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Mechanism of the reaction of allyl amination of Pd(II) allyl complexes containing chelating pyridine–chalcogen ligands. A surprisingly low influence of the chalcogen atom

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Abstract

The rates of amine nucleophilic attack on the allyl ligand (k_2) and the equilibrium constants (K_E) for the displacement of bidentate ligands in Pd(II) allyl complexes of chelating pyridine–chalcogen ethers $[Pd(\eta^3\text{-allyl})(RN–XPh)]^+$ (R = H, Me; X = S, Se) are shown to depend strongly on the steric and electronic requirements of the reactants but are hardly affected by the nature of the chalcogen. Results about the reactivity and solution behaviour of these systems help build up a fairly complete mechanistic picture for this important class of reactions involving coordinated allyl species. In particular the reactivity of the complexes bearing pyridine–thioether ligands is close to that of their pyridine–selenoether analogues, probably owing to a balance of σ and π capabilities of the chalcogen atom. The associative nature of the ligand displacement is markedly affected by steric requirements which depend on the allyl bulkiness. The complexes bearing the ligands with methyl substituted pyridine are the more reactive, due to the destabilisation of the complex ground state induced by the distortion of the starting substrate. We also describe the fluxional behaviour of these species in terms of inversion of the chalcogen absolute configuration and apparent rotation of the allyl ligand.

Keywords: Allylpalladium; Bidentate ligands; Pyridine–chalcogen ethers; Allyl amination mechanism; Solution behaviour

1. Introduction

As a part of the extensive study being currently carried out on the reactivity of Pd(II) allyl complexes [1] (which are still a promising source of synthetic applications) [2], we have undertaken a systematic investigation on the mechanism of nucleophilic attack by amines on the allyl ligand. This has been shown previously to occur on a terminal carbon atom of the η^3-bound allyl fragment on the face opposite with respect to the metal centre [3]. The ancillary ligands we considered were bidentate (L–L′) or terdentate (L–L′–L″) species and the reactions were always carried out in the presence of an activated olefin which leads to a stable Pd(0) olefin complex. The bidentate ligands studied were either labile, as in the case of α-diimine (L–L′ = N–N′) [3b,4] and pyridine–thioethers (L–L′ = N–S) [5], or hemilabile such as imino-phosphine species [6]. The terdentate ligands were similar in nature since the same nucleophilic atoms were used, thus potentially three-coordinating labile pyridine–dithioether (L–L′–L = S–N–S), dipyridine–thioether (L–L′–L = N–S–N) and dipyridine–amine (L–L′–L = N–N–N) or hemilabile pyridine–amino–phosphine (L–L′–L″ = P–N–N) ligands were synthesised and the corresponding Pd(II) allyl complexes were studied [7]. The reactivity and the solution behaviour of Pd(0) olefin complexes, which are the products of the amination reaction, were also widely studied [8]. Moreover it was possible to obtain the Pd(II) allyl complexes by allene insertion into the metal–carbon bond of palladium–alkyl species [9]. We showed that the flexibility and the distortion of the chelate ring of the ancillary

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ligand are of paramount importance in affecting the allene insertion rate [10].

We therefore decided to extend our investigation to palladium complexes containing pyridine–selenium ligands in order to assess the versatility of these new species. In this paper we describe their reactivity and also report on the synthesis and reactivity of new Pd(II) complexes with novel pyridine–thioether ligands. The electronic and steric factors influencing the mechanism of nucleophilic attack on allyl complexes bearing pyridine–chalcogen ligands are discussed in the light of these results.

2. Results and discussion

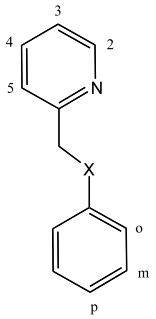
2.1. Synthesis and NMR characterisation of ligands and complexes

The synthesised ligands and complexes, with their numbering scheme (which implies no isomeric preference and only indicates atom locations), are reported in Scheme 1.

The preparation of the pyridine–selenoether ligands follows a similar method to that used for their pyridine–thioether analogues [5]. In the case of the selenium derivatives, the yields were lower than those observed for the sulfur containing ligands owing to the tendency of selenium to give diselenide compounds. As can be seen in Scheme 1, the complexes under study can be divided into three different groups on the basis of symmetry, and consequently the number of possible isomers.

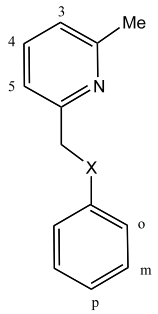
A schematic representation of isomeric distribution for all the species studied is reported in Scheme 2.

Complexes **1a** and **1b** with an unsubstituted allyl ligand can give rise to two rotational isomers due to the relative orientation of the central allyl proton and of chalcogen substituent (it should be recalled that the allyl ligand binds side-on with respect to the main coordination plane). In contrast, complexes **2a**, **2b** and **2b′** (dimethyl substituted allyl fragment) yield four potential rotameric forms on the basis of the arrangements possible for the central allyl proton and the chalcogen substituent and of the position of the dimethyl substituted allyl terminus which can be *cis* or *trans* to sulfur atom as shown in Scheme 2. The com-



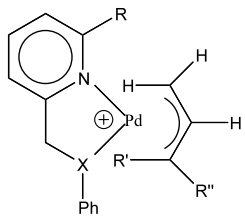
X= Se; HN-SePh (**a**)

X= S ; HN-SPh (**a'**)



X=Se ; MeN-SePh (**b**)

X = S ; MeN-SPh (**b'**)



X = Se; R = H ; R', R"= H (**1a**)

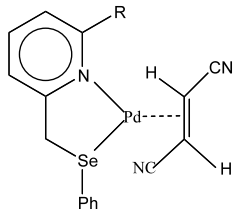
R = H ; R',R" = Me (**2a**)

R = H ; R' = H , R" = Ph (**3a**)

X = Se; R = Me ; R', R"= H (**1b**)

R = Me ; R',R" = Me (**2b**)

R = Me ; R' = H , R" = Ph (**3b**)



X = S; R= H; R' = H , R" =Ph (**3a'**)

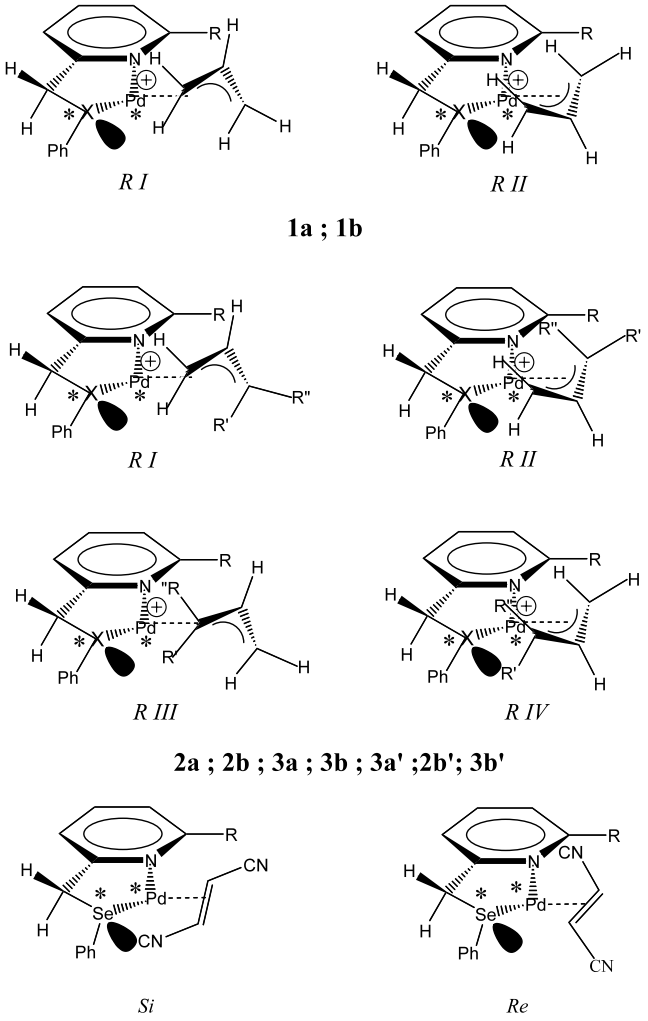
X = S; R = Me; R', R"= Me (**2b'**)

R= Me; R'= H , R" = Ph (**3b'**)

R= H ; (**4a**)

R= Me ; (**4b**)

Scheme 1.



Scheme 2.

plexes **3a**, **3a**′ and **3b**, **3b**′ (phenyl substituted allyl fragment) could produce eight isomers owing to: (i) the position of the central allyl proton and the chalcogen substituent, (ii) the *cis* or *trans* position of the substituted allyl terminus, and (iii) the position of phenyl group which can be *syn* or *anti* within the allyl fragment and consequently with respect to the metal core. However, as already observed for analogous species [6b], no evidence for a phenyl group in *anti* position could be detected since the magnitude of $J(H_{central}-H_{anti\ Ph})$ coupling constant (14–12 Hz) observed at low temperature strongly suggests the *syn* position for this group. Therefore, the exclusion of such an isomeric choice (probably due to steric reasons) halves the number of isomers. The Pd(0) fumaronitrile complexes **4a** and **4b** give two diastereoisomers on the basis of the olefin face coordinated to the metal centre, namely *Re* and *Si* species.

In Fig. 1(a), selected resonances obtained in the low temperature ^{1}H NMR spectrum of complex **1b** are reported. As can be seen, the two expected rotamers, which are present in different populations, are clearly detectable. In particular, the aliphatic zone of such spectra contains particularly diagnostic groups of signals. The four sets of resonances, each with doublet multiplicity, between 3.10 and 3.96 ppm are ascribable to the four allyl *anti* protons ($J = 12.7$ Hz) (two for each rotamer) which differ by their position with respect to the nitrogen atom. The occurrence of two rotameric forms is further supported by the observation of two singlets, corresponding to the methyl substituents in the pyridine ring at 2.71 and 2.74 ppm, respectively. On increasing the temperature several fluxional processes take place, and the ensuing room temperature (r.t.) spectrum shows loss of CH_2–Se diastereotopicity, *syn–syn*, *anti–anti* isomerism and reduction to one singlet of the pyridine-methyl signals. This suggests concomitant chalcogen inversion [11] and apparent allyl fragment rotation [1e,2d] (no *syn–anti* or $\eta^3-\eta^1-\eta^3$ isomerism is observed at r.t.).

In the case of complexes **2a** and **2b** (1,1-Me_2allyl), as already stated, four isomers are expected and this is indeed the case for complex **2a** (unsubstituted pyridine ring) which displays in the low temperature spectrum two sets of doublets (one for each rotamer) in the region 3.00–4.10 ppm. These signals are ascribable to the *anti* protons which can be alternatively *pseudo-cis* or *pseudo-trans* to the chalcogen or nitrogen atom of the ancillary ligand. In the 188 K spectrum of complex **2b** (Fig. 1(b)) only the couple of doublets between 3.60 and 3.85 ppm is detectable, suggesting the presence of only the couple of rotamers in which the dimethyl substituted allyl terminus lies, for steric reasons, *pseudo-trans* to the pyridine nitrogen. The low temperature 2D NOESY confirms this hypothesis since no selective NOE signals from the methyl substituent of the pyridine ring to the methyl substituents of the allyl terminus can be observed.

At variance, positive NOE signals from the methyl substituent of the pyridine ring to both the *syn* and *anti* allyl protons are clearly detectable, except for the case of *anti* allyl protons of the less-populated rotamer which displays an intensity of the crosspeak near the background noise. This fact is probably due to the low concentration of the isomer and/or to the unfavourable position of the proton. Thus the signals in the interval 3.0–3.5 can be assigned to the protons *pseudo-trans* to the pyridine nitrogen; moreover the methyl group on pyridine ring, according to Pregosin's suggestion, can be considered a non-selective but useful 'reporter ' [1e]. The low temperature ^{1}H NMR spectra of complexes **3a** and **3b** (1-phenyl-allyl) display the presence of all the four expected isomers. The isomers distribution is easily determined on the basis of the characteristic features of ^{1}H NMR spectra of the complexes bearing this peculiar allyl fragment. The pair of rotamers bearing the phenyl substituent in the allyl terminus *pseudo-cis* to pyridine

nitrogen displays a marked up-field shift (≈ 7 ppm) of the pyridine 6-H proton caused by the shielding due to phenyl ring currents [6b]. On the other hand, the 6-H pyridine proton of the remaining pair resonates at 8.74 (unresolved doublet). It is possible to establish, therefore, that the more abundant pair of rotamers for complex **3a** place the substituted allyl terminus *pseudo-cis* to pyridine nitrogen. At variance, complex **3b** displays a different situation and the more abundant pair of rotamers contains phenyl substituents that are *pseudo-trans* to the pyridine nitrogen, this phenomenon arising due to steric reasons. These spectra also exhibit a distribution of the *anti* protons in the usual intervals (3.15–3.40 and 3.80–4.10 ppm), thereby confirming the position of the *anti* protons *pseudo-trans* to the pyridine ring (3.00–3.50 ppm). The low temperature ^{1}H NMR signals ascribable to the diagnostic *anti* allyl protons are reported in Table 1.

Palladium(0) fumaronitrile complexes do not deserve detailed comments owing to their customary features and behaviour. As a matter of fact, the ^{1}H NMR spectra of the synthesised Pd(0) complexes (see Section 3) are superimposable to those obtained in the amination reaction in the presence of fumaronitrile. The r.t. spectra show a generalised fluxionality ascribable to selenium inversion [11] and olefin rotation, although other associative mechanisms [12] could not be ruled out. The spectra of complexes **4a** and **4b** differ according to the presence of a singlet ($\delta = 2.93$ ppm; r.t.) due to the methyl substituent on pyridine ring in the case of **4b** complex which also displays a residual coupling between C$\underline{H}_2$–Se protons and ^{77}Se ($^2J_{H-Se} = 13.7$ Hz). This kind of fluxional behaviour was studied in detail in the case of pyridine–thioether Pd(0) fumaronitrile complexes [8a,b] and no particular differences could be detected with respect to these species. The ^{1}H NMR spectrum at 188 K of **4b** complex shows the presence of both *Re* and *Si* isomers as clearly indicated by the couple of singlets due to methyl substituent on the pyridine ring at 2.81 and 2.83 ppm (isomeric ratio 1:2.3), respectively, by the two (one of which not completely resolved) AB systems ascribable to endocyclic C$\underline{H}_2$–Se protons (bs 4.45, AB sys $\delta_A = 4.43$, $\delta_B = 4.53$ ppm, $J_{AB} = 14.2$ Hz), and by the two AB systems ascribable to the olefin protons ($\delta_A = 3.13$, $\delta_B = 3.21$ ppm, $J_{AB} = 9.8$ Hz; $\delta_{A'} = 3.13$, $\delta_{B'} = 3.18$ ppm, $J_{A',B'} = 9.8$ Hz).

2.2. Reactivity

The following allyl amination reactions (Scheme 3) were studied by UV–Vis spectroscopy and ^{1}H NMR spectrometry in $CDCl_3$ at r.t.

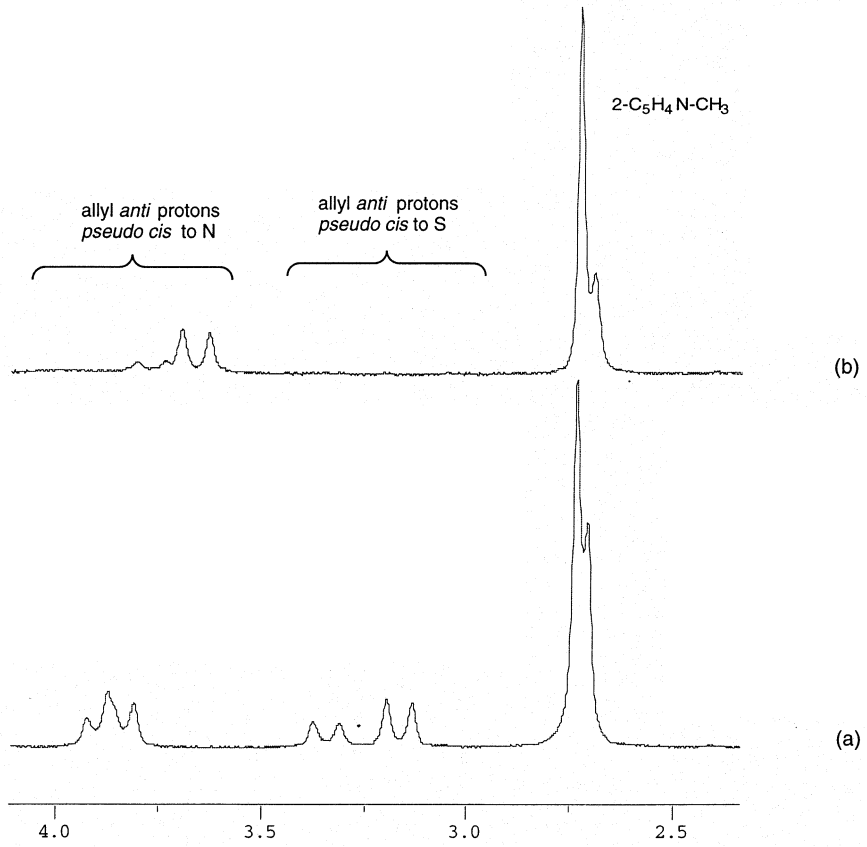


Fig. 1. Aliphatic region of the low temperature ^{1}H NMR spectra of complexes **1b** (a) and **2b** (b) (200 MHz, CD_2Cl_2, 188 K).

Table 1
^{1}H NMR data for allyl *anti* protons and pyridine-substituent methyl protons of selected complexes recorded at 188 K in CD_2Cl_2

Complex	Rotamer (%Major, M; %minor, m)	H_S^{anti} (pseudo-*cis* to S)	H_N^{anti} (pseudo-*cis* to N)	C_5H_4N–CH_3	RIII + RIV / RI + RII
1a	M 60%	3.10 d	4.07 d		100%
	m 40%	3.27 d	4.07 d		
1b	M 60%	3.16 d	3.83 d	2.74 s	100%
	m 40%	3.35 d	3.91 d	2.71 s	
2a	50%		3.90 d		70%
			3.89 d		
		3.21 d			
	50%	3.31 d			30%
2b	50%		3.66 d	2.73 s	100%
			3.77 d	2.70 s	
3a	[a]	[b]	4.14 d		90%
	[a]	[b]	4.14 d		
	M 60%	3.15 d	[b]		10%
	m 40%	3.45 d	[b]		10%
3b	M 55%	[b]	3.92 d	2.74 s	80%
	m 45%	[b]	4.04 d	2.66 s	
	[a]	3.25 bd	[b]	2.50 bs	20%
	[a]	3.25 d	[b]	2.50 bs	

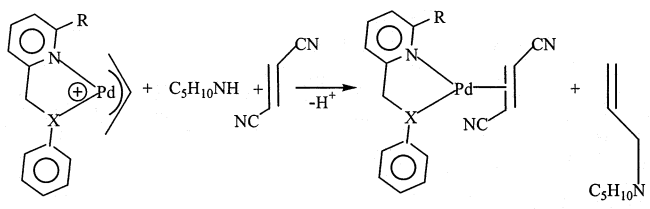
[a] Not separated signals.
[b] Obscured by solvent signal.

In any case the formation of the Pd(0) fumaronitrile complexes together with the corresponding allyl-amines was detected. When the reacting complexes bear unsubstituted allyl, and 1-phenyl-allyl fragments only one allyl-amine isomer was observed. The peculiar reactivity of the complexes bearing the mono-substituted allyl species $[PhCH–CH–CH_2]^-$ which only leads to the formation of the linear amino-olefin $PhCH{=}CH–CH_2NC_5H_{10}$ is not without precedent [6b,13] and probably originates from the extremely low rate of nucleophilic attack by piperidine on the phenyl-substituted allyl terminus which depends on steric and electronic factors. The predominant formation of the linear allyl-amine $PhCH{=}CHCH_2NC_5H_{10}$ could indeed be traced back to its stabilisation via double bond conjugation. As a matter of fact, similar results were also obtained in the palladium catalysed alkylation of 1-arylprop-2-enyl acetates with enolates (Nu) which leads to linear olefins (*E*)-$ArCH{=}CHCH_2Nu$ [14].

The reaction of complexes **2** with piperidine in the presence of fumaronitrile leads to the formation of the usual Pd(0) fumaronitrile complexes and to a mixture of the two allyl-amine isomers ($Me_2C{=}CHCH_2NC_5H_{10}$ (**I1**) and $CH_2{=}CHCMe_2NC_5H_{10}$ (**I2**)). Surprisingly the isomer ratio **I1**/**I2** depends upon the nature of the ancillary ligand. The observed ratio is 5 in the case of complex **2a** (L–L′ = HN–SePh) and 30 (or more) with **2b** and **2b**′ complexes (L–L′ = MeN–XPh). In this latter case significant immediate formation of the inert (with respect to allyl-amination reaction) $[Pd(\eta^3\text{-allyl})(Pip)_2]^+$ complex and a slow isomerisation reaction are observed, so that the 30:1 isomeric ratio is slowly reached. Moreover the complex $[Pd(\eta^3\text{-allyl})(Pip)_2]^+$ is not involved in the isomerisation reaction since in a further experiment no reaction between bispiperidino complex and **I2** (independently synthesised) was observed. This isomerisation phenomenon is easily detected thanks to the characteristic feature of the ^{1}H NMR spectra of the two allyl-amine isomers [5b]. It is noteworthy that similar findings were described by Åkermark et al. in the case of the allyl amination of labile ligand complexes by aliphatic amines [15]. We are not able, at the moment, to propose a mechanism in order to explain such an experimental result but we are still studying this problem and work is still in progress in our laboratory in order to interpret these findings.

2.3. Kinetics and mechanism

The η^3-allyl complexes $[Pd(\eta^3\text{-allyl})(RN–XPh)]^+$ (allyl = C_3H_5, 1,1-Me_2–C_3H_3, 1-Ph–C_3H_4; R = H, Me; X = Se, S) ($[Pd]_0 \approx 10^{-4}$ mol dm^{-3}) react smoothly with a variable excess of piperidine (Pip) ($[Pip]_0 = 1 \times 10^{-3}$–$1.2 \times 10^{-2}$ mol dm^{-3}) in $CHCl_3$ at 25 °C in the



(X = S, Se; $C_5H_{10}NH$ = piperidine)

Scheme 3.

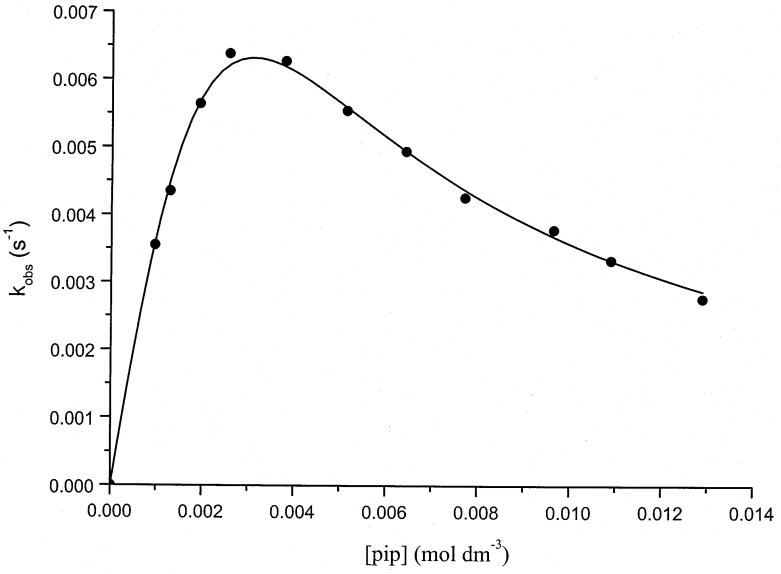


Fig. 2. Fit of k_{obs} to [pip] for the reaction of complex **1a** with piperidine at 25 °C according to Eq. (2).

presence of fumaronitrile (fn) ($[fn]_0 = 2 \times 10^{-4}$–$4 \times 10^{-4}$ mol dm^{-3}) and of pyridine–chalcogenether ligand (RN–XPh) ($[RN–XPh]_0 = 10^{-3}$ mol dm^{-3}) to give the Pd(0) olefin complexes [Pd(η^2-fn)(RN–XPh)] and the allylammine $C_5H_{10}N–C_3H_3R_1R_2$.

The reaction course, which was confirmed by NMR spectrometry (vide supra), was followed by monitoring UV–Vis spectral changes in the wavelength range 280–400 nm as a function of reaction time. Under these conditions the reactions reached completion as indicated by comparison of solution spectra at the end of the reactions with those of the final products independently prepared. The conversion of the reactants into products with time appeared to obey the mono-exponential relationship $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$ which corresponds to a pseudo-first order process

$$-d[[Pd(\eta^3\text{-allyl})(RN-XPh)]^+]/dt = k_{obs}[[Pd(\eta^3\text{-allyl})(RN-XPh)]^+] \quad (1)$$

The k_{obs} values, determined by non-linear regression analysis of A_t (absorbance at time t) versus t (time) data display a bivariate dependence (Eq. (2)) on [Pip] and [RN–XPh] which are considered to be constant with time, being in excess over the metal substrate concentration:

$$k_{obs} = \alpha[Pip]/(1 + \beta[Pip]^2/[RN-XPh]) \quad (2)$$

The parameter values α and β were determined by non-linear regression of rate constants to Eq. (2) (Fig. 2).

In line with the wealth of our previous findings relating to the analogous reactions of Pd(II) η^3-allyl substrates containing labile or hemilabile chelating ligands [4,5], the stepwise mechanism shown in Scheme 4 can be proposed based on the above experimental evidence. This mechanism was also confirmed by NMR experiments carried out either in $CDCl_3$ or CD_2Cl_2.

According to this mechanistic picture the η^3-allyl substrate **S** is in fast pre-equilibrium (K_E) with the inert bisamino species **B** via the displacement of the bidentate ligand RN–XPh. The substrate undergoes concomitant rate-determining bimolecular attack by the amine (k_2 step) to give a labile Pd(0) intermediate species **I** bearing an η^2-bound allyl cation which is displaced rapidly and quantitatively by the activated olefin fumaronitrile (fn) to give the final products **P1** and **P2** (therefore the fn concentration will not influence the overall rate constant). Accordingly, the pseudo-first order rate constant k_{obs} is given by Eq. (3):

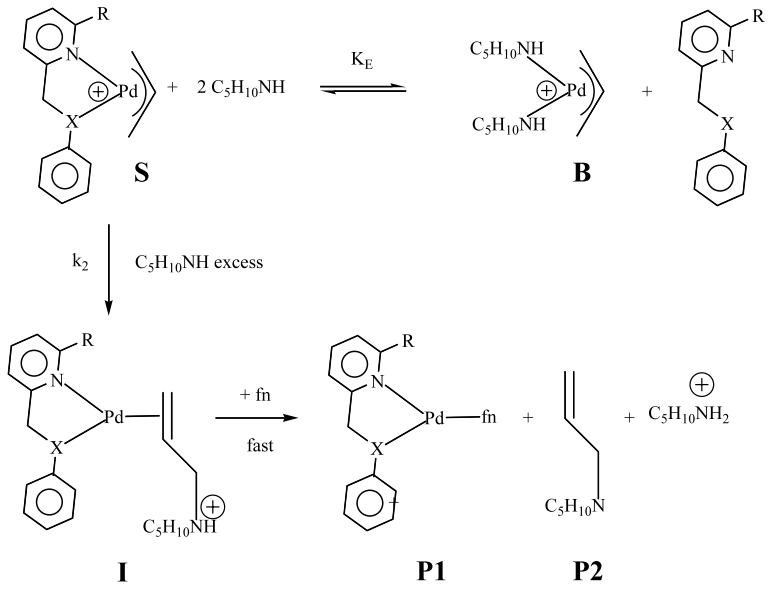
$$k_{obs} = k_2[Pip]/(1 + K_E[Pip]^2/[RN-XPh]) \quad (3)$$

Consequently, the α and β parameters in the observed rate law 2 can be identified as the second-order rate constant k_2 and the equilibrium constant K_E, respectively (Table 2).

The inertness of the bisamino species **B** towards nucleophilic attack of amines on the allyl group is a common feature of this class of reactions and was confirmed by independent reactivity measurements on the authentic isolated species [4,5].

This can be rationalised by the essentially σ-donating ability of the amines (compared with the better π-accepting ability of the bidentate ligands examined), which increases the electron density on the central metal, thereby decreasing the electrophilic character of the allyl ligand.

As can be seen in Table 2 the reactivity of the complexes bearing the pyridine–thioether ligands is very similar to that of the analogous pyridine–sele-



(R = H, Me; X = S, Se; $C_5H_{10}NH$ = piperidine; fn = fumaronitrile)

Scheme 4.

noether species, the k_2 and K_E values being virtually superimposable. This surprising result probably derives from a balance of σ and π capabilities of the chalcogen atoms. Apparently, the slightly higher π ability of the larger selenium atom as compared to sulfur offsets its lower basicity [16]; this characteristic feature could be very important if Pd(0) derivatives are involved.

Within homologous series (same RN–XPh) the K_E values increase in the order:

$[Pd(\eta^3\text{-allyl})(HN\text{–}XPh)]^+$

$> [Pd(\eta^3\text{-1-phenylallyl})(HN\text{–}XPh)]^+$

$\cong [Pd(\eta^3\text{-1,1-Me}_2\text{allyl})(HN\text{–}XPh)]^+$

$[Pd(\eta^3\text{-allyl})(MeN\text{–}XPh)]^+$

$\cong [Pd(\eta^3\text{-1-phenylallyl})(MeN\text{–}XPh)]^+$

$> [Pd(\eta^3\text{-1,1-Me}_2\text{allyl})(MeN\text{–}XPh)]^+$

In the latter case, the K_E values are approximately one order of magnitude higher than in the case of complexes bearing HN–XR ligands.

The associative mechanism of the ligand displacement is strongly influenced by steric requirements which clearly depend on the allyl bulkiness within each homologous series. Moreover the pyridine methyl substituent imparts an instability to the whole molecule which is pointed out by the generalised increase and levelling off of K_E values.

As for the k_2 values, again no influence by the chalcogen atom can be detected. It is convenient to discuss the reactivity of the substrates on the basis of the following reactivity orders:

$[Pd(\eta^3\text{-allyl})(HN\text{–}XPh)]^+$

$> [Pd(\eta^3\text{-1-phenylallyl})(HN\text{–}XPh)]^+$

$> [Pd(\eta^3\text{-1,1-Me}_2\text{allyl})(HN\text{–}XPh)]^+$

$[Pd(\eta^3\text{-allyl})(MeN\text{–}XPh)]^+$

$\cong [Pd(\eta^3\text{-1-phenylallyl})(MeN\text{–}XPh)]^+$

$> [Pd(\eta^3\text{-1,1-Me}_2\text{allyl})(MeN\text{–}XPh)]^+$

The complexes bearing the ligands with the methyl substituted pyridine still come out as more reactive.

Table 2
Second-order rate constants and equilibrium constants for reactions of allyl complexes with piperidine in $CHCl_3$ at 25 °C

Complex	k_2 ($mol^{-1}\ dm^3\ s^{-1}$)	K_E
$[Pd(\eta^3\text{-}C_3H_5)(HN\text{–}SePh)]ClO_4$ (**1a**)	4.07 ± 0.06	107 ± 3
$[Pd(\eta^3\text{-}C_3H_5)(HN\text{–}SPh)]ClO_4$	3.9 ± 0.3 [a]	204 ± 60 [a]
$[Pd(\eta^3\text{-}C_3H_5)(MeN\text{–}SePh)]ClO_4$ (**1b**)	14.3 ± 0.9	2400 ± 200
$[Pd(\eta^3\text{-}C_3H_5)(MeN\text{–}SPh)]ClO_4$	10.0 ± 0.6 [a]	2100 ± 200 [a]
$[Pd(\eta^3\text{-1,1-Me}_2C_3H_3)(HN\text{–}SePh)]ClO_4$ (**2a**)	0.154 ± 0.005	12.7 ± 0.6
$[Pd(\eta^3\text{-1,1-Me}_2C_3H_3)(HN\text{–}SPh)]ClO_4$	0.163 ± 0.002 [a]	18 ± 1 [a]
$[Pd(\eta^3\text{–1,1-Me}_2C_3H_3)\text{-}(MeN\text{–}SePh)]ClO_4$ (**2b**)	0.57 ± 0.01	360 ± 10
$[Pd(\eta^3\text{-1,1-Me}_2C_3H_3)\text{-}(MeN\text{–}SPh)]ClO_4$ (**2b′**)	0.533 ± 0.009	400 ± 10
$[Pd(\eta^3\text{-1-Ph-}C_3H_4)\text{-}(HN\text{–}SePh)]ClO_4$	0.87 ± 0.02	22 ± 1
$[Pd(\eta^3\text{-1-Ph-}C_3H_4)\text{-}(HN\text{–}SPh)]ClO_4$ (**3a**)	0.87 ± 0.03	24 ± 1
$[Pd(\eta^3\text{-1-Ph-}C_3H_4)\text{-}(MeN\text{–}SePh)]ClO_4$ (**3b**)	8.5 ± 0.3	1870 ± 90
$[Pd(\eta^3\text{-1-Ph-}C_3H_4)\text{-}(MeN\text{–}SPh)]ClO_4$ (**3b′**)	9.6 ± 0.8	2700 ± 300

[a] Data from Ref. [5b].

Apparently the destabilisation of the complex ground state also influences the amination reaction. However, the decrease in reactivity within the same series is easily traced back to the influence of steric bulkiness on the rates of bimolecular associative reactions. On the other hand, molecular activation induced by distortion of the starting substrate reflects the increase in k_2 (on going from the first to the second reactivity order) and the levelling off of the reactivity between [Pd(η^3-allyl)-(MeN–XPh)]$^+$ and [Pd(η^3-1-phenylallyl)(MeN–XPh)]$^+$, the latter being slightly less reactive. This phenomenon probably depends on the ground state activation coupled with the electron withdrawing capability of the phenyl group which activates the allyl moiety towards nucleophilic attack, thereby overcoming the steric bulkiness and rendering the complex as reactive as its unsubstituted allyl analogue (if the statistical factor due to the halving of the number of attack sites is taken into account).

3. Experimental

3.1. Preparation of ligands

3.1.1. 2-(Phenyl-selenomethyl)-pyridine (HN–SePh)

To a 10 ml solution of 2.25 g (40.0 mmol) of KOH and 0.943 g (6.00 mmol) of seleno-phenol (HSe–Ph) in DMSO, 0.820 g (5 mmol) of 2-chloromethylpyridine hydrochloride was added and the resulting solution was stirred vigorously for 1 h; 50 ml of water was then added. The organic phase was extracted with diethyl ether (2 × 30 ml) and treated with anhydrous Na_2SO_4 for 12 h. The solution was filtered and concentrated to dryness under reduced pressure and the oily product was flash-chromatographed by eluting with CH_2Cl_2/Et_2O on SiO_2 column. A yellowish oil (0.73 g, 2.98 mmol) was obtained. Yield 59.6%.

Anal. Found: C, 58.12; H, 4.38; N, 5.60. Calc. for $C_{12}H_{11}NSe$: C, 58.09; H, 4.47; N, 5.65%. IR (NaCl, cm^{-1}): $\nu_{C=N}$ 1590. ^{1}H NMR ($CDCl_3$, r.t., ppm): seleno-methyl protons $\delta = 4.23$ (CH_2–Se, s, $J^2_{H-Se} = 12.4$ Hz, 2H); pyridine protons $\delta = 7.53$ (H^4, td, $J = 7.6$, 1.8 Hz, 1H), 8.51 (H^6, dd, $J = 5.4$, 1.8 Hz, 1H); $\delta = 7.06$–7.28 (H^3–H^5–H$_o$–H$_m$–H$_p$, m, 7H). ^{13}C{^{1}H} NMR ($CDCl_3$, r.t., ppm): seleno-methyl carbons $\delta = 33.8$ (*C*H$_2$–Se, $J^1_{C-Se} = 60.2$ Hz); pyridine carbons $\delta = 158.7$ (C^2), 123.0 (C^3), 136.4 (C^4), 121.7 (C^5), 149.5 (C^6); phenyl carbons $\delta = 129.9$ (Se–*C*), 133.6 (C$_o$), 129.0 (C$_m$), 127.3 (C$_p$). ^{77}Se{^{1}H} NMR ($CDCl_3$, r.t., ppm): $\delta = 359$. ^{77}Se NMR ($CDCl_3$, r.t., ppm): $\delta = 359$ (tt, $J_{Se-H} = 12.4$, 3.6 Hz).

3.1.2. 2-Chloro-6-methylpyridine

To a 5.0 g (40.6 mmol) of 2-hydroxymethyl-6-methylpyridine in a 250 ml flask placed into an ice bath, 40 ml of thionyl chloride was slowly added; the resulting solution was stirred for 4 h at 55 °C. The reaction mixture was dried under reduced pressure and the residue was treated with an ice/water mixture and neutralised with Na_2CO_3. The crude product was extracted with CH_2Cl_2 and dried with Na_2SO_4 for 12 h. The filtered solution was dried under reduced pressure by means of a high vacuum line; the oily product (3.76 g, 26.5 mmol, yield 65.3%) was used without further purification.

^{1}H NMR ($CDCl_3$, r.t., ppm): $\delta = 2.57$ (CH_3, s, 3H), 4.65 (CH_2–Cl, s, 2H), 7.10 (H^3, d, $J = 7.7$ Hz, 1H), 7.29 (H^5, d, $J = 7.7$ Hz, 1H), 7.61 (H^4, t, $J = 7.7$ Hz, 1H).

3.1.3. 2-(Phenyl-selenomethyl)-6-methyl-pyridine (MeN–SePh)

The title compound was synthesised in a way similar to that employed in the case of HN–SePh ligand starting from 0.71 g (5.0 mmol) of 2-chloro-6-methylpyridine and 1.57 g (10 mmol) of seleno-phenol in the presence of 2.25 g (40 mmol) KOH in DMSO. The ligand was obtained as a yellowish oil (1.15 g, 4.39 mmol, yield 87.7%).

Anal. Found: C, 59.52; H, 4.96; N, 5.30. Calc. for $C_{13}H_{13}NSe$: C, 59.56; H, 5.00; N, 5.34%. IR (NaCl, cm^{-1}): $\nu_{C=N}$ 1591. ^{1}H NMR ($CDCl_3$, r.t., ppm): selenomethyl protons $\delta = 4.21$ (CH_2–Se, s, $J^2_{H-Se} = 12.1$ Hz, 2H); pyridine protons $\delta = 6.92$ (H^3, d, $J = 7.7$ Hz, 1H), 7.43 (H^4, t, $J = 7.7$ Hz, 1H), 6.97 (H^5, d, $J = 7.7$ Hz, 1H); $\delta = 2.52$ (C$_5$H$_3$N-6-CH_3, s, 3H); $\delta = 7.20$–7.31 (H$_o$–H$_p$, m, 3H); $\delta = 7.45$–7.56 (H$_m$, m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, r.t., ppm): selenomethyl carbons $\delta = 33.7$ (*C*H$_2$–Se, $^1J_{C-Se} = 62.2$ Hz); pyridine carbons $\delta = 157.8$ (C^6), 121.0 (C^5), 136.3 (C^4), 119.6 (C^3), 157.7 (C^2); phenyl carbons $\delta = 129.9$ (Se–*C*), 133.3 (C$_o$, $J^2_{C-Se} = 10$ Hz), 128.7 (C$_m$), 127.0 (C$_p$); C$_5$H$_3$N-6-*C*H$_3$ $\delta = 24.2$. ^{77}Se{^{1}H} NMR ($CDCl_3$, r.t., ppm): $\delta = 358$. ^{77}Se NMR ($CDCl_3$, r.t., ppm): $\delta = 358$ (t, $J_{Se-H} = 12.1$ Hz).

3.2. Preparation of Pd(II) complexes

3.2.1. [Pd(η^3-C_3H_5)(HN–SePh)]ClO_4 (**1a**)

To a solution of 0.126 g (0.308 mmol) of [Pd(η^3-C_3H_5)Cl]$_2$ [17a] in 20 ml of CH_2Cl_2, 0.16 g (0.646 mmol) of HN–SePh and 0.173 g (1.23 mmol) of $NaClO_4 \cdot H_2O$ were added. The solution was stirred for 30 min and concentrated under reduced pressure. The solid was dissolved in CH_2Cl_2, treated with activated charcoal and filtered on celite. The resulting yellow solution was concentrated and the title complex was obtained as an off-white solid (0.298 g, 0.60 mmol, yield 97.6%) by addition of diethyl ether.

Anal. Found: C, 36.51; H, 3.28; N, 2.89. Calc. for $C_{15}H_{16}ClNO_4SePd$: C, 36.39; H, 3.26; N, 2.83%. IR (KBr, cm^{-1}): $\nu_{C=N}$ 1599, ν_{ClO} 1090, δ_{ClO} 623. ^{1}H NMR ($CDCl_3$, r.t., ppm): selenomethyl protons $\delta = 4.77$ (CH_2–Se, s, 2H); allyl protons $\delta = 4.60$ (H$_{syn}$, br s, 2H),

$\delta = 3.76$ (H_{anti}, br s, 2H), $\delta = 5.98$ ($H_{central}$, q, $J = 10.1$ Hz, 1H); pyridine protons $\delta = 7.85$ (H^4, td, $J = 7.8$, 1.6 Hz, 1H), 8.92 (H^6, d, $J = 5.5$ Hz, 1H); pyridine and phenyl protons $\delta = 7.29–7.66$ (H_3–H_5–H_o–H_m–H_p, m, 7H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t., ppm): selenomethyl carbons $\delta = 40.8$ (CH_2–Se, $^1J_{C-Se} = 56$ Hz); pyridine carbons $\delta = 159.3$ (C^2), 124.9 (C^3), 140.0 (C^4), 125.3 (C^5), 155.2 (C^6); phenyl carbons $\delta = 126.0$ (Se–*C*), 130.3 (C_o), 133.6 (C_m), 130.4 (C_p); allyl carbons $\delta =$ 58.2 (C_1, br), 120.3 (C_2), 75.8 (C_3, br).

Complexes **2a**, **3a**, **1b**–**3b** and **3a′**, **2b′**, **3b′** were synthesised similarly to complex **1a** using the appropriate Pd(II) dimer [17b] and ligand.

3.2.2. [Pd(η³-1,1-$Me_2C_3H_3$)(HN–SePh)]ClO_4 (**2a**)

Yield 94.7% (pale yellow microcrystals).

Anal. Found: C, 38.95; H, 3.88; N, 2.90. Calc. for $C_{17}H_{20}ClNO_4SePd$: C, 39.03; H, 3.85; N, 2.88%. IR (KBr, cm^{-1}): $\nu_{C=N}$ 1605, ν_{ClO} 1076, δ_{ClO} 622. ^1H NMR ($CDCl_3$, r.t., ppm): selenomethyl protons $\delta = 4.71$ (CH_2–Se, br s, 2H); allyl protons $\delta = 5.63$ ($H_{central}$, bt, 1H), $\delta = 4.45$ (H_{syn}, br s, 1H), $\delta = 4.01$ (H_{anti}, bs, 1H); allyl methyls $\delta = 1.80$ (Me_{syn}, s, 3H), 1.44 (Me_{anti}, s, 3H); pyridine protons $\delta = 7.85$ (H^4, t, $J = 7.7$ Hz, 1H), 8.85 (H^6, br s, 1H); $\delta = 7.20–7.65$ (H^3–H^5–H_o–H_m–H_p, m, 7H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t., ppm): selenomethyl carbons $\delta = 39.9$ (CH_2–Se, $^1J_{C-Se} = 55.5$ Hz); pyridine carbons $\delta = 159.1$ (C^2), 124.7 (C^3), 139.5 (C^4), 125.1 (C^5), 154.1 (C^6, br); phenyl carbons $\delta =$ 125.6 (Se–*C*), 130.1 (C_o), 133.2 (C_m), 130.1 (C_p); allyl carbons $\delta =$ obscured (C_1), 114.1 (C_2), 66.4 (C_3, br), 27.79 (C_{syn}, br), 21.9 (C_{anti}).

3.2.3. [Pd(η³-1-PhC_3H_4)(HN–SePh)]ClO_4 (**3a**)

Yield 94.0% (Yellow microcrystals).

Anal. Found: C, 44.22; H, 3.58; N, 2.50. Calc. for $C_{21}H_{20}ClNO_4SePd$: C, 44.16; H, 3.53; N 2.45%. IR (KBr, cm^{-1}): $\nu_{C=N}$ 1599, ν_{ClO} 1091.7, δ_{ClO} 623.0. ^1H NMR ($CDCl_3$, r.t., ppm): selenomethyl protons $\delta =$ 4.66 (CH_2–Se, br s, 2H); pyridine protons $\delta = 6.93$ (H^6, br, 1H); allyl protons $\delta = 6.35$ ($H_{central}$, br s, 1H), $\delta = 4.40$ (H_{syn}, br s, 1H), $\delta = 3.42$ ($H_{anti\,H}$, br s, 1H), $\delta = 5.59$ ($H_{anti\,Ph}$, br s, 1H); pyridine and phenyl protons $\delta = 7.17–7.89$ (H_o–H_m–H_p–H^3–H^4–H^5, m, 8H).

3.2.4. [Pd(η³-C_3H_5)(MeN–SePh)]ClO_4 (**1b**)

Yield 96.2% (pale yellow microcrystals).

Anal. Found: C, 37.69; H, 3.61; N, 2.87. Calc. for $C_{16}H_{18}ClNO_4SePd$: C, 37.75; H, 3.56; N, 2.85%. IR (KBr, cm^{-1}):$\nu_{C=N}$ 1601, ν_{ClO} 1090, δ_{ClO} 624. ^1H NMR ($CDCl_3$, r.t., ppm): selenomethyl protons $\delta = 4.85$ (CH_2–Se, s, 2H); pyridine protons $\delta = 7.66$ (H^4, t, $J = 7.7$ Hz, 1H); allyl protons $\delta = 4.76$ (H_{syn}, br s, 2H), $\delta = 5.91$ ($H_{central}$, tt, $J = 12.8$; 7.2 Hz, 1H), $\delta = 3.70$ (H_{anti}, br s, 2H); C_5H_3N-6-CH_3 $\delta = 2.78$ (3H, s, CH_3); phenyl and pyridine protons $\delta = 7.56$ (H_m, m, 2H); $\delta = 7.24–7.35$ (H^3–H^5–H_o–H_p, m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t., ppm): selenomethyl carbons $\delta = 39.8$ (CH_2–Se, $^1J_{C-Se} = 52.2$ Hz); C_5H_3N-6-CH_3 $\delta = 28.9$; pyridine carbons $\delta = 160.0$ (C^2), 121.1 (C^3), 139.2 (C^4), 123.7 (C^5), 157.9 (C^6); phenyl carbons $\delta = 124.3$ (Se–*C*), 129.3 (C_o), 133.0 (C_m), 129.6 (C_p); allyl carbons $\delta = 59.5$ (C^{A1}, b), 116.9 (C^{A2}), 74.1 (C^{A3}, br).

3.2.5. [Pd(η³-1,1-$Me_2C_3H_3$)(MeN–SePh)]ClO_4 (**2b**)

Yield 91.0% (pale yellow microcrystals).

Anal. Found: C, 40.31; H, 4.21; N, 2.58. Calc. for $C_{18}H_{22}ClNO_4SePd$: C, 40.25; H, 4.13; N, 2.61%. IR (KBr, cm^{-1}): $\nu_{C=N}$ 1601, ν_{ClO} 1082, δ_{ClO} 624. ^1H NMR ($CDCl_3$, r.t., ppm): selenomethyl protons $\delta = 4.78$ (CH_2–Se, br d, 2H); allyl protons $\delta = 5.64$ ($H_{central}$, dd, $J = 13.7$, 7.7 Hz, 1H), $\delta = 4.69$ (H_{syn}, d, $J = 7.7$ Hz, 1H), $\delta = 3.77$ (H_{anti}, d, $J = 13.3$ Hz, 1H); allyl methyls $\delta = 1.85$ (Me_{syn}, s, 3H), 1.48 (Me_{anti}, s, 3H); pyridine protons $\delta = 7.63$ (H^4, t, $J = 7.7$ Hz, 1H); C_5H_3N-6-CH_3 $\delta = 2.78$ (CH_3, s, 3H); phenyl protons $\delta = 7.46–7.54$ (H_m, m, 2H); $\delta = 7.20–7.35$ (H^3–H^5–H_o–H_p, m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t., ppm): selenomethyl carbons $\delta = 39.7$ (CH_2–Se, $^1J_{C-Se} = 53.3$ Hz); C_5H_3N-6-CH_3 $\delta = 22.3$; pyridine carbons $\delta = 160.0$ (C^2), 122.5 (C^3), 139.3 (C^4), 124.1 (C^5), 159.0 (C^6); phenyl carbons $\delta = 124.7$ (Se–*C*), 129.9 (C_o), 133.3 (C_m), 129.9 (C_p); allyl carbons $\delta = 96.3$ (C_1, br), 111.6 (C_2), 64.1 (C_3, br), 29.6 (C_{syn}), 22.3 (C_{anti}).

3.2.6. [Pd(η³-1-PhC_3H_4)(MeN–SePh)]ClO_4 (**3b**)

Yield 96.0% (yellow microcrystals).

Anal. Found: C, 45.09; H, 3.78; N, 2.41. Calc. for $C_{22}H_{22}ClNO_4SePd$: C, 45.16; H, 3.79; N, 2.39%. IR (KBr, cm^{-1}):$\nu_{C=N}$ 1604, ν_{ClO} 1087.8, δ_{ClO} 624.9. ^1H NMR ($CDCl_3$, r.t., ppm): selenomethyl protons $\delta =$ 4.76 (CH_2–Se, br s, 2H); allyl protons $\delta = 6.31$ ($H_{central}$, br s, 1H), $\delta = 4.08$ (H_{syn}, br s, 1H), $\delta = 3.93$ ($H_{anti\,H}$, br s, 1H), $\delta = 5.42$ ($H_{anti\,Ph}$, br s, 1H); C_5H_3N-6-CH_3 $\delta =$ 2.63 (CH_3, br s, 3H); pyridine and phenyl protons $\delta = 7.09–7.62$ (H_o–H_m–H_p–H^3–H^4–H^5, m, 8H).

3.2.7. [Pd(η³-1-PhC_3H_4)(HN–SPh)]ClO_4 (**3a′**)

Yield 95.3% (yellow microcrystals).

Anal. Found: C, 48.16; H, 3.88; N, 2.71. Calc. for $C_{21}H_{20}ClNO_4SPd$: C, 48.11; H, 3.84; N, 2.67%. IR (KBr, cm^{-1}): $\nu_{C=N}$ 1601, ν_{ClO} 1093.6, δ_{ClO} 624.9. ^1H NMR ($CDCl_3$, r.t., ppm): thiomethyl protons $\delta = 4.80$ (CH_2–S, br AB system, 2H); allyl protons $\delta = 6.36$ ($H_{central}$, br s, 1H), $\delta = 4.32$ (H_{syn}, br s, 1H), $\delta = 3.49$ ($H_{anti\,H}$, br s, 1H), $\delta = 5.57$ ($H_{anti\,Ph}$, br s, 1H); pyridine and phenyl protons $\delta = 6.85–7.88$ (H_o–H_m–H_p–H^3–H^4–H^5–H^6, m, 9H).

3.2.8. [Pd(η³-1,1-$Me_2C_3H_3$)(MeN–SPh)]ClO_4 (**2b′**)

Yield 97.3% (pale yellow microcrystals).

Anal. Found: C, 44.14; H, 4.55; N, 2.81. Calc. for $C_{18}H_{22}ClNO_4SPd$: C, 44.10; H, 4.52; N, 2.86%. IR

(KBr, cm^{-1}):$\nu_{C\equiv N}$ 1602.8, ν_{ClO} 1082.0, δ_{ClO} 623.0. ^1H NMR ($CDCl_3$, r.t., ppm): thiomethyl protons $\delta_A =$ 4.74, $\delta_B = 4.81$ (CH_2–S, AB system, $J_{AB} = 16$ Hz, 2H); allyl protons $\delta = 5.61$ ($H_{central}$, dd, $J = 13.4$, 7.7 Hz, 1H), $\delta = 4.68$ (H_{syn}, d, $J = 7.7$ Hz, 1H), $\delta = 3.7$ (H_{anti}, d, $J = 13.4$ Hz, 1H); allyl methyls $\delta = 1.75$ (Me_{syn}, s, 3H), 1.43 (Me_{anti}, s, 3H); pyridine protons $\delta = 7.71$ (H^4, t, $J = 7.7$ Hz, 1H); C_5H_3N-6-CH_3 $\delta = 2.80$ (CH_3, s, 3H); pyridine and phenyl protons $\delta = 7.48$–7.53 (H_m, m, 2H); $\delta = 7.31$–7.39 (H_o–H_p–H^3–H^5, m, 5H).

3.2.9. [Pd(η^3-1-PhC_3H_4)(MeN–SPh)]ClO_4 (**3b′**)

Yield 95.0% (yellow microcrystals).

Anal. Found: C, 49.15; H, 4.12; N, 2.58. Calc. for $C_{22}H_{22}ClNO_4SPd$: C, 49.09; H, 4.12; N 2.60%. IR (KBr, cm^{-1}):$\nu_{C\equiv N}$ 1607, ν_{ClO} 1087.8, δ_{ClO} 624.9. ^1H NMR ($CDCl_3$, r.t., ppm): thiomethyl protons $\delta_A =$ 4.63, $\delta_B = 5.04$ (CH_2–S, AB system, $J_{AB} = 16.8$ Hz, 2H); pyridine protons $\delta = 7.71$ (H^4, t, $J = 7.7$ Hz, 1H); allyl protons $\delta = 6.35$ ($H_{central}$, br m, 1H), $\delta = 4.85$ (H_{syn}, br s, 1H), $\delta = 4.07$ ($H_{anti\,H}$, br s, 1H), $\delta = 5.37$ ($H_{anti\,Ph}$, br s, 1H); C_5H_3N-6-CH_3 $\delta = 2.70$ (CH_3, br s, 3H); pyridine and phenyl protons $\delta = 7.14$–7.54 (H_o–H_m–H_p–H^3–H^5, m, 7H).

3.3. Preparation of Pd(0) complexes

3.3.1. [Pd(η^2-fn)(HN–SePh)] (**4a**)

To 0.0746 g (0.30 mmol) of HN–SePh dissolved in 15 ml of anhydrous acetone 0.0246 g (0.315 mmol) of fumaronitrile and 0.148 g (0.143 mmol) of $Pd_2DBA_3{\cdot}CHCl_3$ were added under inert atmosphere (N_2). The solution was stirred for 30 min. Activated charcoal was added and the mixture was filtered on celite.

Reduction to small volume by reduced pressure and addition of diethyl ether yielded 0.102 g (0.236 mmol; yield 82.4%) of the title compound as off-white microcrystals.

Anal. Found: C, 44.50; H, 3.06; N, 9.78. Calc. for $C_{16}H_{13}N_3SePd$: C, 44.42; H, 3.03; N, 9.71%. IR (KBr, cm^{-1}): $\nu_{C\equiv N}$ 2198.7, $\nu_{C=N}$ 1595.1. ^1H NMR ($CDCl_3$, r.t., ppm): selenomethyl protons $\delta = 4.43$ (CH_2–Se, br s, 2H); olefin protons (fumaronitrile) $\delta = 3.24$ (H_{ol}, s, 2H); pyridine protons $\delta = 7.72$ (H^4, td, $J = 7.7$, 1.7 Hz, 1H), 8.89 (H^6, d, $J = 5.2$ Hz, 1H); pyridine and phenyl protons $\delta = 7.69$ (H_m, m, 2H); $\delta = 7.26$–7.42 (H_o–H_p–H^3–H^5, m, 5H).

3.3.2. [Pd(η^2-fn)(MeN–SePh)] (**4b**)

The title complex was prepared in the same way as the **4a** complex. Yield 75.8% (yellow microcrystals). *Anal*. Found: C, 35.71; H, 3.32; N, 9.35. Calc. for $C_{17}H_{15}N_3SePd$: C, 45.72; H, 3.39; N. 9.41%. IR (KBr, cm^{-1}): $\nu_{C\equiv N}$ 2198.7, $\nu_{C=N}$ 1600. ^1H NMR ($CDCl_3$, r.t., ppm): selenomethyl protons $\delta = 4.45$ (CH_2–Se, s, $J_{H-Se} = 13.7$ Hz, 2H); olefin protons (fumaronitrile) $\delta =$ 3.19 (H_{ol}, s, 2H); pyridine protons $\delta = 7.16$ (H^5, d, $J = 7.6$ Hz, 1H); C_5H_3N-6-CH_3 $\delta = 2.93$ (CH_3, s, 3H); pyridine and methyl protons $\delta = 7.24$–7.32 (H_o–H_p–H^3, m, 4H); $\delta = 7.56$–7.63 (H_m–H^4, m, 3H).

3.4. IR and NMR measurements

The IR, ^1H, and $^{13}C\{^1H\}$ NMR spectra were recorded in a Nicolet Magna™ 750 spectrophotometer and in a Bruker™ AC 200 or a Varian ™ 400 Unity spectrometers, respectively. The ^1H 2D NOESY experiments were performed at 188 K in CD_2Cl_2 by means of a Varian™ 400 Unity spectrometer (400 MHz) using a standard three pulse sequence. The mixing time for complex **2b** was 1.8 s. The temperature dependent ^1H NMR spectra were analysed using the SWAN program [18].

3.5. Kinetic and equilibrium measurements

The kinetics of allyl amination were studied by the addition of known aliquots of piperidine solutions to solutions of the complex under study in $CHCl_3$ ($[Pd]_0 \approx 10^{-4}$ mol dm^{-3}) in the presence of fumaronitrile($[fn]_0 \approx 2$–4×10^{-4} mol dm^{-3}) and pyridine–chalcogen ether ($[RN–XPh]_0 \approx 10^{-3}$ mol dm^{-3}) in the thermostated cell compartment of a Lambda 40 Perkin–Elmer™ spectrophotometer at the designed temperature. The reactions were followed by recording spectral changes in the wavelength range of 280–400 nm or at a suitable fixed wavelength.

Mathematical and statistical data analysis was carried out in a personal computer equipped with a locally adapted version of Marquardt's algorithm [19] written in TURBOBASIC™.

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