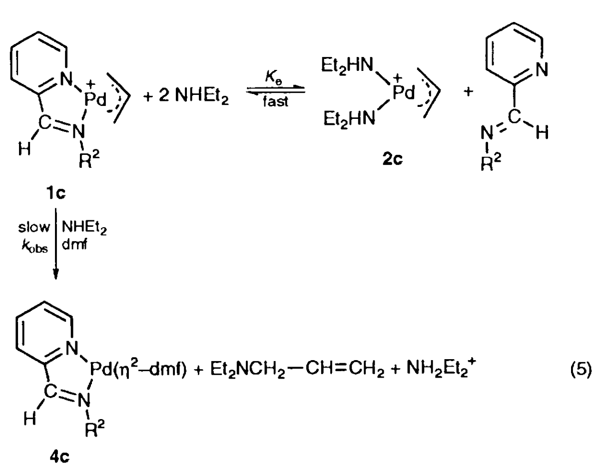
Compound	Allyl carbons C^1,C^3	C^2	C^2CH_3	Imino carbon N=C–H
$[Pd(\eta^3-C_3H_4Me-2)(NHEt_2)_2]BF_4$ [a]	59.1	132.8	23.0	
$[Pd(\eta^3-C_3H_4Me-2)(C_5H_4N-2-CH=NR^2)]ClO_4$ [a] ($R^2 = C_6H_4OMe-4$)	62.7 [b]	135.7	23.6	164.5
$[Pd(\eta^3-C_3H_4Me-2)(C_5H_4N-2-CH=NR^2)]ClO_4$ [c] ($R^2 = C_6H_4OMe-4$)	62.8 [b]	135.2	22.9	166.0
$[Pd(\eta^3-C_3H_5)(C_5H_4N-2-CH=NR^2)]ClO_4$ [c] ($R^2 = C_6H_4OMe-4$)	64.1 [b]	119.5		170.0
$[Pd(\eta^3-C_3H_5)(C_5H_4N-2-CH=NR^2)]ClO_4$ [c] ($R^2 = CMe_3$)	63.7 [b]	118.3		164.4

[a] In $CDCl_3$. [b] A time-averaged singlet for the terminal C^1 and C^3 carbons is observed due to the fast ligand site exchange undergone by the asymmetric $C_5H_4N-2-CH=NR^2$ α-diimine, which is reflected by the fast *syn–syn,anti–anti* exchange of allyl protons in the ^1H NMR spectra. [c] In $(CD_3)_2SO$.

2-CH=NR^2 relative to the corresponding intermediates **2b** can be related to the better π-acceptor abilities of α-diimines[18] (compared to the essentially σ-donating diethylamine ligand) which reduce the electron density on the central metal, thereby increasing the electrophilic character of the allyl moiety. This effect is paralleled by the downfield ^{13}C shifts of the allyl carbon resonances (Table 2) when $NHEt_2$ is replaced by $C_5H_4N-2-CH=NC_6H_4OMe-4$. The relationship between ^{13}C chemical shifts and relative charges on the η^3-allyl carbon has already been established in connection with the ease and regiochemistry of nucleophilic attack.[10b,19] A downfield ^{13}C shift of the terminal allyl carbons is also observed on going from R^3 = Me to R^3 = H in the complexes $[Pd(\eta^3-C_3H_4R^3-2)(C_5H_4N-2-CH=NC_6H_4OMe-4)]ClO_4$, in line with the higher reactivity of the $\eta^3-C_3H_5$ allyl substrate. In the case of R^3 = Me, however, steric hindrance to attack by the amine may also be operative.

From the equilibrium constant values in Table 1 combined with the results of ^1H NMR reactivity studies, it appears that the most suitable substrate for a quantitative kinetic investigation is $[Pd(\eta^3-C_3H_5)(C_5H_4N-2-CH=NR^2)]ClO_4$. The kinetic investigation was carried out by UV/VIS spectrophotometric techniques with an excess of $NHEt_2$ to ensure an effective constancy of its concentration, in the presence of dimethyl fumarate (dmf) to stabilize the resulting palladium(0) product. The use of dmf instead of fn provided much wider spectral changes in the wavelength range around 340 nm in $CHCl_3$ at 25 °C.

The kinetic scheme of equation (5) was assumed where $[\mathbf{1c}]_{tot} = 1 \times 10^{-4}$ mol dm^{-3}, $[NHEt_2] = 1.8 \times 10^{-3}$–$3.6 \times 10^{-2}$ mol dm^{-3} and [dmf] = 1.2×10^{-4}–1×10^{-3} mol dm^{-3}.



(5)

The very slow reaction of **2c** with $NHEt_2$ was neglected in the mathematical treatment (see Experimental section). According to reaction (5), the rate law is given by equation (6), where B =

$$-d[\mathbf{1c}]/dt = k_{obs}[\mathbf{1c}]/(1 + B[\mathbf{1c}]^{-\frac{1}{2}}) \qquad (6)$$

$0.5[NHEt_2]K_e^{\frac{1}{2}}$. Upon integration, the dependence of [**1c**] on time (t) is given by the implicit transcendental equation (7) where $[\mathbf{1c}]_o$ refers to the equilibrium concentration of **1c** at t = 0.

$$[\mathbf{1c}]\exp(-2B[\mathbf{1c}]^{-\frac{1}{2}}) = [\mathbf{1c}]_o\exp(-2B[\mathbf{1c}]_o^{-\frac{1}{2}})\exp(-k_{obs}t) \qquad (7)$$

If the α-diimine concentration is held constant throughout by addition of excess N–N′ to the system, the experimental rate law takes on the customary pseudo-first-order form (8) where $k_{obs'}$ can be expressed by equation (9).

$$-d[\mathbf{1c}]/dt = k_{obs}'[\mathbf{1c}] \qquad (8)$$

$$k_{obs}' = k_{obs}/(1 + K_e[NHEt_2]^2/[N\text{–}N']) \qquad (9)$$

Equation (8) can be integrated to the monoexponential expression $[\mathbf{1c}] = [\mathbf{1c}]_{tot}\exp(-k_{obs}'t)$. With $R^2 = CMe_3$, the equilibrium (K_e) was driven almost completely to the left, so that $1 \gg K_e[NHEt_2]^2/[N\text{–}N']$ and thus $k_{obs}' = k_{obs}$. The latter values were found to be in a good agreement with those derived from equation (7) (Table 3), thereby providing a check on the internal consistency of the treatment. A plot of $k_{obs}/[NHEt_2]$ *vs.* $[NHEt_2]$ gives a straight line with intercept $k_2 = (1.23 \pm 0.04) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and slope $k_2' = 1.47 \pm 0.02$ dm^6 mol^{-2} s^{-1} (Fig. 3), indicating a two-term relationship of type given by equation (10).

$$k_{obs} = k_2[NHEt_2] + k_2'[NHEt_2]^2 \qquad (10)$$

With $R^2 = C_6H_4OMe-4$, the equilibrium could not be shifted completely to the left due to the larger K_e value (Table 1). In this case the bis(amine) complex **2c** was also present in appreciable concentration throughout and rate equation (9) was observed. A plot of k_{obs}' *vs.* $[NHEt_2]$ reveals a curvilinear relationship (Fig. 4) which can be fitted by expression (11).

$$k_{obs}' = (k_2[NHEt_2] + k_2'[NHEt_2]^2)/(1 + K_e[NHEt_2]^2/[N\text{–}N']) \qquad (11)$$

Non-linear regression of k_{obs}' *vs.* $[NHEt_2]$ yields the parameters $k_2 = (4.43 \pm 0.01) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, $k_2' = 4.8 \pm 0.2$ dm^6 mol^{-2} s^{-1} and $K_e = 4.0 \pm 0.3$ dm^3 mol^{-1}, the latter value being in very good agreement with that determined by equilibrium studies (Table 1).

Table 3 Rate data for reaction (5) at 25 °C in chloroform

Compound $[Pd(\eta^3\text{-}C_3H_5)(N\text{-}N')]ClO_4$ N-N' = $C_5H_4N\text{-}2\text{-}CH{=}NR^2$	$10^2[NHEt_2]$/mol dm^{-3}	10^4[dmf]/mol dm^{-3}	10^2[N-N']^a/mol dm^{-3}	$10^4k_{obs}/s^{-1}$
$R^2 = CMe_3$^{b}	0.50	1.2	0	1.01^c
	1.00	1.2	0	2.70^c
	1.51	1.2	0	5.24^c
	2.01	1.2	0	8.41^c
	3.02	1.2	0	17.15^c
$R^2 = CMe_3$	0.50	1.2	1.68	1.01^d
	1.00	1.2	1.68	2.71^d
	1.51	1.2	1.68	5.23^d
	2.01	1.2	1.68	8.42^d
	3.02	1.2	1.68	17.15^d
$R^2 = C_6H_4OMe\text{-}4$^{b}	0.18	1.2	0.103	0.95^e
	0.36	1.2	0.103	2.11^e
	0.90	1.2	0.103	5.99^e
	1.44	1.2	0.103	9.05^e
	1.80	1.2	0.103	10.42^e
	2.40	1.2	0.103	11.83^e
	3.00	1.2	0.103	12.57^e
	3.60	1.2	0.103	12.96^e
$R^2 = C_6H_4OMe\text{-}4$	2.40	5.0	0.103	11.85^e
	2.40	10.0	0.103	11.82^e

^{a} Concentration of α-diimine added in excess. ^{b} $[Pd]_{tot} = 1 \times 10^{-4}$ mol dm^{-3}. ^{c} k_{obs} Values in equation (7). ^{d} k_{obs} Values in equation (10). ^{e} k_{obs}' Values in equation (11).

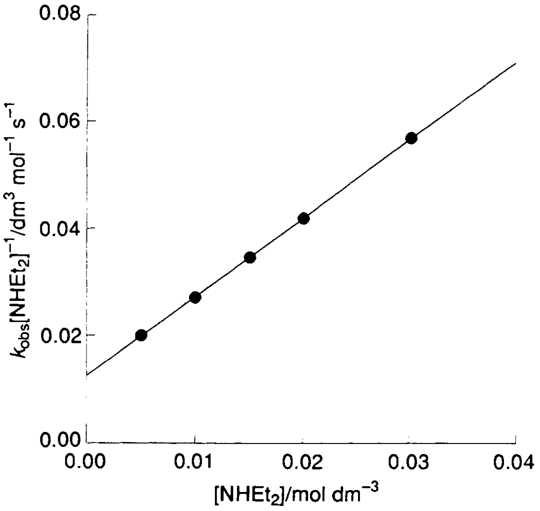


Fig. 3 Fit of $k_{obs}/[NHEt_2]$ to $[NHEt_2]$ for the reaction of $[Pd(\eta^3\text{-}C_3H_5)(C_5H_4N\text{-}2\text{-}CH{=}NCMe_3)]ClO_4$ with $NHEt_2$ in $CHCl_3$ at 25 °C [equation (10); concentration of excess N-N' added = 1.68×10^{-2} mol dm^{-3}; other conditions as in Table 3]

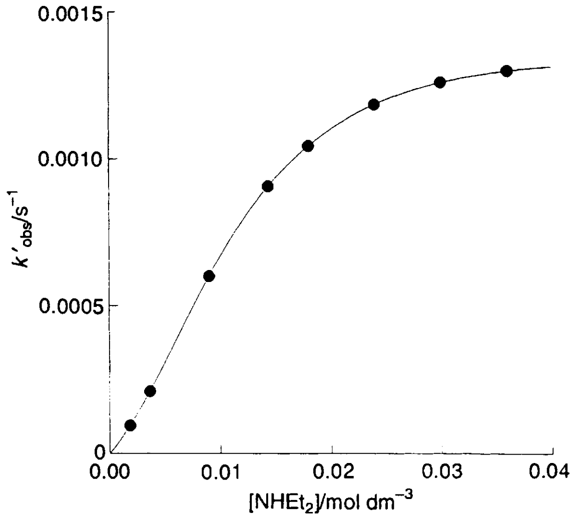


Fig. 4 Fit of k_{obs}' to $[NHEt_2]$ for the reaction of $[Pd(\eta^3\text{-}C_3H_5)(C_5H_4N\text{-}2\text{-}CH{=}NC_6H_4OMe\text{-}4)]ClO_4$ with $NHEt_2$ in $CHCl_3$ at 25 °C {equation (11); [dmf] = 1.2×10^{-4} mol dm^{-3}; other conditions as in Table 3}

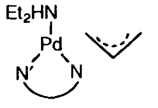
In both cases, the rate-determining step (k_{obs}) of reaction (5) involves both a first- and a second-order term in diethylamine. Moreover, the rates were found to be independent of dmf concentration up to a Pd : dmf molar ratio of 1 : 10, suggesting that the activated olefin serves as a mere stabilizing agent for the palladium(0) fragment in a fast subsequent step. The k_2 term can be related to a direct bimolecular attack of $NHEt_2$ on the terminal allyl carbon of **1c**. The k_2' term may be interpreted on the basis of a parallel nucleophilic attack by a hydrogen-bonded diethylamine dimer in fast association equilibrium with the monomer [equation (12)]. The presence of such dimers in

$$2NHEt_2 \overset{K_D}{\rightleftharpoons} Et_2N\text{-}H \cdots NHEt_2 \qquad (12)$$

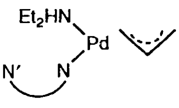
chlorinated solvents is well established[20] and their role as nucleophiles in organic[20,21] and organometallic[22] reactions is well documented. According to this interpretation, the k_2' term in equations (10) and (11) is the product K_Dk_2'', where k_2'' is the second-order rate constant for direct attack by the dimer. Alternatively, the quadratic dependence on amine concentration might be viewed in the context of a base-catalysed bimolecular attack involving a concerted three-centre activated complex.[22]

The higher k_2 value for $R^2 = C_6H_4OMe\text{-}4$ is in line with the higher electrophilic character of the allyl group, as suggested by ^{13}C NMR data (Table 2). A corresponding increase of k_2' is also observed on going from $R^2 = CMe_3$ to $R^2 = C_6H_4OMe\text{-}4$, which lends support to the above mechanistic picture. The much higher values of k_2' relative to k_2 may arise from an enhanced nucleophilic power of the dimer[23] compounded with the presence of the K_D term.

An alternative mechanism might involve parallel nucleophilic attacks of the monomeric $NHEt_2$ on both **1c** and a labile intermediate containing a co-ordinated diethylamine, such as **II** or **III**.



II



III

On the basis of the available experimental evidence, however, no intermediates of this type were detected in our systems. At present further kinetic studies are underway with the use of tertiary amines as nucleophiles in an effort to discriminate between these mechanisms.

Experimental

The cationic complexes **1**, [Pd(η^3-allyl)(N–N')]ClO_4 (allyl = 4-methoxycyclohexenyl, allyl, 2-methylallyl; N–N' = α-diimine), were prepared by published methods.[14,15] Diethylamine was distilled over anhydrous K_2CO_3 under nitrogen. All other chemicals and solvents were reagent grade and were used without further purification. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

Preparation of Complexes [Pd(η^3-allyl)($NHEt_2$)$_2$]BF_4 **2**.—Addition of silver tetrafluoroborate (0.390 g, 2 mmol) dissolved in acetone (10 cm^3) to a stirred solution of [{PdCl(η^3-C_3H_5)}$_2$][24] (0.366 g, 1 mmol) and $NHEt_2$ (0.366 g, 5 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C caused the immediate precipitation of AgCl. After stirring for 10 min, the mixture was treated with activated charcoal and filtered. The clear solution was concentrated to small volume without heating and diluted with Et_2O to precipitate the product [Pd(η^3-C_3H_5)($NHEt_2$)$_2$]BF_4 as a pearl-white solid (0.46 g, 60.4% yield based on the theoretical amount). This compound must be stored in a freezer (−20 °C) to prevent rapid decomposition. It was characterized by conductivity (Λ_M 94.8 S cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} MeOH solution at 25 °C), by elemental analysis (Found: C, 34.2; H, 7.2; N, 7.3. $C_{11}H_{27}BF_4N_2Pd$ requires C, 34.70; H, 7.15; N, 7.35%) and by ^{1}H NMR spectra in $CDCl_3$ [allyl protons, δ 5.52 (1 H, m, CH_2CHCH_2), 3.62 (2 H, d, *J* 7.5, H_{syn}), 2.79 (2 H, d, *J* 12.3, H_{anti}); diethylamine protons, δ 3.73 (2 H, br m, NH), 3.2–2.5 (8 H, m, CH_2), 1.38 (6 H, t, *J* 7.2, CH_3) and 1.20 (6 H, t, *J* 7.2 Hz, CH_3)].

By the same procedure the homologue [Pd(η^3-C_3H_4Me-2)($NHEt_2$)$_2$]BF_4 was isolated in 68.5% yield and identified by ^{1}H and ^{13}C NMR spectra in $CDCl_3$ [allyl protons, δ 3.42 (2 H, s, H_{syn}), 2.71 (2 H, s, H_{anti}), 2.10 (3 H, s, CH_3); diethylamine protons, δ 3.65 (2 H, br m, NH), 3.2–2.5 (8 H, m, CH_2), 1.40 (6 H, t, *J* 7.2, CH_3), 1.25 (6 H, t, *J* 7.2 Hz, CH_3); allyl carbons, δ 132.8 (CH_2CMeCH_2), 59.1 (CH_2CMeCH_2), 23.0 (CH_3); diethylamine carbons, δ 49.3 (CH_2), 49.1 (CH_2), 15.1 (CH_3) and 14.8 (CH_3)].

In an attempt to prepare the analogous cationic complex with the 4-methoxy-1–3-η^3-cyclohexenyl group starting from [{PdCl(η^3-C_6H_8OMe)}$_2$],[5] the above method yielded an oily product whose ^{1}H NMR spectrum in $CDCl_3$ is fully consistent with its formulation as [Pd(η^3-C_6H_8OMe)($NHEt_2$)$_2$]BF_4 [4-methoxy-1–3-η^3-cyclohexenyl protons, δ 5.61 (1 H, t, H^2), 4.69 (1 H, t, H^1), 4.47 (1 H, d, H^3), 3.44 (1 H, br s, OCH), 3.30 (3 H, s, OCH_3), 1.92 (1 H, m, CH_2), 1.81 (1 H, m, CH_2), 1.43 (1 H, m, CH_2), 1.08 (1 H, m, CH_2); diethylamine protons, δ 3.35 (2 H, br m, NH), 3.1–2.5 (8 H, m, CH_2), 1.33 (3 H, t, CH_3), 1.31 (3 H, t, CH_3), 1.21 (3 H, t, CH_3) and 1.17 (3 H, t, CH_3)].

Isolation of cis-*3-diethylamino-6-methoxycyclohexene* **3a**.—Diethylamine (1.024 g, 14 mmol), was added to a stirred solution of [Pd(η^3-C_6H_8OMe)(C_5H_4N-2-CH=NC_6H_4OMe-4)]ClO_4 **1a** (1.059 g, 2 mmol) and fumaronitrile (0.187 g, 2.4 mmol) in $CHCl_3$ (30 cm^3). After standing for 24 h, Et_2O was added to complete the precipitation of [Pd(η^2-fn)(C_5H_4N-2-CH=NC_6H_4OMe-4)] **4a**.[15a] After filtration of **4a** (0.62 g), the solvents were evaporated and the residue was worked up as described in the literature[5] to isolate **3a** as an oil, which was further purified by chromatography on a silica gel column ($CHCl_3$–MeOH 95:5 v/v; R_f = 0.4, 0.275 g, 75.0%). ^{1}H NMR spectrum in $CDCl_3$: δ 5.95–5.80 (2 H, m, CH=CH), 3.60 (1 H, m, OCH), 3.34 (3 H, s, OMe), 3.31 (1 H, m, NCH), 2.60–2.40 (4 H, m, NCH_2), 1.65–1.45 (4 H, m, CH_2–CH_2) and 1.03 (3 H, t, CCH_3).

Reactions of [Pd(η^3-allyl)(N–N')]ClO_4 **1** *with* $NHEt_2$.—These reactions were carried out in $CDCl_3$ at 25 °C and their progress was monitored by ^{1}H NMR spectroscopy using known amounts of dichloromethane or toluene as internal standards.

Fumaronitrile (0.06 mmol) and diethylamine (0.35 mmol) were added to a stirred solution or suspension of **1** (0.05 mmol) in $CDCl_3$ (2 cm^3). The less soluble complexes **1** (allyl = C_3H_5) dissolved progressively in *ca.* 2 h. In the course of the reaction some precipitation of [Pd(η^2-fn)(N–N')] also occurred, which was filtered off before the NMR measurements. In no case was noticed formation of metallic palladium.

The reaction with the η^3-C_6H_8OMe derivative **1a** was nearly complete (*ca.* 90% conversion) in 10 h. In the reaction mixture, the amination product **3a** was identified by its typical ^{1}H NMR resonances, which occurred at the same chemical shifts as for the isolated sample.

The reactions with the η^3-C_3H_5 derivatives **1b** were almost complete (*ca.* 90% conversion) in 4 h for N–N' = C_5H_4N-2-CH=NC_6H_4OMe-4 and in 5 h for N–N' = C_5H_4N-2-CH=$NCMe_3$. In the reaction mixtures, the amination product, diethylprop-2-enylamine, was identified by its ^{1}H NMR spectrum [propen-2-yl protons, δ 5.31 (m, C=CH–C), 5.15–5.0 (m, C=CH_2), 3.04 (d, *J* 7.3, CCH_2); ethyl protons, δ 2.47 (q, *J* 7.2 Hz, CH_2), 1.02 (t, CH_3)].

The reactions with the η^3-C_3H_4Me-2 derivatives **1b** were much slower (75–80% conversion after 24 h). In the reaction mixtures, the amination product diethyl(2-methylprop-2-enyl)amine was identified by its ^{1}H NMR spectrum [2-methylprop-2-enyl protons, δ 4.84 and 4.79 (s, C=CH_2), 2.90 (s, CCH_2), 1.72 (s, CCH_3); ethyl protons, δ 2.46 (q, *J* 7.2 Hz, CH_2), 1.00 (t, CH_3)], which is in good agreement with that reported in CCl_4 solution for the isolated amine.[25]

Physical Measurements and Instrumentation.—The conductivity was measured with a CDM83 conductivity meter. The ^{1}H and ^{13}C NMR spectra were run on Bruker AM400 and Bruker WP80SY spectrometers at 25 °C, using tetramethylsilane as an internal standard. Equilibrium and kinetic measurements were carried out on a Perkin Elmer Lambda 5 spectrophotometer using 1 cm quartz cells.

Determination of Equilibrium Constants.—Equilibrium constants for equation (3) were determined spectrophotometrically by adding known amounts of $CHCl_3$ solutions of $NHEt_2$ of known concentration to a solution of **1** in the thermostatted cell compartment of the spectrophotometer and by recording the absorption spectra of the reaction solutions in the wavelength range 250–600 nm immediately after mixing. The analytical concentrations of palladium substrate and $NHEt_2$ were in the range 5×10^{-5}–2×10^{-4} and 9×10^{-6}–0.1 mol dm^{-3}, respectively.

The absorbance data were fitted by non-linear least-squares[26] to a mathematical model underlying equation (3).[27]

Spectrophotometric Kinetic Measurements.—The kinetics of reaction (5) was studied by adding known aliquots of $NHEt_2$ solutions to freshly prepared solutions of **1c** in the presence of dmf and recording the absorbance readings at 340 nm with time. An excess of $NHEt_2$ over the palladium substrate was used throughout to ensure the constancy of $[NHEt_2]$. Rate equation (6) was derived from the equilibrium-rate scheme of equation (5), which serves to define the gross rate constant used in the integrated rate equation, but does not imply anything about a detailed mechanism [equations (13)–(15)], $\{[NHEt_2]$ = constant $\gg [\mathbf{1c}]_{tot}$, $[\mathbf{2c}] = [N–N']\}$, whence $-d[\mathbf{1c}]/dt = k_{obs}[\mathbf{1c}]/(1 + B[\mathbf{1c}]^{-\frac{1}{2}})$ with $B = 0.5[NHEt_2]K_e^{\frac{1}{2}}$. Integration of this differential equation yields equation (7). The absorbance *vs.* time data $A_t = \varepsilon_{1c}[\mathbf{1c}] + \varepsilon_{4c}[\mathbf{4c}] + (\varepsilon_{2c} + \varepsilon_{N-N'})[\mathbf{2c}]$ were fitted by non-linear regression, the implicit equation (7) being solved numerically in each iterative cycle by bisection.[28] The parameters fitted were k_{obs} and the absorption coefficients, whereas K_e was kept fixed at the value determined by equilibrium studies (Table 1). The initial concentration $[\mathbf{1c}]_o$ in equation (7) was obtained by analytically solving the equilibrium equation system at $t = 0$, under the prevailing concentration conditions.

$$[\mathbf{1c}]_{tot} = [\mathbf{1c}] + [\mathbf{2c}] + [\mathbf{4c}] \qquad (13)$$

$$K_e = [\mathbf{2c}][N–N']/[\mathbf{1c}][NHEt_2]^2 \qquad (14)$$

$$d[\mathbf{4c}]/dt = -(d[\mathbf{1c}]/dt + d[\mathbf{2c}]/dt) = k_{obs}[\mathbf{1c}] = -d[\mathbf{1c}]/dt + (\tfrac{1}{2}[NHEt_2]K_e^{\frac{1}{2}}[\mathbf{1c}]^{-\frac{1}{2}})d[\mathbf{1c}]/dt \qquad (15)$$

For the kinetic runs in which the α-diimine concentration was held constant by adding excess N–N′, the kinetic model can be described by equations (13) and (14), where [N–N′] and $[NHEt_2]$ can be regarded as constant. Thus, $d[\mathbf{4c}]/dt = k_{obs}[\mathbf{1c}] = -(1 + K_e[NHEt_2]^2/[N–N'])d[\mathbf{1c}]/dt$, whence equation (16) follows [see equations (8) and (9)].

$$-d[\mathbf{1c}]/dt = k_{obs}[\mathbf{1c}]/(1 + K_e[NHEt_2]^2/[N–N']) = k_{obs}'[\mathbf{1c}] \qquad (16)$$

The model reduces therefore to the customary first-order monoexponential rate law $A_t = A_\infty + (A_o - A_\infty)\exp(-k_{obs}'t)$ from which k_{obs}' can be obtained by non-linear regression of absorbance *vs.* time data. The term $1/(1 + K_e[NHEt_2]^2/[N–N'])$ is simply the fraction of unreacted palladium that is present as the substrate **1c**.

Data Reduction and Analysis.—Mathematical and statistical analysis of equilibrium and kinetic data was carried out on an IBM PS/2 70 personal computer equipped with an INTEL 80387 math coprocessor by the use of a locally adapted version of Marquardt's non-linear regression algorithm[26] written in TURBOBASIC (Borland). Two- and three-dimensional plots were obtained with the SIGMAPLOT (Jandel) and SURFER (Golden Software) packages.

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