Palladium-Induced Intramolecular Pyridine-Allyl Coupling Reactions: Formation of N-Bridgehead Heterocycles with a Stable C–N Bond

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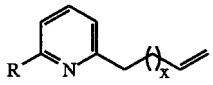
In the presence of stoichiometric amounts of bis(acetonitrile)dichloropalladium(II) the *ortho*-alkenylpyridines 2-but-3′-en-1′-ylpyridine (**1**), 2-pent-5′-en-1′-ylpyridine (**2**), 2-hex-5′-en-1′-ylpyridine (**3**), 2-hept-6′-en-1′-ylpyridine (**4**) and 2-methyl-6-pent-4′-en-1′-ylpyridine (**5**) led to a mixture of coordination compounds such as 2-alken-1′-ylpyridine-κ*N*:κ²*C*-dichloropalladium(II) and bis(2-alken-1′-ylpyridine-κ*N*)-dichloropalladium(II) together with 2-pent-4-ene-1′,3′-diylpyridine-κ*N*:κ³*C*-chloropalladium(II) and 2-hex-4-en-1′,3′-diylpyridine-κ*N*:κ³*C*-chloropalladium(II) in the case of **2** and **3** respectively. The latter were quantitatively demetallated in the presence of an excess of triphenylphosphane to yield tris(triphenylphosphane)palladium(0), 2-vinyl-2,3-dihydroindolizinium chloride and 2-prop-1′-en-1′-yl-2,3-dihydroindolizinium chloride, respectively, by a regioselective addition of the pyridine unit onto the more congested terminal carbon atom of the allyl fragment.

Introduction

The formation of an intramolecular C−N bond between an amine and an olefin activated in the presence of palladium complexes, has been extensively studied. Indeed, Hegedus and co-workers[1] have shown that for primary and secondary amines this amine-olefin coupling reaction, yielding a new C−N bond, results mainly from the addition of the amine to the alkene which has been activated towards nucleophilic addition through coordination to the palladium center. Moreover, recent studies from our group revealed that tertiary amines could also be used as nucleophiles in a different type of C−N coupling reaction to afford cationic and neutral heterocyclic compounds[2]. Here the key step is the formation of an (η^3-allyl)Pd^{II} intermediate by a palladium-assisted C−H activation process. We deemed it of great importance to check whether this coupling reaction could be extended to other nitrogen-containing systems such as those containing an sp^2-hybridised nitrogen atom. We were especially interested in nitrogen nucleophiles in pyridinic systems in these heterocyclisation reactions. It is noteworthy that prior to the work described herein the intramolecular C−N coupling of a nitrogen atom at an allylic position was limited mainly to primary or secondary amines as nitrogen-containing nucleophiles[3]. We can note that heterocycles obtained in this novel way [i.e. by intramolecular addition of a pyridine unit onto a (allyl)Pd derivative] would furnish N-bridgehead heterocycles, many of which display interesting biological properties[4].

The substrates we have chosen for this study are *ortho*-alkenylpyridine derivatives bearing a terminal olefin separated by a chain of carbon atoms of variable length, in the *ortho* position of the pyridine (Scheme 1).

Scheme 1. *ortho*-Alkenyl pyridines (*o*-AlkPy)



1: x = 1; R = H
2: x = 2; R = H
3: x = 3; R = H
4: x = 4; R = H
5: x = 2; R = Me

We report herein the reactivity of the pyridine derivatives **1**−**5** (they are called *o*-AlkPy from now on) in the presence of a palladium(II) complex and base, and we compare this to the reactions observed previously for tertiary amines. We will also describe the interactions between the nitrogen atom and/or the alkene unit and the Pd^{II} center, define under which structural conditions an allylic C−H activation can take place, and, finally study the depalladation of the thus formed organopalladium species affording the anticipated heterocyclic compounds.

Results

Synthesis of the *ortho*-Alkenylpyridines

The *o*-AlkPy ligands **1**−**5** are synthesised according to a known procedure[5]. It is based principally on a C−C coupling reaction between a 2-methylpyridyllithium derivative (prepared in situ) and an alkenyl bromide (Scheme 2).

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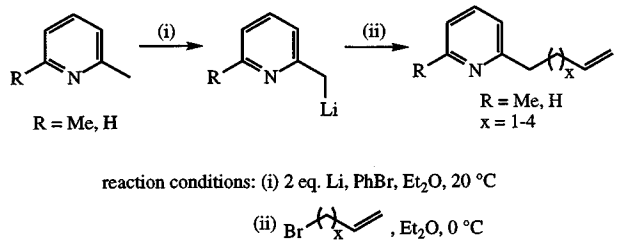
Scheme 2. Synthesis of *ortho*-alkenylpyridines

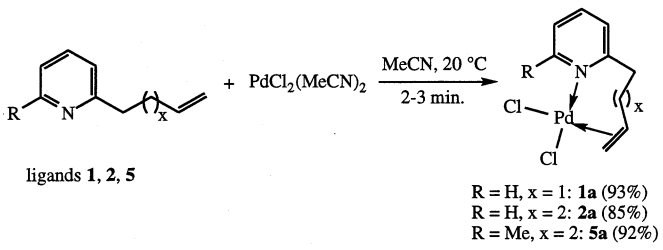


Ligand-Pd^{II} Interaction

The reaction of the *ortho*-alkenylpyridines **1**−**5** with stoichiometric amounts of $PdCl_2(MeCN)_2$ (1:1) leads to the formation of new coordination chelate complexes (Scheme 3). The stability of these compounds (**1a**, **2a** and **5a**) enabled their characterisation both in the solid state and in solution. This is in marked contrast to the corresponding derivatives obtained previously with *ortho*-alkenylaniline or -benzylamine which were only characterised in solution as they were too unstable to be isolated in the solid state.[2a] The structure of compound **2a** was determined by ^{1}H-NMR and IR spectroscopy, microanalysis and mass spectrometry while compounds **1a** and **5a** were identified by comparison of their ^{1}H-NMR spectra with that of **2a** and confirmed by their combustion analyses.

The downfield shift of the *ortho* proton of the pyridine ring in the proton-NMR spectrum of **2a** indicates that the nitrogen atom is coordinated to the Pd atom. The coordination of the olefinic double bond is evidenced by the shielding of all the protons in the lateral chain. Moreover, this is confirmed by the fact that when the chelate complexes are treated with one equivalent of PPh_3 or NEt_3, used to displace the alkene-Pd interaction, the chemical shifts of the latter protons are indeed almost identical to the values observed for the free ligand. In addition, the elemental analysis of **2a** gave a ratio of 1:2:1 with respect to palladium, chlorine and the *o*-AlkPy ligand **2**; the mass spectrum is in agreement with a monomeric species which was expected due to its solubility. Finally, two absorptions with mean intensities corresponding to the frequencies of two Pd−Cl vibrations are seen in the far-IR spectrum: the higher value is assigned to the vibration frequency of the Pd−Cl bond *trans* to N, and the lower one, to the Pd−Cl bond *trans* to the olefin[6][7].

Scheme 3. Chelate-type interaction between the *o*-AlkPy ligands and Pd^{II}



In order to check whether it would be possible to generate an (η^3-allyl)Pd^{II} complex by deprotonation at the allylic position, as it was observed in the case of tertiary amines[2a][2b], the chelate adduct **2a** was treated with a base. Indeed, the corresponding (η^3-allyl)Pd^{II} analogue was formed. Nevertheless, its poor yield (less than 10%) due to the formation of a secondary product of the type $PdCl_2(\mathbf{2})_2$ (see below), incited us to investigate optimum conditions to generate the (allyl)Pd complex.

Ligand-Pd^{II}-Base Interaction: Formation of (η^3-Allyl)Pd^{II} Complexes

The products of the one-pot reaction of the *o*-AlkPy ligands **1**−**5** with one equivalent of $PdCl_2(MeCN)_2$ and a base were studied. The reaction conditions and the products formed are indicated in Table 1 below. Several important remarks can be made concerning these results. Firstly, the nature of the final products seems to depend not only on the number of carbon atoms (*n*) between the nitrogen atom and the terminal olefin but also on the nature of R (R = Me, H). In fact, the formation of an (η^3-allyl)palladium(II) complex, analogous to that obtained in the case of tertiary amines, is limited to the cases where R = H and *n* = 4, 5. In other terms, no allylpalladium complex is observed for *n* larger than 5: the same observation was made in the case of tertiary amines where a different reactivity was noticed for the same length of the carbon chain separating the terminal olefin and the sp^3-hybridised nitrogen atom[2a][2b]. Given that the number of carbon atoms between the nitrogen atom and the allylic fragment in these two (η^3-allyl)Pd^{II} complexes (**2d** and **3d** in Table 1) is the same, we are inclined to believe that in the case of pyridino-olefins, the formation of the allyl complex is under thermodynamic control. However, the formation, in all cases and whatever the reaction conditions, of an important quantity of a secondary product (existing as two isomers except for **5c**) consisting of two *o*-AlkPy ligands and two chlorine atoms coordinated to the same palladium center, limits the yield of the allyl complex for *n* = 4, 5 and R = H. The latter organopalladium compounds **2d** and **3d** are indeed the minor products obtained during this reaction. All attempts (use of different reaction conditions, solvents or bases) to optimise its yield were unsuccessful: 18% was the maximum yield obtained for **2d** [the $PdCl_2(\mathbf{2})_2$ adduct remained the major product of the reaction] when heating a mixture of **2**, 1 equivalent of $PdCl_2(MeCN)_2$ and 2.5 equivalents of NaOAc in MeCN at 65°C for 3 h.

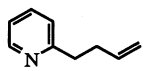
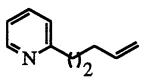
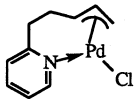
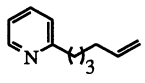
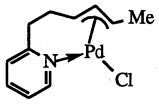
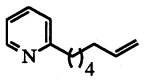
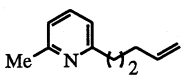
It is worth noting that the stability of these $PdCl_2$(ligand)$_2$ adducts depends on the value of *n*. For *n* < 4 (i.e for **1**), this adduct was not stable and was not isolated although a proton-NMR spectrum of the reaction mixture revealed unambiguously its presence in solution. When *n* increases, a higher yield of the adducts reflects an increase in their stability. A plausible explanation, based on observations from L. D. Pettit's group[5], is the increase in the basicity of the nitrogen atom as it moves further away from the olefinic

double bond with a negative inductive effect. Consequently, the donor ability of the nitrogen atom, via its lone pair of electrons, increases. This is confirmed by the chemioselective formation of this adduct in the case $n = 6$ (compounds **4b** and **4c**). In addition, for longer aliphatic chains ($n = 5$ and 6) this adduct is obtained with an isomerisation of the double bond in the lateral carbon chain of the pyridino-olefin ligand. The latter reaction is rationalised by a classical 1,3-hydrogen shift as described by Sen[8] and others[9]. Finally, the simplicity of the ^{1}H- and ^{13}C-NMR spectra (compared to those obtained for a mixture of the two isomers) suggests the formation of only one isomer of the $PdCl_2$(*o*-AlkPy)$_2$ adduct for ligand **5**. An increase in the steric bulk around the nitrogen atom resulting from the presence of a methyl group in the second *ortho* position of the pyridine ring would most probably favour the formation of the *anti* isomer **5c** rather than the *syn* isomer.

As shown in Scheme 4, ligand **2** is metallated by the palladium salt $PdCl_2(MeCN)_2$ in the presence of 2 equivalents of K_2CO_3 in MeCN to afford the (η^3-allyl)Pd^{II} complex **2d** and the two isomers **2b** and **2c** of the adduct $PdCl_2$(**2**)$_2$ as the main products, along with some palladium black and traces of unidentified products. After Celite filtration, **2d** (15%) and a mixture of isomers **2b** and **2c** (30%) were isolated by column chromatography on silica gel using ethyl acetate as eluant.

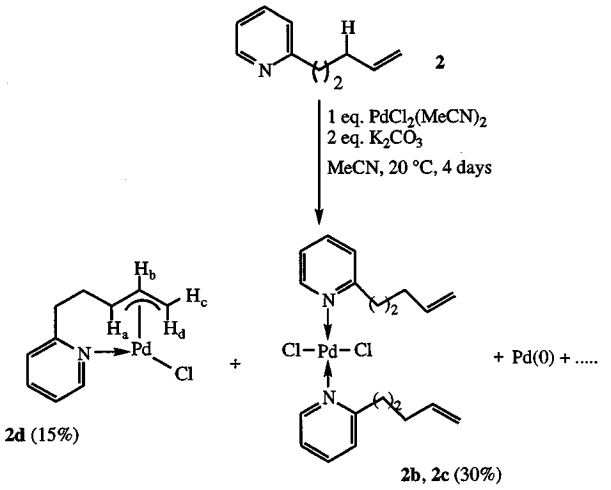
The (η^3-allyl)Pd^{II} complex **2d** was structurally characterised by microanalysis and ^{1}H- and ^{13}C-NMR spectroscopy. The ^{1}H-NMR spectrum shows the presence of the expected signals for an η^3-allyl fragment: a multiplet at $\delta \approx 5.5$ corresponding to H_b, coupled to H_a, H_c and H_d (Scheme 4); the terminal CH_2 group with the characteristic *syn* ($^3J_{HbHc}$ = 6.68 Hz), *anti* ($^3J_{HbHd}$ = 11.87 Hz) and *gem* ($^2J_{HcHd}$ = 1.1 Hz) couplings. The intramolecular coordination of the ni-

Table 1. Ligand-Pd^{II}-base interaction

Entry	Ligands (o-AlkPy)	Products formed	Conditions / yield [a]
1	 **1** (n = 3)	$PdCl_2$(**1**)$_2$ (**1b**, **1c**)	1,5 eq.K_2CO_3, MeCN, 65°C, 2h / [b]
2	 **2** (n = 4)	 **2d** + $PdCl_2$(**2**)$_2$ (**2b**, **2c**)	2 eq. K_2CO_3, MeCN, 20 °C, 4 days / (**2b** + **2c**): 30% **2d** : 15%
3	 **3** (n = 5)	 **3d** + $PdCl_2$(**3**)$_2$ (**3b**, **3c**)	2 eq. NaOAc, MeCN, 20 °C, 1 night / (**3b** + **3c**): 34% **3d** : 10%
4	 **4** (n = 6)	$PdCl_2$(**4**)$_2$ (**4b**, **4c**)	1,5 eq. NaOAc, MeCN, 65 °C, 1 night / (**4b** + **4c**): 40%
5	 **5** (n = 4)	$PdCl_2$(**5**)$_2$ (**5c**)	1,5 eq. NaOAc, MeCN, 65 °C, 3h / 41%

[a] Yield of the pure products after a column chromatography on silica gel. – [b] Unstable product, not isolated but characterised in solution by ^{1}H NMR.

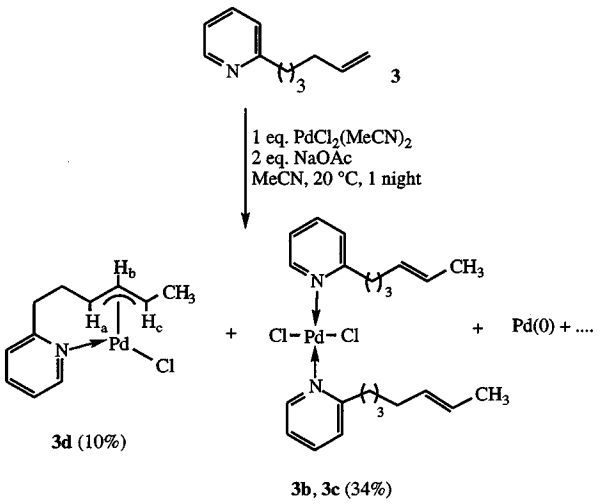
Scheme 4



trogen atom is evidenced by the deshielding of the *ortho* proton (δ = 9.4 compared to 8.4 for the free ligand). The ^{1}H-NMR spectrum of **2d** indicates the presence of only one isomer in which the coupling constant between H_b and H_a is characteristic for two protons in an *anti* position ($^3J_{HaHb}$ = 11.5 Hz) suggesting that the carbon chain is in a *syn* position to H_b.

The $PdCl_2$(**2**)$_2$ adduct results from the higher affinity of a palladium(II) center for an sp^2-nitrogen atom. This compound was characterised by ^{1}H and ^{13}C NMR, elemental analysis and IR. The ^{1}H-NMR spectrum shows two distinct doublets of doublets in a 1:1 ratio at $\delta \approx 9$. In the presence of a drop of deuterated pyridine this spectrum remained unchanged but with a larger excess, the free *o*-AlkPy ligand **2** and the yellow adduct $PdCl_2$(pyr-D_5)$_2$ were formed. All these observations seem to indicate that the terminal olefin of the lateral chain is not coordinated and that a simple adduct is formed by the coordination of *o*-AlkPy ligand **2** on the palladium(II) center. The combustion analysis is in agreement with the presence of two chlorine atoms and two ligands around one atom of palladium. The far-IR spectrum of this compound shows only one large and intense band at 347 cm^{-1}: this vibration frequency is characteristic of a Pd−Cl bond *trans* to a chlorine atom[6][7]. Thus these data indicate that the $PdCl_2$(**2**)$_2$ adduct is a mixture of two isomers, in a 1:1 ratio. For one of these isomers, the two lateral carbon chains are on the same side of the coordination plane of the palladium center (*syn* isomer) and in the other isomer, they are opposite each other with respect to this plane (*anti* isomer). The (η^3-allyl)Pd^{II} complex **3d** and the mixture of isomers **3b** and **3c** (Scheme 5) were isolated in an analogous way to that described for **2d**, **2b** and **2c**. Their structures were determined mainly by ^{1}H and ^{13}C NMR. The proton NMR of **3d** shows the presence of only one compound where the multiplet at δ = 5.5 characteristic of H_b, the central proton of the allylic unit is no longer observed. Instead a triplet at δ = 5.3 was found, indicating that H_b is coupled with H_a and H_c, two magnetically equivalent protons. This suggests that the (η^3-allyl)Pd^{II} complex has the *syn* configuration. The presence of the methyl group is confirmed by a doublet integrating for three protons at δ = 1.55 and with a coupling constant $^3J_{HHc}$ of 6.3 Hz. Finally, evidence for the intramolecular coordination of the nitrogen atom comes from the shielding of the *ortho* proton (δ = 9.41 compared to 8.47 for the free ligand). The structure of the *syn*-(η^3-allyl)Pd^{II} complex **3d** was confimed by ^{13}C-DEPT NMR.

Scheme 5



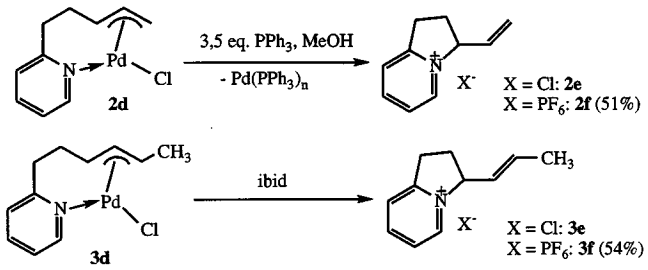
The aspect of the ^{1}H-NMR spectrum of the mixture **3b** and **3c** is also markedly different from that observed for the mixture of isomers **2b** and **2c**: the integration of the multiplets in the olefinic region indicates the presence of fewer olefinic protons (8 instead of 12). On the other hand, we noticed the appearence of a new multiplet integrating for 12 protons at δ = 1.7 and corresponding to the methyl groups. In addition, the ^{13}C-DEPT NMR spectrum shows a signal for methyl groups, thereby confirming the isomerisation of the olefinic double bond in ligand **3** during the course of the reaction and prior to the allylic deprotonation leading to the allyl complex. The same isomerisation process was observed in the case of ligand **4** and the analogous mixture of isomers **4b** and **4c** was isolated and characterised (see Table 1).

Formation of Cationic N-Bridgehead Heterocycles

The (η^3-allyl)Pd^{II} complexes **2d** and **3d** are stable in air and in solution. However, in the presence of an excess (3.5−4 equivalents) of triphenylphosphane in MeOH or MeCN at room temperature, they can be easily demetallated[10]. An orange-yellow solution was obtained together with the precipitation of a pale yellow solid. A proton NMR of the reaction mixture indicated the presence of only one organic compound and the characteristic signals of the phosphane ligands in a Pd^0 complex, Pd(PPh_3)$_n$. After filtration through Celite and anion exchange using KPF_6 in MeOH, the cationic N-heterocycles **2f** and **3f** (Scheme 6) were obtained as pure beige solids. These heterocyclic com-

pounds are indolizinium derivatives incorporating an sp^2-hybridised nitrogen atom shared between a pyridine ring and a 5-membered ring.

Scheme 6



The structures of compounds **2f** and **3f** were deduced from ^1H and ^{13}C NMR, mass spectrometry and combustion analysis. The proton-NMR spectrum of **2f** is rather simple and shows not only that all the protons are different but also that the protons of the lateral carbon chain resonate at lower frequencies compared to those observed for compound **2d**: this general shielding is best explained by the presence of a positive charge on the nitrogen atom. The diastereotopicity of the protons of both CH_2 groups in **2f** is due to the presence of a stereogenic center α to the nitrogen atom. The structure of compound **3f** was deduced by comparaison of its ^1H- and ^{13}C-NMR spectra with those of **2f**.

Discussion

This study was aimed at defining the reactivity of *ortho*-alkenylpyridine ligands with a Pd^{II} center in the presence of a base. We intended to extend the scope of the unusual reactions that were observed for the related *ortho*-alkenylanilines or -benzylamines under similar conditions, i.e. the palladium-mediated heterocyclisation of these ligands which occured via the formation of C−N bonds at the allylic position[2].

We have noticed one major similarity between tertiary amines and pyridine derivatives concerning the above-mentioned heterocyclisation process: the addition of the nucleophile (amine or pyridine) always takes place at an allylic terminal (i.e. after an allylic deprotonation in the presence of a base) instead of a direct nucleophilic addition on the activated olefin due to its coordination to a Pd^{II} center, as observed in the case of primary and secondary amines[1]. Indeed, the results we have obtained clearly demonstrate that there is very little similarity between these types of nitrogen ligands and the corresponding pyridine derivatives, since in the present work we have mainly observed the formation of stable pyridine−palladium adducts. This result is not surprising as it is well known that Pd^{II} has a much larger affinity to a pyridine nitrogen atom as compared to an sp^3-hybridised tertiary amine nitrogen atom[11].

However, in two cases we could observe the formation of some (η^3-allyl)Pd-containing complexes by a C−H activation reaction. It is interesting to note that (i) this moiety has only been observed for two ligands and (ii) that both compounds do have the same geometry around the (Py-allyl)Pd unit: in both cases a CH_2-CH_2 chain is found between the pyridine ring and one extremity of the allylic unit. This is due to the stabilisation of the π-allyl fragment by an intramolecular coordination of the pyridine, thereby confering an ideal coordination geometry for the palladium atom in an analogous manner to that observed for a Pd(benzylamine-allyl) derivative[2a].

Moreover, for ligand **3** a prior C−H migration is essential in order to obtain the same type of stabilised (Py-allyl)Pd compound observed for ligand **2** (see Table 1). However, this C−H migration occurs only once since for ligand **4**, we observed only the formation of the bis(*ortho*-alkenylpyridine)palladium adduct. This behaviour is in marked contrast to that of the corresponding ligands bearing an sp^3-hybridised tertiary amine unit[2a][2b], for which the formation of the (η^3-allyl)Pd moiety was always possible (although it could not be isolated in each case studied) regardless of the number of carbon atoms between the olefin and the N atom. We interpret this as a consequence of the strong coordination of the sp^2-hybridised nitrogen atom of the pyridine moiety to the Pd center prior to the C−H activation at the allylic position by this metal, whereas for the tertiary amine alkene derivatives the interaction of the alkene to the palladium center seems to be the key step of the metallation process, yielding the (π-allyl)Pd derivatives in a quantitative way.

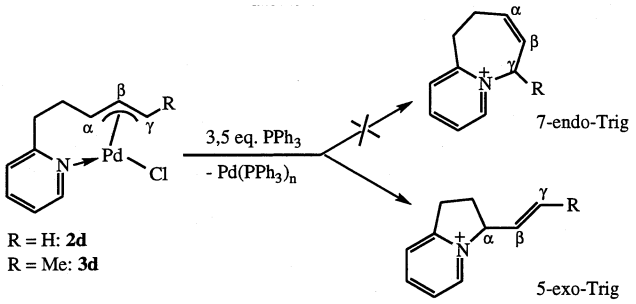
Although the corresponding (η^3-allyl)Pd^{II} complexes have been observed for pyridine derivatives, their yields are low (less than 20%) compared to those for tertiary amine analogues. These compounds are most likely formed by the intermediacy of the monomeric chelate adduct where both the nitrogen atom and the olefin are coordinated to the palladium atom (its presence in solution was unambiguously identified by ^1H NMR of the reaction mixture at the beginning of the reaction). However, the C−H activation process takes place only partially since the compounds with two ligands per palladium, $PdCl_2$(*o*-AlkPy)$_2$, are the major products of the reaction. Nevertheless, once they are formed no reverse reaction could be envisaged to transfer one species into the other; this result seems to indicate clearly the absence of any type of equilibrium between these two Pd^{II} compounds. One may anticipate, from our failed attempts to increase the yields of the allylic compounds starting from **2a** for instance, that the formations of these two classes of compounds are in competition with each other; however, in the absence of any reliable kinetic data we cannot conclude about this important mechanistic point.

It is, however, interesting to note the ease with which the allylic compounds can be demetallated to yield quantitatively heterocyclic compounds with a stable C−N bond even in the presence of Pd^0 formed. Indeed, even if some rare examples of (allyl)Pd^{II} complexes analogous to that observed for the pyridino-olefins are known for quinoline derivatives[12], the cyclisation reaction by the addition of an sp^2-nitrogen atom on an allylic fragment has never been

studied until now. One of the reasons is, most probably, a reversible reaction implying a C−N bond rupture, between the pyridinium ion formed and the simultaneous obtention of Pd^0 during the demetallation reaction. Indeed, allylpyridinium moities synthesised by other methods are used to generate in the presence of Pd^0 an (η^3-allyl)Pd^{II} complex and a trisubstituted pyridine (playing the role of a neutral leaving group) by an oxidative addition of the C−N bond on the Pd^{II} center[13]. Moreover, another reason which may justify that hitherto only few studies have been carried out concerning pyridine-allyl coupling reactions yielding new C−N bonds, is the result of the recent study carried out on the reversible intermolecular addition of a pyridine on an allylic unit[14]. Thus, this reversibility reflects the instability of the $C-N^+$ bond formed during this study.

The demetallation of the (η^3-allyl)Pd^{II} compounds is induced by an intramolecular attack of the sp^2-hybridised nitrogen atom on the allylic fragment and this can occur either as an endo- or exocyclisation yielding different cyclic products. In the case of substrate **2d** or **3d**, only one heterocycle is obtained by the formation of a new C−N bond between the sp^2-nitrogen and the more substituted carbon atom C_α to give a 5-membered heterocycle (Scheme 7). We have, therefore, a remarkably high regioselectivity when taking into account the two possible electrophilic centers on the allylic fragment.

Scheme 7



According to Baldwin rules governing the formation of cyclic products[15], both the formation of the 5-membered heterocycle and that of the 7-membered one are favoured processes. It is, however, accepted that the formation of 5-membered rings is more frequent than that of 7-membered derivatives[16]. An important observation is the fact that in the case of tertiary amines, for the closely related (π-allyl)Pd compounds (i.e. those having 3 carbon atoms between the N atom and the allylic fragment) the endocyclisation process was exclusively observed[2a]. This highlights the difference of the strength of the N−Pd bond in the latter case as compared to the pyridine compounds: the endocyclisation could only take place via an intermediate in which the NR_2 unit was not coordinated to the palladium atom. On the other hand, for the pyridine-containing compounds the exocyclisation could be achieved without dissociation of the Py−Pd bond by a *cis* migration of the N atom to the more substituted allylic carbon atom; however, this assumption merits a more substantial mechanistic study.

Moreover, in the case of substrate **3d**, the exocyclisation should be even more favorable owing to the steric effect of the methyl group at the external (C_γ) allylic carbon atom. Consequently, the nucleophilic attack at this position becomes more difficult[17].

Conclusion

The present study shows that even if there is a remarkable difference in affinity to a palladium(II) center between a pyridinic sp^2-nitrogen and a tertiary amino sp^3-nitrogen atom, it is possible to generate the (η^3-allyl)Pd^{II} analogue of the pyridino-olefin derivative. The demetallation of the latter complex yields, regioselectively and in mild conditions, a stable cationic N-heterocycle by the intramolecular formation of a C−N bond between the pyridinic nitrogen atom and the allylic C_3 unit. Nevertheless, the low yield of the allylpalladium complex associated with the fact that it is observed in only a few cases, considerably limits the scope of this elegant cyclisation reaction for the formation of cationic N-bridgehead heterocycles. Consequently, new methods to generate selectively and quantitatively the key (η^3-allyl)Pd^{II} intermediate are under investigation.

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Experimental Section

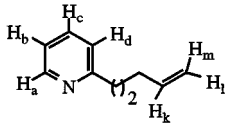
General: All the reactions described herein were carried out without any particular precaution unless otherwise stated. All the solvents used were dried beforehand and distilled under nitrogen. The other commercial starting materials were utilised without further purification. Filtrations to remove the black deposit of metallic palladium formed during the depalladation reactions, were performed using Celite pads. Column chromatography was carried out either on silica gel (Geduran SI 60; 0.063−0.200 mm) or on alumina 90 (Activity II−III mesh; 0.063−0.200 mm) from Merck. ^{1}H- (300.13 or 200.13 MHz), ^{13}C- (75.47 or 50.32 MHz) and ^{31}P-NMR spectra (81 MHz) were recorded with AC 300 and AC 200 Bruker instruments and externally referenced to TMS. Coupling constants (*J*) are given in Hertz. All deuterated solvants were dried with molecular sieves (4 Å) and stored under nitrogen. Combustion analyses were performed by the Service Central de Microanalyses du CNRS, Université Louis Pasteur, Strasbourg, France or by that of Vernaison, France. All Mass spectra were performed by the Laboratoire de Spectroscopie de Masse de l'Université Louis Pasteur, Strasbourg. IR spectra were recorded with an IRFT Bruker instrument and the absorption bands are given in cm^{-1}.

Ligands Synthesis: Ligands **1** and **2** were prepared according to published procedures[5]. Ligands **3**, **4** and **5** were synthesised in an analogous manner. The analytical data for these ligands are listed below.

Ligand **1**: Yellow oil (83%). − ^{1}H NMR ($CDCl_3$): δ = 8.45−8.43 (m, 1 H, H_o), 7.48 (td, 1 H, H_m, ^3J = 8.4 Hz, ^4J = 1.9 Hz), 7.09 (d, 1 H, H_m, ^3J = 19.2 Hz), 7.04−6.97 (m, 1 H, Ar, H_p), 5.86−5.73 (m, 1 H, HC=C), 5.01−4.87 (m, 2 H, $C=CH_2$, $^3J_{trans}$ = 17.1 Hz, $^3J_{cis}$ = 10.2 Hz), 2.83−2.78 (m, 2 H, Ar-CH_2), 2.47−2.39 (m, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 161.4, 149.2, 137.7, 136.2, 123.0, 121.0, 115.1 (aromatic and olefinic), 37.7, 33.7 (CH_2).

Ligand **2**: Pale yellow oil (78%). − The indices allocated to certain protons are given in Figure 1. − ^{1}H-NMR ($CDCl_3$): δ = 8.45 (d, 1 H, H_a, $^3J_{HaHb}$ = 3.4 Hz), 7.52 (m, 1 H, H_c), 7.03 (m, 2 H, H_b + H_d), 5.80 (m, 1 H, H_k, $^3J_{HkHm}$ = 18.8 Hz, $^3J_{HkHl}$ = 9.3 Hz), 4.92 (m, 2 H, H_l + H_m, $^2J_{HlHm}$ = 1.8 Hz), 2.74 (t, 2 H, Ar-CH_2), 2.06 (m, 2 H, CH_2−CH=), 1.80 (m, 2 H, CH_2-CH_2-CH=).

Figure 1. Numbering scheme for the protons of ligand **2**



Ligand **3**: Orange yellow oil (94%). − ^{1}H NMR ($CDCl_3$): δ = 8.47 (d, 1 H, H_o, ^3J = 4.8 Hz); 7.54 (td, 1 H, H_m, ^3J = 7.7, Hz, ^4J = 1.8 Hz), 7.10 (d, 1 H, H_m, ^3J = 7.8 Hz); 7.07−7.02 (m, 1 H, H_p), 5.82−5.71 (m, 1 H, HC=C), 5.01−4.88 (m, 2 H, H_2C=C), 2.76 (t, 2 H, Ar-CH_2, ^3J = 7.7 Hz), 2.11−2.03, 1.78−1.67, 1.49−1.38 (3 m, 6 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 162.3, 149.2, 138.8, 136.3, 122.7, 120.9 (aromatic and olefinic), 38.3, 33.6, 29.4, 28.7 (CH_2). − MS; *m/z*: 162 (M^+ + H), 120 (M^+ − C_3H_5), 106 (M^+ − C_4H_7), 93 (M^+ − C_5H_8).

Ligand **4**: Yellow oil (93%). − ^{1}H NMR ($CDCl_3$): δ = 8.52−8.50 (m, 1 H, Ar, H_o), 7.56 (td, 1 H, Ar, ^3J = 7.7 Hz, ^4J = 1.9 Hz), 7.12 (d, 1 H, Ar, ^3J = 7.8 Hz), 7.09−7.05 (m, 1 H, Ar), 5.86−5.72 (m, 1 H, HC=C), 5.01−4.89 (m, 2 H, C=CH_2), 2.77 (t, 2 H, Ar−CH_2, ^3J = 7.6 Hz), 2.09−2.01, 1.78−1.68, 1.48−1.32 (3 m, 8 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 162.3, 149.1, 138.9, 136.1, 122.6, 120.8 (aromatic and olefinic CH), 114.2 (olefinic CH_2), 38.3, 33.6, 29.7, 28.8, 28.7 (CH_2).

Ligand **5**: Pale yellow oil (80%). − ^{1}H NMR ($CDCl_3$): δ = 7.45 (t, 1 H, Ar, ^3J = 7.7 Hz), 6.94−6.90 (m, 2 H, Ar), 5.87−5.75 (m, 1 H, HC=C), 5.04−4.92 (m, 2 H, C=CH_2), 2.74 (t, 2 H, Ar-CH_2, ^3J = 7.7), 2.51 (s, 3 H, CH_3), 2.14−2.07, 1.84−1.74 (2 m, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 161.5, 157.7, 138.5, 136.4, 120.4, 119.5, 114.8 (aromatic and olefinic), 37.9, 33.5, 29.3 (CH_2), 24.6 (CH_3). − MS; *m/z*: 161 (M^+), 160 (M^+ − H), 120 (M^+ − C_3H_5), 107 (M^+ − C_4H_6).

Synthesis of the Chelate Adducts

Compound **2a**: To a suspension of $PdCl_2(MeCN)_2$ (0.93 g; 3.6 mmol) in acetonitrile (40 ml) was added dropwise a solution of ligand **2** (0.525 g; 3.6 mmol). The yellow suspension became gradually homogeneous with increasing amounts of the ligand. The reaction mixture was stirred for 10 min at room temperature. After removal of the solvent by evaporation, drying, washing with ether (2 × 40 ml), compound **2a** was obtained as a fine, orange-coloured powder (0.985 g; yield 85%). − ^{1}H NMR ($CDCl_3$): δ = 8.63 (d, 1 H, H_{ortho}, ^3J = 5.5 Hz), 7.83 (t, 1 H, H_{para}, ^3J = 7.7 Hz), 7.38−7.34 (m, 2 H, H_{meta}), 6.43−6.31 (m, 1 H, CH_2=C*H*), 5.78 (dd , 1 H, CH_2=CH, ^3J = 7.7 Hz, ^2J = 2.1 Hz), 4.95−4.83 (m, 1 H, Ar−CH_2), 4.68 (d, 1 H, CH_2=CH, ^3J = 14.7 Hz), 3.39−3.32 (m, 1 H, Ar−CH_2), 2.61−2.48, 2.34−2.16, 2.07−1.89, 0.95−0.88 (4 m, 4 H, CH_2). − IR (polyethylene pellet): 341 (br, m, νPd−Cl *trans* to N); 308 (br, m, νPd−Cl *trans* to the olefin). − MS (FAB); *m/z*: 328 (M^+ + 3H), 254 [M^+ − 2 Cl)]. − $C_{10}H_{13}Cl_2NPd$ (324.5): calcd. C 37.01, H 4.04, N 4.32; found C 37.10, H 4.12, N 4.38.

Compounds **1a** and **5a** were synthesised in the same way as described for compound **2a** above.

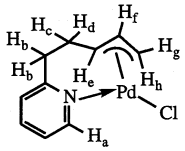
Compound **1a**: Dark yellow solid (93%). − ^{1}H NMR ($CDCl_3$): δ = 8.93 (d, 1 H, H_o, ^3J = 5.6 Hz), 7.85 (t, 1 H, H_m, ^3J = 7.5 Hz), 7.40−7.26 (m, 2 H, H_p + H_m), 6.91−6.78 (m, 1 H, C=CH), 5.85 (d, 1 H, C=CH_2, $^3J_{cis}$ = 8.2 Hz), 4.41 (d, 1 H, C=CH_2, $^3J_{trans}$ = 14.1 Hz), 3.92 (td, 1 H, CH_2, ^3J = 12.6 Hz), 3.34−3.27, 2.80−2.77, 1.70−1.54 (3 m, 3 H, CH_2). − $C_9H_{11}Cl_2NPd$ (310.5): calcd. C 34.79, H 3.54, N 4.51; found C 34.65, H 3.36, N 4.71.

Compound **5a**: Orange yellow solid (92%). − ^{1}H NMR ($CDCl_3$): δ = 7.71 (t, 1 H, Ar, ^3J = 7.5 Hz), 7.24 (d, 1 H, Ar, ^3J = 8.3 Hz), 7.17 (d, 1 H, Ar, ^3J = 7.7 Hz), 6.55−6.35 (m, 1 H, C=CH), 5.65 (d, 1 H, C=CH_2, ^3J = 7.1 Hz), 5.18−5.07 (m, 1 H, CH_2), 4.57 (d, 1 H, C=CH_2, ^3J = 14.5 Hz), 3.40−3.32 (m, 1 H, CH_2), 3.28 (s, 3 H, CH_3), 2.63−2.43, 2.25−2.10, 2.05−1.85, 1.05−0.82 (4 m, 4 H, CH_2). − $C_{11.6}H_{16.4}Cl_2NPd$ (**5a** + 0.1 C_6H_{14}) (the solvent was detected in the ^{1}H-NMR spectrum) (347.2): calcd. C 40.11, H 4.70, N 4.03; found C 40.14, H 4.45, N 4.11.

Synthesis of the (η^3-Allyl)palladium Complex **2d** *and of the Mixture* **2b** + **2c**: A suspension containing ligand **2** (1.3 g, 8.8 mmol), $PdCl_2(MeCN)_2$ (2.3 g, 8.8 mmol) and 2 equiv. of NaOAc (1.45 g, 17.6 mmol) in acetonitrile (50 ml) was heated at 65°C for 3 h. A red solution with a considerable deposit of metallic palladium was thus obtained. After filtration of the Pd^0 so formed through Celite, the clear solution was concentrated to dryness. The brown oily residue was then extracted with CH_2Cl_2 (ca. 5 ml). A column chromatography using silica gel and ethyl acetate as eluant allowed the migration of a first yellow band corresponding to the mixture **2b** + **2c**. After solvent evaporation, a yellow solid was obtained (1.25 g; yield 30%). Then a second yellow fraction containing compound **2d** was collected (0.412 g; yield 16%).

Compound **2d**: Figure 2 indicates the indices attributed to certain protons.

Figure 2. Numbering scheme for the protons of ligand **2d**



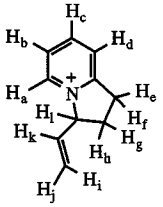
^{1}H NMR ($CDCl_3$): δ = 9.36 (d, 1 H, H_a, $^3J_{HaH}$ = 5.2 Hz), 7.73, 7.30 (2 m, 3 H, *meta* and *para* protons), 5.45 (m, 1 H, H_f, $^3J_{HfHh}$ = 11.87 Hz, $^3J_{HfHg}$ = 6.68 Hz, $^3J_{HfHe}$ = 11.5 Hz), 3.94 (d, 1 H, H_g), 3.72 (m, 1 H, H_e, $^3J_{HeHc}$ = 5.6 Hz), 3.12 (m, 2 H, H_b, $^3J_{HbHc}$ = 6.74 Hz, $^3J_{HbHd}$ = 3.15 Hz), 2.88 (d, 1 H, H_h), 2.05 (m, 1 H, H_c), 1.85 (m, 1 H, H_d). − ^{13}C NMR ($CDCl_3$): δ = 158.2, 152.2, 138.7, 124.9, 122.9 (aromatic), 111.7, 81.4, 55.9 (allylic), 41.6, 26.4 (CH_2). − $C_{12}H_{16}ClNOPd$ (**2d** + 0.5 $C_4H_8O_2$) (the solvent was detected in the ^{1}H-NMR spectrum) (332.1): calcd. C 43.37, H 4.82, N 4.22; found C 43.74, H 4.81, N 4.42.

Compounds **2b** + **2c**: ^{1}H NMR ($CDCl_3$): δ = 9.02 (d, 2 H, H_o, ^3J = 5.0 Hz), 8.90 (d, 2 H, H_o, ^3J = 4.9 Hz), 7.68 (td, 4 H, H_m, ^3J = 7.5 Hz, ^4J = 1.6 Hz), 7.30−7.18 (m, 8 H, H_m + H_p), 6.05−5.93 (m, 4 H, C=CH), 5.29−5.05 (m, 8 H, C=CH_2), 3.96−3.92 (m, 8 H, CH_2), 2.42−2.18 (m, 16 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 164.0, 152.7, 152.2, 138.2, 138.0, 125.4, 124.5, 122.6 (aromatic carbon atoms and olefinic CH), 115.7 (olefinic CH_2), 39.5, 38.9, 33.8, 33.4, 28.2 (CH_2). − IR (polyethylene pellet): 347 (br, s, νPd−Cl *trans* to Cl). − $C_{20}H_{26}Cl_2N_2Pd$ (471.7): calcd. C 50.91, H 5.52, N 5.94; found C 51.62, H 5.52, N 5.63.

Synthesis of Indolizinium Derivatives **2e** *and* **2f**: The reaction of the allylpalladium complex **2d** (220 mg, 0.76 mmol) with 3.5 equivalents of triphenylphosphane (700 mg, 2.66 mmol) in methanol (20 ml), at room temperature and under nitrogen, gave an orange solu-

tion together with a yellow solid that precipitated after only a few minutes of reaction. The reaction mixture was allowed to stir for 1 h. Then after filtration of the fine yellow solid, the filtrate was concentrated to dryness to give an orange oily residue. Column chromatography on alumina using a mixture of ether and methanol (80:20) as eluant, enabled the migration of a yellow band corresponding to the cationic heterocycle **2e** (100 mg, crude yield 72%). Compound **2f** (PF_6^- as conter anion) was obtained pure as a beige solid by treating **2e** with KPF_6 in methanol (112 mg, yield 51%). The indices attributed to the different protons in compounds **2e** and **2f** are indicated in Figure 3.

Figure 3. Numbering scheme for the protons of ligand **2e**



Compound **2e**: ^{1}H NMR ($CDCl_3$): δ = 8.97 (d, 1 H, H_a, ^3J = 5.9 Hz), 8.42 (t, 1 H, H_c, ^3J = 7.7 Hz), 8.09 (d, 1 H, H_d, ^3J = 7.9 Hz), 7.93 (t, 1 H, H_b, ^3J = 6.7 Hz), 6.13 (dd, 1 H, H_l, ^3J = 15.2, 7.6 Hz), 6.00−5.88 (m, 1 H, H_k), 5.68 (d, 1 H, H_i, $^3J_{trans}$ = 16.8 Hz), 5.54 (d, 1 H, H_j, $^3J_{cis}$ = 10.0 Hz), 3.70−3.59, 2.83−2.77, 2.31−2.24 (4 m, 4 H, H_e + H_f + H_g + H_h). − ^{13}C NMR ($CDCl_3$): δ = 158.1, 145.7, 140.7, 132.8, 126.3, 125.3 (aromatic and olefinic CH), 124.6 (olefinic CH_2), 73.4 (N−CH), 31.6, 28.6 (CH_2). − MS (without Cl^-); *m/z*: 146 (M^+), 117 [M^+ − (vinyl + 2H)].

Compound **2f**: ^{1}H NMR ([D_6]acetone): δ = 8.89 (d, 1 H, H_a, ^3J = 6.4 Hz), 8.64 (t, 1 H, H_c, ^3J = 8.6 Hz), 8.24 (d, 1 H, H_d, ^3J = 7.8 Hz), 8.11 (t, 1 H, H_b, ^3J = 6.8 Hz), 6.28−6.17 (m, 1 H, H_k), 5.81−5.68 (m, 1 H, H_l), 5.75 (d, 1 H, H_i, $^3J_{trans}$ = 17.0 Hz), 5.69 (d, 1 H, H_j, $^3J_{cis}$ = 10.2 Hz), 3.83−3.58, 3.05−2.85, 2.62−2.42 (3 m, 4 H, H_e + H_f + H_g + H_h). − $C_{10}H_{12}F_6NP$ (291.2): calcd. C 41.24, H 4.12, N 4.81; found C 40.76, H 4.01, N 4.58.

Synthesis of the (η^3-Allyl)palladium Complex **3d** *and of the Mixture* **3b** + **3c**: To a mixture containing ligand **3** (0.76 g, 4.7 mmol) and $PdCl_2(MeCN)_2$ (1.22 g, 4.7 mmol) in acetonitrile (50 ml) were added 2 equiv. of NaOAc (0.77 g, 9.4 mmol). The reaction mixture was stirred overnight at room temperature. A red solution along with a deposit of black metallic palladium was obtained. After filtration through Celite and concentration of the filtrate to dryness, the brown oily residue was extracted with a minimum amount of CH_2Cl_2. Column chromatography on silica gel using a mixture of ether and acetone (85:15) as eluant, allowed the migration of a first yellow band containing a mixture of isomers **3b** + **3c** (0.473 g, yield 34%), followed by the migration of a second yellow fraction corresponding to the allylpalladium complex **3d** (0.142 g, yield 10%).

Compound **3d**: ^{1}H NMR ($CDCl_3$): δ = 9.41 (d, 1 H, Ar, H_o, ^3J = 5.3 Hz), 7.73 (td, 1 H, Ar, ^3J = 7.7 Hz, ^4J = 1.8 Hz), 7.34−7.27 (m, 2 H, Ar), 5.30 (t, 1 H, $H_{central\ allylic}$, ^3J = 10.8 Hz), 3.83−3.65 (m, 1 H, $H_{allylic}$), 3.53−3.43 (m, 1 H, $H_{allylic}$), 3.19−3.01 (m, 2 H, CH_2), 2.13−1.98 (m, 1 H, CH_2), 1.91−1.71 (m, 1 H, CH_2), 1,55 (d, 3 H, CH_3, ^3J = 6.3 Hz). − ^{13}C NMR ($CDCl_3$): δ = 158.4, 152.7, 138.5, 124.9, 122.8 (aromatic), 112.6, 76.9, 73.7 (allylic), 41.3, 26.4 (CH_2), 17.9 (CH_3).

Compounds **3b** + **3c**: ^{1}H NMR ($CDCl_3$): δ = 9.13−8.80 (m, 4 H, Ar, H_o), 7.67 (t, 4 H, Ar, H_m, ^3J = 6.4 Hz), 7.40−7.08 (m, 8 H, Ar, H_p),, 5.75−5.40 (m, 8 H, C=CH), 3.90 (br s, 8 H, H_2C−C=), 2.60−2.03 (m, 16 H, CH_2), 1.85−1.58 (m, 12 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 164.3, 160.6, 152.5, 152.1, 138.2, 130.4, 126.3, 126.1, 125.3, 122.4, 121.4 (aromatic and olefinic), 39.6, 39.1, 32.6, 28.9, 26.6, 23.0, 22.5 (CH_2), 18.1,14.1 (CH_3). − $C_{22.6}H_{31.2}Cl_{3.2}N_2Pd$ (**3b**, **3c** + 0.6 CH_2Cl_2) (the solvent was detected in the ^{1}H-NMR spectrum) (550.8): calcd. C 49.27, H 5.67, N 5.09; found C 49.18, H 5.35, N 5.28.

Synthesis of the Indolizinium Derivatives **3e** *and* **3f** : Compound **3e** was prepared by a similar procedure to that described for **2e**, starting from **3d** (70 mg; 0.23 mmol) and yielding **3e** (36 mg). Compound **3f**, with PF_6^- as counterion instead of Cl^-, was obtained pure as a pale yellow solid (38 mg; yield 54%), by treating a methanol solution of **3e** with KPF_6, followed by a column chromatography on alumina using the same system of eluant as for **2e**.

Compound **3e**: ^{1}H NMR ($CDCl_3$): δ = 8.95 (d, 1 H, H_o, ^3J = 6.1 Hz), 8.37 (td, 1 H, H_m, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 7.99 (d, 1 H, H_m, ^3J = 7.9 Hz), 7.93 (t, 1 H, H_p, ^3J = 6.8 Hz), 6.49−6.37 (m, 1 H, C=C*H*Me, ^3J = 6.5 Hz), 6.23 (dd, 1 H, N−C*H*, ^3J = 8.4, 16.6 Hz), 5.59−5.50 (m, 1 H, *H*C=C), 3.87−3.73, 3.61−3.51, 2.92−2.82, 2.33−2.20 (4 m, 4 H, CH_2), 1.85 (dd, 3 H, CH_3, ^3J = 6.6 Hz, ^4J = 1.6 Hz). − MS (without Cl^-); *m/z*: 160 (M^+), 132 ($M^+ - C_2H_4$), 106 ($M^+ - C_4H_6$), 95 ($M^+ - C_5H_7$).

Compound **3f**: ^{1}H NMR ([D_6]acetone): δ = 8.86 (d, 1 H, H_o, ^3J = 6.2 Hz), 8.60 (t, 1 H, H_m, ^3J = 7.7 Hz), 8.19 (d, 1 H, H_m, ^3J = 7.7 Hz), 8.06 (t, 1 H, H_p, ^3J = 6.6 Hz), 6.37−6.26 (m, 1 H, C=C*H*Me), 5.86−5.77 (m, 1 H, *H*C=C), 5.69 (dd, 1 H, N−C*H*, ^3J = 8.1, 16.3 Hz), 3.78−3.61, 2.95−2.70, 2.51−2.38 (3 m, 4 H, CH_2),1.87 (dd, 3 H, CH_3, ^3J = 6.6 Hz, ^4J = 1.6 Hz). − ^{13}C NMR (CD_3OD): δ = 160.5, 146.5, 141.0, 138.9, 127.4, 127.0 (aromatic and olefinic CH), 126.0 (CH_2 olefinic), 75.2 (N−CH), 32.1, 30.0 (CH_2), 18.1 (CH_3). − $C_{11}H_{14}F_6NP$ (305.2): calcd. C 43.28, H 4.59, N 4.59; found: C 43.02, H 4.41, N 4.37.

Synthesis of the Mixture of Isomers **4b** *and* **4c**: To a solution containing $PdCl_2(MeCN)_2$ (0.78 g, 3.0 mmol) and ligand **4** (0.528 g, 3.0 mmol) in acetonitrile (40 ml) were added 1.5 equiv. of NaOAC (0.37 g, 4.5 mmol). The reaction mixture was heated at 65°C overnight. The black deposit of palladium(0) thereby formed was filtered off using a Celite pad. Then, after evaporation of the solvent, the brown oily residue obtained was extracted using a minimum of CH_2Cl_2. Column chromatography on silica gel with ethyl acetate as eluant allowed the migration of a yellow band containing the mixture **4b** + **4c** (0.335 g, yield 42%). − ^{1}H NMR ($CDCl_3$): δ = 9.00 (d, 2 H, H_o, ^3J = 4.5 Hz), 8.89 (d, 2 H, H_o, ^3J = 5.0 Hz), 7.67 (t, 4 H, Ar, ^3J = 3.7 Hz), 7.26 (br t, 4 H, Ar), 7.19 (t, 4 H, Ar, ^3J = 6.5 Hz), 5.40−5.60 (m, 8 H, HC=CH), 3.92 (t, 8 H, H_2C−C=, ^3J = 7.6 Hz), 2.43−1.95 (m, 24 H, CH_2), 1.80−1.55 (m, 12 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 159.5, 147.7, 147.3, 133.2, 126.2, 126.1, 120.5, 120.1, 117.6 (aromatic and olefinic), 35.2, 34.6, 27.6, 24.9,24.7, 24.0, 23.4 (CH_2), 13.1 (CH_3). − $C_{24}H_{34}Cl_2N_2Pd$ (527.9): calcd. C 54.61, H 6.45, N 5.31; found C 53.58, H 5.97, N 4.76.

Synthesis of Compound **5c**: A mixture containing ligand **5** (0.72 g, 4.5 mmol), $PdCl_2(MeCN)_2$ (1.17 g, 4.5 mmol) and 1.5 equiv. of NaOAc (0.55 g, 6.8 mmol) in 50 ml of acetonitrile was heated at 65°C for 3 h. An orange solution containing some black palladium was observed. After filtration through a Celite pad, the solvent was evaporated and the brown oily residue formed was extracted using a minimum of CH_2Cl_2. Column chromatography on silica gel with a mixture of CH_2Cl_2 and hexane (90:10) as eluant allowed the migration of a yellow band. After evaporation of the solvents, compound **5c** was obtained as a beige solid (0.93 g, yield 41%). − ^{1}H

NMR ($CDCl_3$): δ = 7.56 (td, 2 H, Ar, ^3J = 7.7 Hz, ^4J = 3.4 Hz), 7.10 (d, 4 H, Ar, ^3J = 7.6 Hz), 6.03−5.90 (m, 2 H, HC=C), 5.21−5.06 (m, 4 H, C=CH_2), 4.30−4.23 (m, 4 H, CH_2), 3.63 (s, 6 H, CH_3), 2.37−2.44, 2.21−2.11 (2 m, 8 H, CH_2). − ^{13}C NMR ([D_6]acetone): δ = 165.0, 161.2, 139.8, 139.1, 124.3, 123.1, 115.7 (aromatic and olefinic), 40.1, 34.3, 29.1 (CH_2), 27.9 (CH_3). − $C_{25}H_{37}Cl_2N_2Pd$ (**5c** + 0.5 C_6H_{14}) (the solvent was detected in the ^{1}H-NMR spectrum) (542.9): calcd. C 55.31, H 6.82, N 5.16; found C 55.32, H 6.39, N 5.22.

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