Palladium-Mediated Intramolecular C-N Bond Formation between Tertiary Amines and Alkenes

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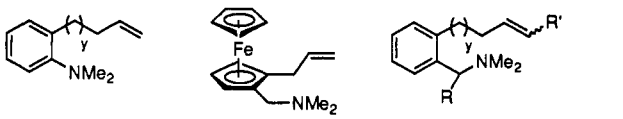
Abstract: The reaction of terminal alkenylarenes having either *o*-(dimethylamino) or *o*-[(dimethylamino)methyl] substituents with $PdCl_2(MeCN)_2$ in MeOH in the presence of NaOAc and PPh_3 has been studied. This reaction affords allylic phosphonium compounds for those substrates having more than six carbon atoms between the alkene function and the tertiary amine nitrogen atom. In those cases where the alkene is closer to the NMe_2 unit, this reaction leads, *via* allylic metalation, to intramolecular cyclization that involves generation of a new C–N bond and results in the formation of cationic 5-, 6-, or 7-membered heterocyclic ammonium compounds. For example, $C_6H_4(CH_2CH{=}CH_2)$-1-$(CHMeNMe_2)$-2 can be converted to the *endo*-cyclization product $[C_6H_4\{CH{=}CHCH_2NMe_2CH(Me)\}$-1,2]Cl in 86% yield with this Pd(II)-based system. The cyclization reaction is highly selective and occurs either at the terminal, less substituted olefinic carbon atom (C_γ), affording *endo*-cyclization, or at the allylic C_α carbon atom, resulting in the formation of *exo*-cyclic products. The cyclization reaction is thought to proceed *via* a palladium-assisted C–H activation route: in most cases it was possible to isolate and characterize an η^3-allylpalladium complex as a key intermediate and then allow it to react further with PPh_3 to afford a cyclized end product. The X-ray crystal structures of a palladium–allyl complex, *i.e.*, $\mathbf{2i}_{syn}$, and a quinolinium derivative, **3a**, are described. Crystal data for $\mathbf{2i}_{syn}$: monoclinic, space group $P2_1/c$, with $a = 8.902(1)$, $b = 20.587(1)$, and $c = 9.702(1)$ Å, $\beta = 95.52(1)°$, $Z = 4$, $R = 0.038$. Crystal data for **3a**: monoclinic, space group $P2_1/n$ with $a = 13.032(1)$, $b = 6.544(1)$, and $c = 13.415(1)$ Å, $\beta = 114.72(1)°$, $Z = 4$, $R = 0.042$.

Introduction

The intramolecular amination of olefins mediated by palladium compounds has been extensively investigated by Hegedus and co-workers.[1] They have found that primary and secondary amines form a new C–N bond as a result of nucleophilic addition of the amine to an alkene that is η^2-bonded to a palladium(II) center. After release of one proton, this leads, without any noticeable exceptions, to the formation of neutral heterocycles, wherein the new C–N bond has been formed at the most substituted olefinic carbon center. To the best of our knowledge, the synthetic utility of this selective reaction has not been investigated for related olefins bearing a tertiary amine function, most probably because the expected products would be cationic heterocycles. We have already observed that palladium complexes can indeed mediate intramolecular C–N bond formation between a polysubstituted alkene and a tertiary amine and that this reaction affords cationic heterocycles. These reactions proceed *via* intramolecular nucleophilic addition of the amino unit to an alkene which is η^2-bonded to the palladium center.[2] However, the scope and limitations of this reaction were unknown, and we believed it to be of interest to study a series of substrates which have as a common attribute a terminal olefin separated from a NMe_2 group by hydrocarbon chains with different degrees of flexibility.



1a: y = 0 **1b**: y = 1 **1c**: y = 2 **1d**: y = 3 **1e**: y = 4

1f

1g: y = 0, R = R' = H **1h**: y = 0, R = Me, R' = H **1i**: y = 0, R = H, R' = $SiMe_3$ **1j**: y = 1, R = R' = H **1k**: y = 2, R = R' = H

Figure 1. *o*-Alkenyl(tertiary-aminoalkyl)arenes and ferrocene **1a–k**.

This paper reports on the reactivity of a specific class of such amino olefins, namely 1,2-disubstituted benzenes, in which there is an $(CH_2)_yCH_2CH{=}CH_2$ substituent positioned ortho to either a dimethylamino (NMe_2) or a (dimethylamino)methyl (CH_2NMe_2) function. The allyl and amine functions are thus connected by a carbon skeleton chain containing a rigid C sp^2 – C sp^2 arene linker which favorably orientates them for intramolecular coupling. In order to study the factors which govern the heterocyclization process, we have varied the nature of the N-donor atom, (aryl)N *vs* (benzyl)N, and the mobility of the alkene function by varying the number of CH_2 (spacer) units ($y = 0$–4) between the arene ring and the allyl moiety, see Figure 1.

An understanding of these factors is also timely in view of our ongoing study of heterocyclization reactions of palladium complexes containing ortho-amine-substituted aryl ligands[3a,b] with alkynes;[3c,d] in this system an alkenyl functionality is built up by successive insertion of alkyne molecules into the palladium–aryl carbon bond.[3] Finally, the present results provide an interesting

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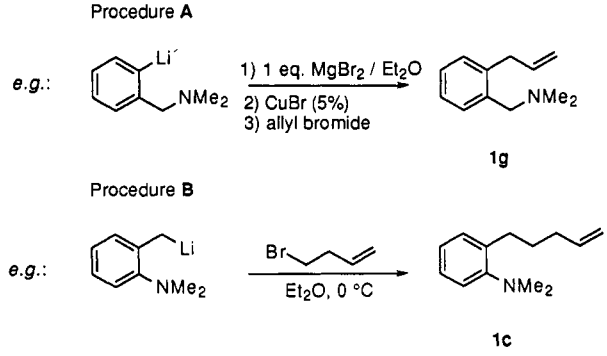
Scheme 1



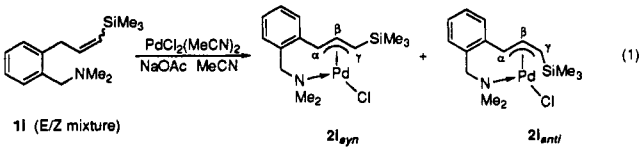
comparison with those obtained previously[1] for the palladium-mediated heterocyclization reaction of related primary and secondary aminoarenes.

Results

***o*-Alkenyl(tertiary-aminoalkyl)arenes.** The general procedure for the synthesis of the *o*-alkenyl(tertiary-aminoalkyl)arenes is based on a C–C coupling reaction of a (tertiary-aminoalkyl)-substituted aryllithium or benzyllithium compound with an alkenyl bromide, either with (procedure A) or without (procedure B) 1 equiv of $MgBr_2$ and a catalytic amount of CuBr. The $MgBr_2$/CuBr-mediated reaction is particularly useful for the coupling of allyl bromide with an aryllithium compound.[4] Both procedures A and B (Scheme 1) afford high yields of the *o*-alkenyl(tertiary-aminoalkyl)arene compounds **1a–k** (see Table 1). The amino olefin substrates **1a–k**, have been reacted with stoichiometric amounts of $PdCl_2(MeCN)_2$. In most cases organic products were formed, sometimes directly and sometimes *via* isolable organopalladium intermediates; in the latter case, depalladation to afford the organic products was induced with additional reagents such as PPh_3.

The most characteristic aspect of the interaction of these alkenyl(tertiary-aminoalkyl)arenes with palladium(II) salts is the intermediacy of an η^3-allylpalladium species. With the substrates based on *N,N*-dimethylanilines **1a–c**, this was indirectly expressed primarily in the organic products produced, but in the other cases, **1d–k**, it was directly evident in the generation of stable, isolable palladium complexes. The nature of these intermediate organometallic species is important in understanding the type of organic products that are finally produced from **1a–k**, so in the following sections we describe the preparation and characterization of these intermediate organopalladium species (and some independently prepared η^3-allylpalladium complexes) and then present the reactions that afford organic compounds.

η^3-Allylpalladium Complexes. The benzylamine substrates **1f–j** are metalated by the palladium(II) salt $PdCl_2(MeCN)_2$ under the correct reaction conditions (in MeCN for substrates **1f,g,i** and in MeOH for **1j,h**) to afford the corresponding stable η^3-allylpalladium compounds **2f–j**,[5a] in which the *o*-alkenyl(tertiary-aminoalkyl)arene substrate is η^1-N,η^3-allyl-bonded to the metal center. These are examples of palladium-mediated C–H activation reactions in which there is abstraction of a proton that is delivered to the basic reaction medium. Complexes **2f–j** could be isolated in good yield (60–93%) and were structurally characterized by ^1H and ^{13}C NMR and, for one isomer of **2i**, also by a single crystal X-ray diffraction study. Complex **2i** obtained from **1i**, which has a terminal CH=CHSiMe$_3$ group, is a mixture of two allylic isomers, $\mathbf{2i}_{syn}$ and $\mathbf{2i}_{anti}$, in a 9:4 ratio (see eq 1)that could be separated by fractional crystallization from diethyl ether



(1)

at −30 °C. The ^1H NMR spectrum of the major isomer is consistent with it having the *syn* conformation ($^3J_{HH}$ = 9.9 and 14.1 Hz) in solution, *i.e.*, it is $\mathbf{2i}_{syn}$. Furthermore, an X-ray crystal structure determination of this isomer showed unambiguously that also in the solid state it has the *syn* conformation. An ORTEP drawing of $\mathbf{2i}_{syn}$, together with the adopted numbering scheme, is presented in Figure 2, and some selected geometric data are given in Table 2.

The molecular structure of $\mathbf{2i}_{syn}$ shows it to be a mononuclear palladium(II) complex in which the ligands are the alkenyl moiety, bonded as an η^3-[Ar-C(1)-C(2)-C(3)-SiMe$_3$] allylic unit, a chlorine atom, and the N-donor atom of the intramolecularly coordinating CH_2NMe_2 fragment. The overall (pseudo-four-coordinate) geometry about the palladium center is like that commonly observed in related allylic (d^8) metal derivatives.[6] In $\mathbf{2i}_{syn}$, the 2-[(dimethylamino)methyl]phenyl and SiMe$_3$ groups occupy *syn* positions, with the N-donor and Cl atoms "trans" to allylic carbons C(1) and C(3), respectively. The phenyl ring makes a dihedral angle with the plane of the allylic unit of 41.9(5)° that helps to reduce the interaction between the aryl ortho proton, H(16), and the central β-allyl proton, H(2), which are separated by 2.58 Å. It is worth mentioning that the closest intramolecular nonbonding separation present is 2.42 Å between the allylic proton H(1) and proton H(4) of the CH_2NMe_2 methylene group.

The second isomer of **2i**, $\mathbf{2i}_{anti}$, differs from $\mathbf{2i}_{syn}$ with respect to the position of the bulky SiMe$_3$ group, which is now *anti*-bonded to the allylic grouping, where it has a sterically unfavorable positioning with respect to the Pd–Cl function. Surprisingly, $\mathbf{2i}_{anti}$ does not isomerize to $\mathbf{2i}_{syn}$ (or *vice versa*) even at elevated temperatures (70 °C in $CDCl_3$), although thermal isomerization of allylic groups with bulky, *anti*-positioned substituents is well documented.[7] This conclusion seems to be corroborated by the fact that for the synthesis of **2i** an *E*/*Z* mixture of 1.6/1.0 molar ratio of **1i** was used, suggesting that $\mathbf{2i}_{anti}$ and $\mathbf{2i}_{syn}$ were formed directly from the respective *Z*- and *E*-isomers of **1i**.

The three complexes **2f–h** are all η^3-allylpalladium species that exist as only one isomer and whose structures in solution were easily determined by ^1H NMR spectroscopy. In these complexes the methyl groups of the NMe_2 unit afford two signals, *i.e.*, they are diastereotopic, and this confirms amine–palladium coordination. From the $^3J_{HH}$ coupling constant values within the allylic fragment, one can conclude that the ferrocenyl group in **2f** and the aryl groups of **2g** and **2h** are in allylic *syn* positions.

The direct palladation of alkenylaminoarene **1j** by $PdCl_2(MeCN)_2$ in MeOH also affords an η^3-allylpalladium intermediate, **2j**, which could be definitively identified in solution by ^1H NMR. Unfortunately, this species was not stable enough to allow its isolation, and its solutions decomposed quickly to metallic palladium and an organic heterocyclic product.

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(5) (a) **2h** was also obtained when **1h** was treated under Hegedus' conditions.[8] (b) *Acta Chem. Scand.* **1984**, *38*, 91.

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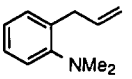
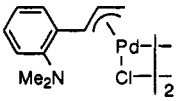
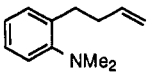
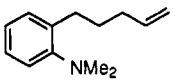
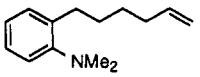
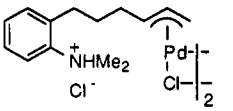
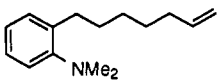
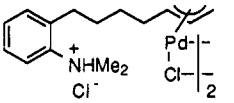
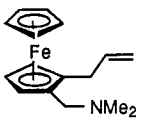
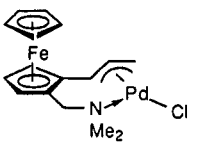
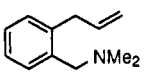
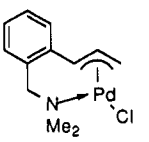
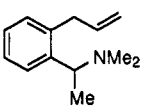
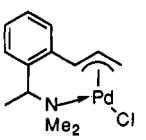
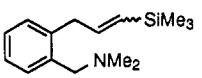
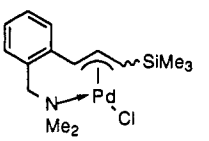
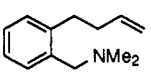
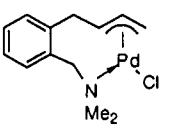
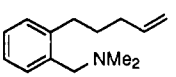
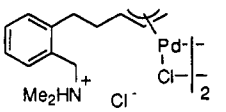
Table 1. Representation of Substrates **1a–k** and their η^3-Allylpalladium Derivatives

entry	substrate	procedure[a]	yield (%)	η^3-allyl Pd derivative	yield (%)[b]
1	**1a** 	A	94	**2a**[c] 	36
2	**1b** 	A	78	not observed	
3	**1c** 	B	62	not observed	
4	**1d** 	B	80	**2d**[d] 	e
5	**1e** 	B	92	**2e**[d] 	e
6	**1f** 	A	58	**2f** 	93
7	**1g** 	A	84	**2g** 	62
8	**1h** 	A	72	**2h** 	68
9	**1i** 	A[f]	78	**2i** 	52
10	**1j** 	A	90	**2j**[g] 	g
11	**1k** 	B	82	**2k**[d] 	e

[a] Procedure A (Scheme 1): aryl Li derivative, $MgBr_2$, CuBr (5%), allyl bromide. Procedure B: benzyl Li derivative, alkenyl bromide. [b] Yields refer to isolated, analytically pure product. [c] Obtained from the reaction of the allyl Li derivative with $PdCl_2(SMe_2)_2$. [d] Obtained when the reaction with $PdCl_2(MeCN)_2$ is performed in CH_2Cl_2. [e] Could not be isolated as a single compound. [f] *E*:*Z* ratio is 1.6:1. [g] Not isolated due to its instability in solution.

Compared to **1f–j**, the substrates **1d**, **1e**, and **1k** have longer aliphatic chains ($y = 3$ or 4), and this leads to a dramatic change in their behavior with a palladium(II) salt. Their reactions with $PdCl_2(MeCN)_2$ in MeOH with NaOAc at room temperature, instead of forming an η^3-allylpalladium complex, invariably produced metallic palladium and a very complex mixture of organic compounds. (Unfortunately we have been unable to separate and characterize these products.) However, the same

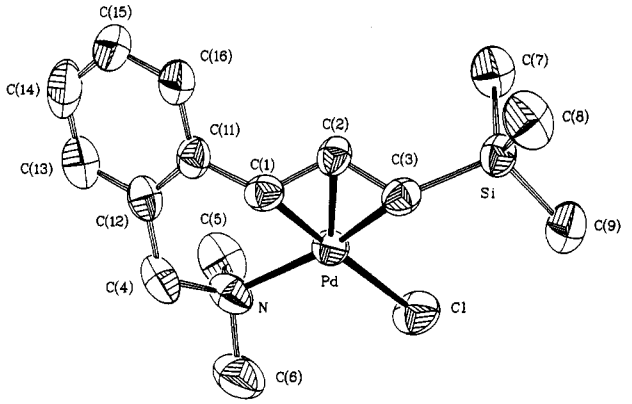


Figure 2. ORTEP drawing of $\mathbf{2i}_{syn}$ and adopted numbering scheme, with thermal ellopsoids drawn at the 50% probability level.

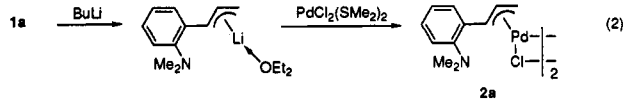
Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex $\mathbf{2i}_{syn}$

Pd–C(1)	2.086(4)	Pd–Cl	2.372(1)	C(2)–C(3)	1.403(6)
Pd–C(2)	2.114(4)	Pd–N	2.171(4)	C(1)–C(11)	1.482(6)
Pd–C(3)	2.183(5)	C(1)–C(2)	1.404(6)	C(3)–Si	1.872(4)
C(11)–C(1)–C(2)		121.9(4)	C(1)–Pd–Cl		172.6(1)
C(2)–C(3)–Si		123.8(4)	C(2)–Pd–Cl		136.9(1)
C(1)–C(2)–C(3)		119.9(4)	C(3)–Pd–Cl		104.3(1)
N–Pd–Cl		94.07(11)	C(1)–Pd–N		91.8(2)
C(1)–Pd–C(2)		39.0(2)	C(2)–Pd–N		127.2(2)
C(1)–Pd–C(3)		69.3(2)	C(3)–Pd–N		160.1(2)
C(2)–Pd–C(3)		38.1(2)			

reaction of **1d**, **1e** and **1k**, when performed under different conditions, *i.e.*, at 0 °C and in CH_2Cl_2, afforded a Bordeaux-red colored solution and no metallic palladium. Increasing the temperature to 20 °C now resulted in the precipitation of brownish powders whose formation was not influenced by the addition of bases such as NEt_3 or 2,6-di(*tert*-butyl)pyridine. Although unambiguous characterization of these powders has been hindered by their low solubility in common NMR solvents and irreproducible elemental microanalyses, we do have some data which point to them being primarily η^3-allylpalladium species (**2d**, **2e**, or **2k**) with chloride-bridged, dimeric structures. Firstly, addition of pyridine (4 equiv per palladium) to a slurry of these powders in $CDCl_3$ gave solutions whose ^1H NMR spectra showed an ammonium proton (singlet at 11.5 ppm) and further resonances characteristic for the free alkenylaminoarene (**1d**, **1e**, or **1k**) and for the corresponding η^3-allyl species (**2d**, **2e**, or **2k**) in a *ca.* 1:4 molar ratio. Futhermore, infrared spectra all show an intense absorption band at *ca.* 2900–3000 cm^{-1}, which is characteristic for a protonated dimethylamine unit, *i.e.*, in complexes **2d**, **2e**, and **2k**, intramolecular coordination of the nitrogen to the palladium is being blocked as a result of protonation of the amino group.

The reaction of aniline derivatives **1a–c** with $PdCl_2(MeCN)_2$ in the presence of sodium acetate in MeOH or MeCN affords metallic palladium and a single organic heterocycle (see below). The organopalladium intermediates for **1a** and **1c** are transient species that could not be isolated. With **1b**, however, the first step is the formation of an insoluble yellow complex which, when isolated and treated with pyridine, gave instantaneously and quantitatively $PdCl_2(Py)_2$ (Py = pyridine) and free alkenylaminoarene **1b**. This insoluble intermediate is probably an adduct [$PdCl_2$(**1b**)], which is the expected precursor to an η^3-allylpalladium species.

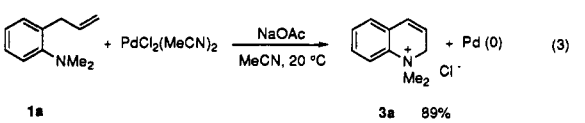
Because of the above evidence for the formation of η^3-allylpalladium species from substrates **1d–k**, we believed it to be important to discover whether analogous species derived from **1a–c** were indeed accessible. To this end, amino olefin **1a** was deprotonated with butyllithium to afford an allyllithium derivative, and this was found to transmetalate with $PdCl_2(SMe_2)_2$ to give a stable dimeric η^3-allylpalladium complex, **2a** (see eq 2). For



(2)

this complex, the $^3J_{HH}$ coupling constant values within the allylic fragment indicate that the aryl group is bonded in a *syn* position. No spectroscopic evidence was found for amine–palladium coordination; for example, the methyl groups of the NMe_2 unit appear as one singlet in the ^1H NMR spectrum, even at temperatures as low as –80 °C. We therefore conclude that, in contrast to the mononuclear η^3-allylpalladium complexes **2f–i**, complex **2a** has a chloride-bridged dimeric structure. For comparative purposes, this indirect lithiation route was also applied to substrate **1i**. This afforded the mononuclear complex **2i** (as a mixture of the isomers $\mathbf{2i}_{syn}$ and $\mathbf{2i}_{anti}$) identical to that obtained by the direct palladium route described above (eq 1).

Formation of Heterocyclic Products. When the amino olefin substrates **1a–c** and 1 equiv of $PdCl_2(MeCN)_2$ were reacted (in MeOH or MeCN) in the presence of sodium acetate, see Experimental Section, a heterocyclization reaction occurred and metallic palladium was formed.[8] A summary of these reactions is given in Table 3. Specifically, for aniline derivative **1a** this reaction gave high yields of 2*H*-*N*,*N*-dimethylquinolinium chloride, **3a** (see eq 3). The structure of this heterocylic product was

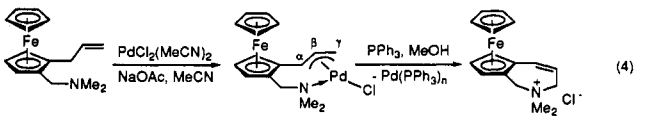


(3)

deduced from analytical and spectroscopic data and was unambiguously established in the solid state by an X-ray diffraction study. An ORTEP drawing of the organic cation and the adopted numbering scheme is presented in Figure 3, and some selected geometric data are given in Table 4.

When the amino olefin substrate is an aniline with longer olefinic chains, **1b** (y = 1) and **1c** (y = 2), the reaction with $PdCl_2(MeCN)_2$ as described above for **1a** gave high yields of an indolinium derivative **3b** (72%) and a quinolinium derivative **3c** (72%), respectively. With **1b** the reaction affording **3b** required about 4 days to reach completion and as such is significantly slower than the reactions of **1a** or **1c** that are complete within a matter of hours. The slow conversion of **1b** into **3b** is probably due to the formation of an adduct between **1b** and $PdCl_2$ that is insoluble in the reaction mixture (*vide supra*). The cyclization of amino olefin substrates based on *N*,*N*-dimethylbenzylamine, **1g** (y = 0) and **1j** (y = 1) to afford six- and seven-membered nitrogen heterocycles, **3g** and **3j**, respectively (see Table 3, entries 7 and 10) was readily achieved under similar conditions to those described for **1a**. However, the yields of **3g** and **3j** from these reactions could be considerably improved by adding triphenylphosphine to the reaction mixture after 2 h of reaction time.

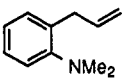
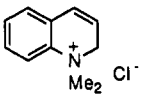
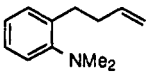
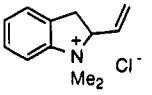
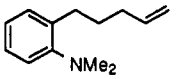
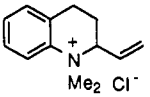
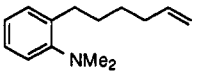
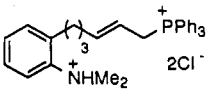
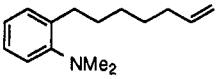
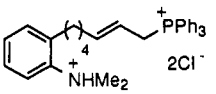
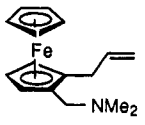
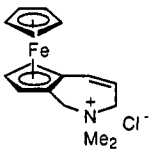
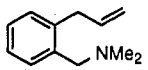
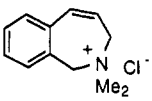
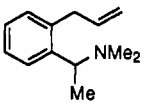
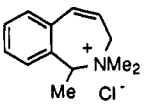
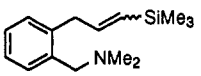
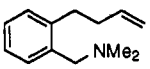
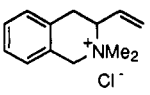
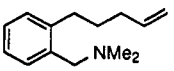
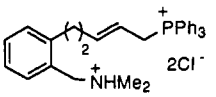
The stable η^3-allylpalladium complexes **2f–h**, isolated from the reactions of **1f–h** with $PdCl_2(MeCN)_2$, can be quantitatively depalladated in MeOH by the addition of PPh_3 (eq 4). This new



(4)

methodology for the removal of palladium from the product of palladium-mediated coupling reactions[2c,9] affords insoluble Pd-$(PPh_3)_n$ and the seven-membered heterocycles **3f–h**, respectively. Under the same conditions, addition of PPh_3 to η^3-allylpalladium

Table 3. Representation of Organic Products

entry	substrate	PPh_3[a]	organic product	yield (%)[b]
1	**1a** 	no	**3a** 	89[c]
2	**1b** 	no	**3b** 	72[c,d]
3	**1c** 	no	**3c** 	72[c]
4	**1d** 	yes[e]	**4d** 	32[c]
5	**1e** 	yes[e]	**4e** 	30[c]
6	**1f** 	yes[e]	**3f** 	98
7	**1g** 	yes	**3g** 	79
8	**1h** 	yes[e]	**3h** 	86
9	**1i** 	yes[f]		
10	**1j** 	yes	**3j** 	90[c]
11	**1k** 	yes[e]	**4k** 	35[c]

[a] Added to induce or accelerate the depalladation process. [b] Yield of the analytically pure product. [c] Yield related to the aminoalkenylarene. [d] After 4 days reaction time. [e] The η^3-allyl Pd complex was used as starting material. [f] In the presence of PPh_3 in MeOH decomposition occurs; no identifiable organic products observed.

complex **2a**, synthesized *via* the butyllithium route, led to quantitative formation of the quinolinium derivative **3a**. However, this procedure was unsuccessful for the depalladation of **2i**.

(8) When **1a** was treated under the reaction conditions used by Hegedus *et al.* (*i.e.*, $PdCl_2(MeCN)_2$ in THF with NEt_3 as base) for the corresponding primary or secondary 2-allylaniline derivatives, it afforded an insoluble material which proved to be an adduct of **1a** and Pd(II) (see the reaction of **1b** with Pd(II)).

Formation of Phosphonium Products. In order to study whether the cyclization procedure could also be applied for the synthesis of medium ring-size heterocycles (containing 8–10 ring atoms), we also reacted the organopalladium complexes obtained from the amino olefin substrates **1d**, **1e**, and **1k** with PPh_3. However,

(9) Pfeffer, M.; Sutter, J.-P.; Rotteveel, M. A.; De Cian, A.; Fischer, J. *Tetrahedron* **1992**, *48*, 2427.

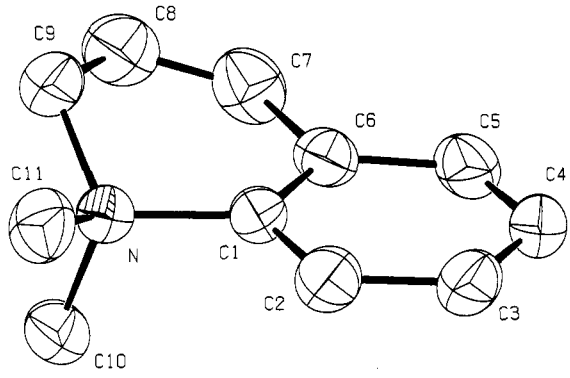
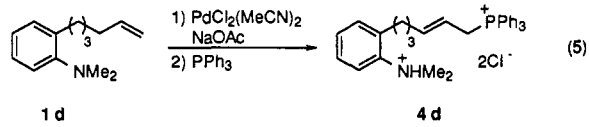


Figure 3. ORTEP drawing of the cation (chloride anion not shown) **3a** and adopted numbering scheme, with thermal ellipsoids drawn at the 50% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound **3a**

C(6)–C(7)	1.455(3)	C(9)–N	1.518(3)
C(7)–C(8)	1.320(4)	C(10)–N	1.510(3)
C(8)–C(9)	1.476(4)	C(11)–N	1.506(3)
C(1)–N	1.496(3)		
C(1)–N–C(9)	110.39(15)	C(10)–N–C(11)	108.51(17)
N–C(9)–C(8)	112.3(2)	C(9)–C(8)–C(7)	120.2(2)
C(8)–C(7)–C(6)	120.7(2)	C(7)–C(6)–C(1)	120.2(2)
C(9)–N–C(11)	106.74(18)	C(1)–N–C(11)	112.68(18)
C(9)–N–C(10)	110.05(19)	C(1)–N–C(10)	108.44(17)

instead of the desired heterocycles, the corresponding allylic phosphonium compounds **4d**, **4e**, and **4k** were formed. This is illustrated for the formation of **4d** from **1d** (see eq 5).



(5)

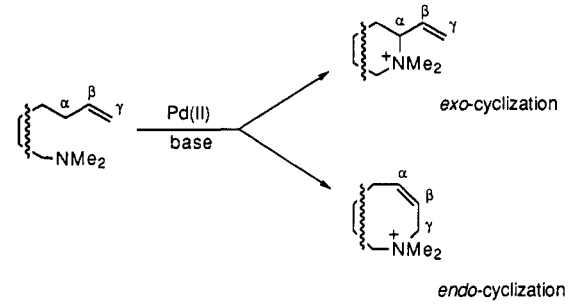
1d **4d**

Discussion

The present results show that controlled intramolecular coupling between an alkene and a tertiary amine can be successfully induced by Pd(II). This reaction, affording cationic heterocycles, has so far clearly escaped general attention, and only a few examples have been reported in the literature.[2a,b,10] In the heterocycles obtained, formation of the new C–N bond has occurred either at the terminal, less substituted, olefinic carbon atom, C_γ (affording **3a**, **3f–h**; *endo*-cyclization), or at the allylic C_α carbon atom (affording **3b**, **3c**, and **3j**; *exo*-cyclization), as summarized in Scheme 2. In none of the reactions studied here is the more substituted olefinic carbon atom, C_β, involved in the coupling reaction, and our results for this cyclization reaction point to a palladium-assisted C–H activation route. This contrasts with the results obtained for the related palladium-mediated cyclization reactions of alkenes that have primary or secondary amine substituents.[1] For the latter reactions, the operative mechanism invoked involves direct C–N bond formation by nucleophilic addition of the primary or secondary amine to the alkene which is η^2-bonded to, and activated by, the palladium atom. This type of addition is also possible with tertiary amines; earlier we demonstrated in an organopalladium compound intramolecular addition of a NMe_2 unit to an η^2-bonded alkene that lacked allylic protons.[2] Intermolecular aminopalladium of alkenes by amines has been shown to be a reversible process with the reverse reaction increasingly faster in the series primary < secondary[5b] < tertiary amine. Thus, the reversible attack of the tertiary amine on the alkene η^2-coordinated to Pd should be nonproductive in the aminopalladation process. The C–H activation step, which is likely to be mediated by the presence of the intramolecular NMe_2 group, should then lead to the irreversible formation of the π-allylpalladium complexes (see below) from which the C–N bond formation can take place.

For our reaction, crucial evidence regarding the C–H activation reaction pathway comes from the nature of isolated, stable, η^3-allylpalladium complexes (**2f–i**) which were shown to be true reaction intermediates, since depalladation, induced with PPh_3, leads to heterocyclic products. Even in reactions, such as with substrate **1a**, where an organometallic intermediate could not be isolated directly, *i.e.*, where it was probably a transient species, supporting evidence for the formation of such a species has been obtained by indirect synthesis. Thus, η^3-allylpalladium complex **2a**, synthesized *via* a transmetalation route, could be depalladated by PPh_3 to afford the heterocycle **3a**, which is identical to that resulting from the reaction of substrate **1a** with $PdCl_2(MeCN)_2$ in the presence of NaOAc (see Scheme 2).

Scheme 2



The general feature of the reactions of aminoalkenes **1a–k** with a palladium(II) salt is that when a terminal olefinic unit is present, one invariably finds C–H activation at the C_α–allylic position leading to an η^3-allylpalladium complex. This process, which follows after η^1-N,η^2-alkene coordination to the metal, may be related to the well-established synthesis of η^3-allylpalladium complexes from alkyl-substituted alkenes and palladium(II).[7e] Recently we reported a related formation of η^1-*N*,η^3-allylpalladium complexes starting with compounds bearing an intramolecular η^1-*N*,η^2-alkene coordination to palladium by metal insertion into a C–H allylic bond.[6b] The stability of the formed complexes seems to depend on the nonnucleophilicity of the NMe_2 group, and isolation or observation of these intermediates could be achieved only when either N–Pd coordination (*i.e.*, **2f–j**) or N-protonation occurred (*i.e.*, **2d,e,k**).

In our study, from both the nature of the heterocycles formed and the structure of the organopalladium intermediates, we can deduce that the C–N bond-forming step in the heterocyclization reactions most probably involves an intramolecular nucleophilic addition of the noncoordinated tertiary amine function on a palladium-bonded η^3-allyl unit.[11] This process will depend on the nature of the η^3-allyl, N-chelate ring. The intermediates with the stereochemically more favorable chelate rings (*i.e.*, **2f–i**), for which the Pd–N dissociation process is more difficult, require added phosphine for heterocyclization. For the stereochemically more strained chelate rings, the distance between the η^3-allyl Pd and N is too short or the N–Pd interaction too weak (*i.e.*, **2a–c**); Pd–N coordination is thus unfavorable and results in a rapid intramolecular nucleophilic addition of the noncoordinated NMe_2 grouping onto the η^3-allyl moiety. This also underlines the role of PPh_3 in these reactions, since added phosphine displaces by substitution the coordinated tertiary amine

(10) Barelle, M.; Apparu, M. *Tetrahedron* **1977**, *33*, 1309.

(11) (a) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 799–938. (b) Trost, B. M. *Angew. Chem.* **1989**, *101*, 1199; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173.

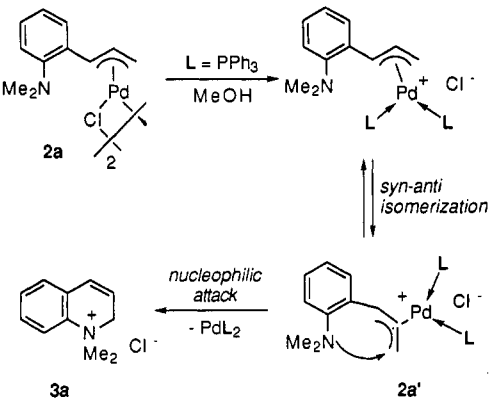
grouping from the palladium center and so generates the tertiary alkylamine nucleophile (see Scheme 3).

In all of the observed intermediates, the thermodynamically more stable *syn* conformation of the η^3-allyl unit was found. However, in **3a**, as well as in the seven-membered ring compounds **3f–h**, the geometry of the endocyclic C=C bond is always *cis*. To rationalize this, it is necessary to assume that the η^3-allyl unit of the intermediate organopalladium precursor undergoes *syn–anti* isomerization prior to the C–N bond formation step.[7] An illustration of the likely reaction pathway including this isomerization step, based on the formation of **3a** from **2a**, is presented in Scheme 3.

***Endo-* versus *exo*-Cyclization.** The carbon–nitrogen coupling reaction we have studied is of a rare type for which only a few examples have been previously reported,[9] and various factors relating to the chemo- and regioselectivity are worth comment. Firstly, the palladium-mediated functionalization of the terminal alkene in the substrates **1a–k** exhibits a high degree of chemoselectivity, and in each case only one substrate-specific organic product is obtained. One sees in those cases where heterocyclic products are formed (**3a–c**, **3f–h**, and **3j**) that these are the result of coupling of the NMe_2 group with either C_α or C_γ of the palladium-bonded η^3-allyl unit, *i.e.*, *exo*- or *endo*-cyclization. Here the regioselectivity is also remarkably high, since for a given alkenylaminoarene substrate only one of the two possible heterocyclic rings is produced, and the origin for this specificity appears to lie in the steric bulk of the substituents of the allyl unit. Thus, exo cyclic C–N coupling does not take place when the C_α carbon atom carries bulky phenyl or ferrocenyl groups; in these cases the formation of the larger heterocyclic ring is preferred, and the products (**3a**, **3f–h**) are six- or seven-membered heterocycles with an endocyclic alkenyl unit. The results obtained with the particular substrate **1i** that carries a terminal $SiMe_3$ substituent further serve to stress the importance of steric bulk in these reactions. Here the palladium-bonded η^3-allyl complex, in which both C_α and C_γ are substituted by bulky groups (an aryl and a $SiMe_3$ group, respectively), is very stable, and depalladation of this complex to afford organic products could not be induced with PPh_3. It is worth noting that the regioselectivity in these intramolecular *endo*-cyclizations is like that usually found in intermolecular nucleophilic addition reactions on palladium-bonded allyl units.[12] Our other examples of C–N bond formation all involve addition of the tertiary amine function at C_α and produce five- or six-membered heterocyclic rings bearing an exocyclic olefin unit. Finally, it has to be noted that in the PPh_3-induced cyclization reaction, $Pd^0(PPh_3)_n$ is formed. Recently, Pfeffer *et al.* established that the reaction of the next higher homologue of **1f** (having one extra CH_2 grouping separating the Cp ring and the allyl fragment) with PPh_3 in MeOH produces a 1:2 mixture of the *exo*- and *endo*-cyclized products. In the presence of $Pd^0(PPh_3)_n$ these two heterocycles are in equilibrium, and in acetone this leads to complete isomerization of the endo- into the *exo*-heterocyclic product.[6c] This observation points to the occurrence of Pd^0-catalyzed allylic C–N bond cleavage and to the fact that in the present study *endo-/exo*-product formation takes place under thermodynamic control.[12e]

Limitation to Heterocyclization. One very noticeable difference in reactivity is observed on going from an alkenylaminoarene substrate in which the olefinic bond is three or four carbon atoms away from the amine donor atom to one in which this separation is five or six carbon atoms. In the first case, discussed above, we find heterocyclization reactions; in the second case, *i.e.*, substrates **1d**, **1e**, and **1k**, the formation of analogous larger ring-size heterocycles *via* intramolecular amination does not take place. With these substrates we do find an initial selective reaction with the palladium(II) salt (when CH_2Cl_2 is used as a solvent) that affords CH_2Cl_2-insoluble organopalladium products **2d**, **2e**, and **2k**, which would appear to be η^3-allyl species resulting from a C–H activation reaction. Since palladium at the allyl function occurs irrespective of whether an external base is used or not, we believe that the dimethylamino group in the substrates **1d**, **1e**, and **1k** plays the role of an internal base that can bind HCl, so assisting the C–H activation process. These η^3-allyl complexes thereby contain an ammonium unit ($-NHMe_2^+$) which was not deprotonated by the external base present in the reaction mixture. Without detailed information on the structures of these complexes (*e.g.*, with N–H···Pd or N–H···Cl bridge bonding motives),[13] it is unwise to speculate on the reason for this behavior, but this is a limiting factor for the application of our procedure to the synthesis of larger ring heterocycles.

Scheme 3



However, the complexes (with a tether of five (**2d**, **2e**) or six carbon atoms (**2k**) between the amine and the alkene function) do give rise to selective nucleophilic addition of PPh_3 at C_γ to afford phosphonium derivatives (**4d**, **4e**, and **4k**, respectively). This contrasts with the PPh_3 depalladation reactions that resulted in heterocyclization, where the intermediates have a tether of three or four carbon atoms. The type of addition with phosphines which affords phosphonium species has been reported previously and generally occurs when η^3-allylpalladium complexes are reacted with excess phosphine in the absence of a stronger nucleophile.[7e,14] Accordingly, the behavior of the organopalladium intermediates **2d,e,k** supports the view that the NMe_2 group in these complexes is no longer nucleophilic, *i.e.*, is protonated, and is fully consistent with the presence of a protonated amino group in the resulting organic phosphonium products **4d,e,k**. Further studies to elucidate the anomalous behavior of **1d**, **1e**, and **1k** are in progress.

Conclusions

The reason why in our present system allylic functionalization is preferred with tertiary amine units is still being investigated. Certainly, entropy and a conformational effect (analogous to the *gem*-dimethyl effect)[15] contribute in a positive way to the high chemo- and regioselectivity observed in the present reactions. Also, the stability of intramolecular Pd–N coordination is an important factor. In the case of the palladium complexes with favorable chelate ring stereochemistry, the N atom is blocked for

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intramolecular nucleophilic addition at the allylic function. The stability of that latter η^1-N,η^3-allylpalladium interaction may also be proof that the C–N bond formation results not from a pseudo-reductive elimination process between these two palladium-bound atoms but follows the *trans*-to-palladium addition pathway as expected for the N-nucleophile,[16] the latter process taking place as soon as PPh_3 is added.

The present study demonstrates that intramolecular nucleophilic addition of a tertiary amine to a palladium-bound η^3-allyl unit is possible, and, with aminoalkene substrates, it appears to have synthetic potential for the preparation of heterocyclic ring systems. Recently a catalytic process based on the present findings was developed; see note added in proof.

Experimental Section

General. All reactions were carried out in an atmosphere of dry, deoxygenated nitrogen, using standard Schlenk techniques. All solvents were dried and distilled in a nitrogen atmosphere prior to use. Commercially available reagents were used as supplied (allyl bromide was distilled and dried on 4-Å molecular sieves). Lithium compounds[17,18] and $C_3H_5(Me_3Si)Br$[19] were prepared by standard literature methods. ^1H (300.13 or 200.13 MHz), ^{13}C (75.47 or 50.32 MHz), and ^{31}P (81 MHz) NMR spectra were recorded variously on Bruker AC 300 and AC 200 spectrometers. δ values are given in ppm and J in Hz. Mass spectra were recorded on a Jeol-AX 505w mass spectrometer. Elemental analyses were carried out at the Institute for Applied Chemistry TNO, Zeist, The Netherlands, and the Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim a.d. Ruhr, Germany, as well as at the Service Central de Microanalyses du CNRS, Universit'e Louis Pasteur, Strasbourg, France.

Synthesis of the *o*-Alkenyl[(dimethylamino)alkyl]arenes. Procedure A, *o*-(2-Propenyl)-*N*,*N*-dimethylaniline (1a). A solution of $[LiC_6H_4NMe_2\text{-}2]\cdot 1/2(tmeda)$ (7.87 g, 42.5 mmol) in Et_2O (40 mL) was slowly added to a suspension of anhydrous $MgBr_2$ (7.91 g, 42.9 mmol) in Et_2O (30 mL) at 0 °C. After the mixture was stirred for 30 min, a catalytic amount of CuBr (300 mg) was added, followed by addition of allyl bromide (5.15 g, 42.6 mmol) in *ca.* 10 min. The resulting reaction mixture was stirred at room temperature for 2 h. The solvent was then removed *in vacuo* and the resulting gray residue extracted with pentane (3 × 20 mL). The crude product was obtained after evaporation of the pentane. Further purification by flash distillation *in vacuo* yielded 6.4 g (94%) of pure **1a** as a colorless liquid.

The aminoalkenes **1b** (78%), **1g** (84%), **1h** (72%), **1i** (1.6/1.0 *E*/*Z* mixture, 78%), and **1j** (90%) were obtained as described for **1a**.

A slightly modified procedure was needed for **1f**. An excess of anhydrous $MgBr_2$ (5.50 g, 30 mmol) was added to a stirred suspension of 2-[(dimethylamino)methyl]ferrocenyllithium[18] (4.89 g, 19.6 mmol) in Et_2O at 0 °C. After continuous stirring of the mixture for 10 min, CuBr (150 mg) was added, followed by allyl bromide (2 mL, 23 mmol) in *ca.* 10 min. The reaction mixture was then stirred at room temperature for 1 h. The resulting yellow suspension was hydrolyzed with H_2O (50 mL) and extracted with pentane (2 × 20 mL). The organic layer was dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was chromatographed through an alumina column (activity I) with ethyl acetate as eluent. After removal of the solvent, **1f** (3.28 g, 58%) was obtained as an amber oil.

Procedure B, *o*-(4-Pentenyl)-*N*,*N*-dimethylaniline (1c). 4-Bromo-1-butene (0.8 mL, 8 mmol) in Et_2O (10 mL) was added dropwise to a suspension of $[LiCH_2C_6H_4NMe_2\text{-}2]$ (1.1 g, 7.8 mmol) in Et_2O (30 mL) at 0 °C. The mixture was warmed up to room temperature, stirred for 4 h, hydrolyzed with H_2O (20 mL), and extracted with Et_2O (2 × 20 mL). The combined ether fractions were evaporated to dryness *in vacuo*, yielding NMR-pure **1c** as a yellow oil (0.91 g, 4.8 mmol, 62%).

The aminoalkenes **1d** (80%), **1e** (92%), and **1k** (82%) were obtained as described for **1c**.

^1H NMR ($CDCl_3$) data for the **1** compounds. **1a**: δ 7.28 (m, 2 H, Ar); 7.19 (dd, 1 H, Ar, $^3J_{HH}$ = 7.9 $^5J_{HH}$ = 1.2); 7.11 (dt, 1 H, Ar, $^3J_{HH}$ = 7.3, $^5J_{HH}$ = 1.4); 6.11 (m, 1 H, HC=); 5.20 (m, 2 H, $=CH_2$); 3.62 (d, 2 H, CH_2, $^3J_{HH}$ = 6.5); 2.78 (s, 6 H, NMe_2). **1b**: δ 7.29–7.04 (m, 4 H, Ar); 5.99 (m, 1 H, CH=); 5.11 (m, 2 H, $=CH_2$; 2.86 (m, 2 H, CH_2); 2.74 (s, 6 H, NMe_2); 2.45 (m, 2 H, CH_2). **1c**: δ 7.26–7.02 (m, 4 H, Ar); 5.90 (m, 1 H, CH=); 5.02 (m, 2 H, $=CH_2$; 2.74 (m, 2 H, CH_2Ar); 2.71 (s, 6 H, NMe_2); 2.17 and 1.81 (2m, 4 H, CH_2). **1d**: δ 7.26–6.99 (m, 4 H, Ar); 5.92 (m, 1 H, =CH); 5.04 (m, 2 H, $=CH_2$); 2.74 (m, 2 H, CH_2); 2.71 (s, 6 H, NMe_2); 2.19 and 1.80 (2 m, 4 H, CH_2). **1e**: δ 7.26–6.99 (m, 4 H, Ar); 5.86 (m, 1 H, =CH); 5.88 (m, 2 H, $=CH_2$); 2.73 (m, 2 H, CH_2); 2.70 (s, 6 H, NMe_2); 2.10, 1.68, and 1.47 (3m, 8 H, CH_2). **1f**: δ 6.0 (m, 1 H, HC=); 5.06 (m, 2 H, H_2C=); 4.17 (t, 1 H, C_5H_3, $^3J_{HH}$ = 1.8); 4.04 (s, 7H, $C_5H_5 + C_5H_3$); 3.35 and 3.22 (2d, 2 H, CH_2N, $^2J_{HH}$ = 12.85); 3.10 (m, 2 H, CH_2); 2.10 (s, 6 H, NMe_2). **1g**: δ 7.37–7.22 (m, 4 H, Ar); 6.04 (m, 1 H, =CH); 5.08 (m, 2 H, $=CH_2$); 3.60 (d, 2 H, CH_2, $^3J_{HH}$ = 7.8); 3.45 (s, 2 H, CH_2N); 2.29 (s, 6 H, NMe_2). **1h**: δ 7.45 (d, 1 H, Ar, $^3J_{HH}$ = 8.5); 7.16 (m, 3 H, Ar); 5.95 (m, 1 H, HC=); 5.0 (m, 2 H, H_2C=); 3.45 (m, 3 H, CH_2 + *H*CMe); 2.18 (s, 6 H, NMe_2); 1.27 (d, 3 H, CH_3, $^3J_{HH}$ = 6.6). **1i**: (*E*-isomer) δ 7.25 (m, 4 H, Ar); 6.30 (dt, 1 H, HC=, $^3J_{HH}$ = 18.2); 5.72 (m, 1 H, =CHSi); 3.65 (d, 2 H, CH_2C, $^3J_{HH}$ = 3.0); 3.45 (s, 2 H, CH_2N); 2.30 (s, 6 H, NMe_2); 0.15 (s, 9 H, $SiMe_3$); (*Z*-isomer) δ 7.25 (m, 4 H, Ar); 6.56 (m, 1 H, HC=, $^3J_{HH}$ = 13.8); 5.72 (m, 1 H, =CHSi); 3.75 (d, 2 H, CH_2, $^3J_{HH}$ = 3.7); 2.30 (s, 6 H, NMe_2); 0.27 (s, 9 H, $SiMe_3$). **1j**: δ 7.29–7.15 (m, 4 H, Ar); 5.90 (m, 1 H, HC=); 5.03 (m, 2 H, H_2C=); 3.40 (s, 2 H, CH_2N); 2.80 (m, 2 H, $ArCH_2$); 2.36 (m, 2 H, CH_2); 2.24 (s, 6 H, NMe_2). **1k**: δ 7.32–7.16 (m, 4 H, Ar); 5.90 (m, 1 H, =CH; 5.05 (m, 2 H, $=CH_2$); 3.41 (s, 2 H, CH_2N); 2.75 (m, 2 H, $ArCH_2$); 2.26 (s, 6 H, NMe_2); 2.17, 1.71 (2 m, 4 H, CH_2).

^{13}C NMR ($CDCl_3$) data for the **1** compounds. **1a**: δ 152.6, 134.5, 130.2, 126.8, 123.1, 119.2 (Ar); 137.9, 115.5 (C=); 45.0 (NMe_2); 35.0 (CH_2). **1b**: δ 152.9, 136.8, 129.5, 126.7, 123.4, 119.6 (Ar); 138.9, 114.5 (C=); 45.3 (NMe_2); 34.6, 30.3 (CH_2). **1c**: δ 152.8, 137.3, 129.6, 126.4, 123.3, 119.4 (Ar); 138.9, 114.4 (C=); 45.1 (NMe_2); 33.9, 30.2, 29.9 (CH_2). **1d**: δ 152.9, 137.6, 129.6, 126.5, 123.4, 119.5 (Ar); 139.1, 114.4 (C=); 45.3 (NMe_2); 33.8, 30.5, 30.2, 29.1 (CH_2). **1e**: δ 152.9, 137.7, 129.6, 126.4, 123.4, 119.5 (Ar); 139.2, 114.3 (C=); 45.3 (NMe_2); 33.9, 30.7, 30.6, 29.4, 29.0 (CH_2). **1f**: δ 137.2, 115.4 (C=); 86.8, 82.3 (C_5H_3); 68.9 (C_5H_5); 69.9, 68.0, 66.0 (3 CH, C_5H_3); 57.4 (CH_2N); 45.2 (NMe_2); 32.2 (CH_2). **1g**: δ 138.7, 137.0, 130.1, 129.5, 127.2, 125.9 (Ar); 137.4, 115.3 (C=); 61.7 (CH_2N); 45.4 (NMe_2); 36.7 (CH_2). **1j**: δ 141.0, 136.7, 130.2, 129.3, 127.1, 125.7 (Ar); 138.5, 114.7 (C=); 61.7 (CH_2N); 45.6 (NMe_2); 35.3, 31.9 (CH_2). **1k**: δ 141.7, 136.8, 130.3, 129.4, 127.2, 125.7 (Ar); 138.8, 114.8 (C=); 61.9 (CH_2N); 45.6 (NMe_2); 33.9, 32.0, 30.6 (CH_2).

Synthesis of the η^3-Allylpalladium Complexes. $[PdCl\text{-}syn\text{-}\eta^3\text{-}\{C_3H_4\text{-}2\text{-}(\alpha\text{-}C_6H_4NMe_2)\}]_2$ (2a). A 1.5 M solution of *n*-BuLi (9.0 mL, 13.5 mmol) in hexane was added to a solution of **1a** (2.2 g, 13.6 mmol) in Et_2O (25 mL). The reaction mixture was heated at reflux for 2 h and stirred overnight at room temperature. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a yellow solid. This solid was recrystallized at −30 °C from a saturated Et_2O solution to give $Li\{C_3H_4\text{-}2\text{-}(\alpha\text{-}C_6H_4NMe_2)\}$ as its etherate complex (2.6 g, 79%). ^1H NMR (C_6D_6): δ 7.4–6.7 (m, 4 H, Ar); 6.6 (m, 1 H, HC=); 4.5–3.3 (br s, 3 H); 3.2 (q, 4 H, OCH_2); 2.3 (s, 6 H, NMe_2); 1.05 (t, 6 H, CH_3). A water quench of $Li\{C_3H_4\text{-}2\text{-}(\alpha\text{-}C_6H_4NMe_2)\}$ yields *o*-(1-propenyl)-*N*,*N*-dimethylaniline and *o*-(2-propenyl)-*N*,*N*-dimethylaniline in a 1:3 ratio.

A solution of $Li\{C_3H_4\text{-}2\text{-}(\alpha\text{-}C_6H_4NMe_2)\}(OEt)$ (0.23 g, 0.95 mmol) in Et_2O (25 mL) was added dropwise to a suspension of $PdCl_2(MeCN)_2$ (0.29 g, 0.96 mmol) in Et_2O (50 mL). The reaction mixture was filtered through a Celite column (2 cm) after 2 h of reflux. The solvent was removed *in vacuo*, and the residue was dissolved in $CHCl_3$ (3 mL). Complex **2a** was obtained as orange crystals by slow distillation of pentane into this solution (yield 36%). ^1H NMR ($CDCl_3$): δ 7.49 (d, 1 H, Ar, $^3J_{HH}$ = 7.8); 7.32 (m, 1 H, Ar); 7.08 (m, 2 H, Ar); 5.72 (m, 1 H, HC_β); 5.03 (d, 1 H, HC_α, $^3J_{HH}$ = 11.0); 3.97 (dd, 1 H, $C_\gamma H_{syn}$, $^2J_{HH}$ = 1.1, $^3J_{HH}$ = 5.5); 3.0 (d, 1 H, $C_\gamma H_{anti}$, $^3J_{HH}$ = 11.8); 2.85 (s, 6 H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 132.5, 129.0, 127.8, 125.5, 120.2 (Ar); 108.0 (C_β); 82.0 (C_α); 57.0 (C_γ); 47.0 (NMe_2).

$[PdCl\text{-}\eta^3\text{-}\{C_6H_{10}\text{-}2\text{-}(C_6H_4NMe_2HCl)\}]_2$ (2d). A solution of **1d** (1.05 g, 5.17 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a suspension of $PdCl_2(MeCN)_2$ (1.35 g, 5.20 mmol) in CH_2Cl_2 (30 mL) at 0 °C, and after a few minutes a clear Bordeaux-red solution was obtained. This solution was stirred for 1 h at 0 °C, warmed up to room temperature, and stirred for an additional hour, yielding a precipitate (1.09 g) which was separated from the solution by filtration and dried *in vitro*. ^1H

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NMR ($CDCl_3$ + Py-d_5): δ 7.10 (m, 4 H, Ar); 5.41 (dt, 1 H, C_β, $^3J_{HH}$ = 11.16, $^3J_{HH}$ = 6.8); 3.90 (m, 1 H, C_αH); 3.82 (d, 1 H, $C_\gamma H_2$); 2.94 (d, 1 H, $C_\gamma H_2$); 2.78 (m, 2 H, $ArCH_2$); 2.69 (s, 6 H, NMe_2); 1.86 (m, 4 H, $2CH_2$). ^{13}C NMR ($CDCl_3$ + Py-d_5): δ 136.6, 129.6, 126.6, 123.6, 119.4 (Ar); 113.0 (C_β); 82.5 (C_α); 58.0 (C_γ); 45.3 (s, 2 C, NMe_2); 32.1, 30.3, 30.0 (3 C, CH_2). IR (KBr): 3061 cm^{-1} (NMe_2H^+).

[PdCl-η³-{C_7H_{12}-2-($C_6H_4NMe_2HCl$)}]₂ (2e). This compound was prepared *via* a similar procedure to that described for **2d**, starting from **1e** (1.04 g) and yielding **2e** (0.98g). ^1H NMR ($CDCl_3$ + Py-d_5): δ 9.55 (br s, $^+HNMe_2$); 7.18 (m, 4 H, Ar); 5.37 (dt, 1 H, C_βH, $^3J_{HH}$ = 11.6, $^3J_{HH}$ = 6.9); 3.81 (m, 1 H, C_α); 3.76 (d, 1 H, $C_\gamma H_2$); 2.91–2.84 (m, 9 H, C_γ, CH_2, NMe_2); 2.00–1.50 (m, 6 H, CH_2). ^{13}C NMR ($CDCl_3$ + Py-d_5): δ 136.7, 130.4, 127.0, 125.6, 119.5 (Ar); 112.9 (C_β); 82.5 (C_α); 58.1 (C_γ); 46.0 (2 C, NMe_2); 32.0, 30.6, 30.5, 29.3 (4 C, CH_2). IR (KBr): 3061 cm^{-1} (NMe_2H^+).

[PdCl-*syn*-η³-{C_3H_4-2-($C_5H_5FeC_5H_3CH_2NMe_2$)}] (2f). A solution of **1f** (1.2 g, 4.3 mmol) in MeCN (5 mL) was added dropwise to a suspension of $PdCl_2(MeCN)_2$ (1.12 g, 4.3 mmol) in MeCN (20 mL), followed by sodium acetate (0.37 g, 4.5 mmol). The reaction mixture was stirred for 2 h. The solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2 (3 × 10 mL). The combined solutions were concentrated, and **2f** (1.69 g, 93%) was precipitated as a yellow solid by addition of pentane. ^1H NMR ($CDCl_3$): δ 5.45 (m, 1 H, HC_β); 4.58 (d, 1 H, HC_α, $^3J_{HH}$ = 10.6); 4.32, 4.19, 4.10 (3m, 3 H, C_5H_3); 4.14 (s, 5 H, C_5H_5); 3.93 (d, 1 H, $C_\gamma H_{syn}$, $^3J_{HH}$ = 7.04); 2.99 (d, 1 H, $C_\gamma H_{anti}$, $^3J_{HH}$ = 12.30); 3.93, 2.83 (2d, 2 H, CH_2N, $^2J_{HH}$ = 12.47); 2.96, 2.02 (2s, 6 H, NMe_2). Anal. Calcd for $C_{16}H_{20}ClFeNPd$: C, 45.31; H, 4.72; N, 3.30. Found: C, 45.14; H, 4.79; N, 3.36.

[PdCl-*syn*-η³-{C_3H_4-2-($C_6H_4CH_2NMe_2$)}] (2g): This complex was prepared *via* a procedure similar to that described for **2f**. Recrystallization from a $CHCl_3$–pentane solution gave **2g** (62%) as colorless crystals. ^1H NMR ($CDCl_3$): δ 7.40 (m, 4 H, Ar); 5.62 (m, 1 H, HC_β); 4.66 (d, 1 H, HC_α, $^3J_{HH}$ = 10.4); 4.15 (d, 1 H, $C_\gamma H_{syn}$, $^3J_{HH}$ = 7.1); 4.06 (d, 1 H, CH_2N, $^2J_{HH}$ = 12.0); 3.23 (d, 2 H, CH_2N + $C_\gamma H_{anti}$, J_{obsd} = 12.0); 3.09 and 2.11 (2 s, 6 H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 137.8, 136.6, 130.8, 129.9, 128.0, and 126.3 (Ar); 114.9 (C_β); 76.7 (C_α); 68.1 (C_γ); 59.8, 51.4 (NMe_2); 46.2 (CH_2N). Anal. Calcd for $C_{12}H_{16}ClNPd$: C, 45.59; H, 5.10; N, 4.43. Found: C, 45.27; H, 5.11; N, 4.42.

[PdCl-*syn*-η³-{C_3H_4-2-($C_6H_4CH(Me)NMe_2$)}] (2h). This complex was prepared *via* a procedure similar to that described for **2f**. Reaction of **1h** (0.95 g, 5 mmol) with $PdCl_2(MeCN)_2$ (1.3 g, 5 mmol) and sodium acetate (0.41 g, 5 mmol) in MeOH yielded **2h** as a yellow solid (1.12 g, 68%). ^1H NMR ($CDCl_3$): δ 7.5–7.1 (m, 4 H, ArH); 5.50 (m, 1 H, HC_β); 4.70 (d, 1 H, HC_α, $^3J_{HH}$ = 10.3); 4.11 (d, 1 H, $C_\gamma H_{syn}$, $^3J_{HH}$ = 7.0); 3.31 (q, 1 H, MeC*H*); 3.17 (d, 1 H, $C_\gamma H_{anti}$, $^3J_{HH}$ = 12.4); 2.96, 2.05 (2 s, 6 H, NMe_2); 1.65 (d, 3 H, HC*Me*). ^{13}C NMR ($CDCl_3$): δ 142.6–127.8 (Ar); 112.9 (C_β); 76.1 (C_α); 72.3 (*C*HMe); 59.7 (C_γ); 49.1, 48.2 (2 s, NMe_2); 20.0 (Me). Anal. Calcd for $C_{13}H_{18}ClNPd$: C, 47.29; H, 5.50; N, 4.24. Found: C, 47.18; H, 5.59; N, 4.28.

[PdCl-η³-{C_3H_3-γ-$SiMe_3$-(α-$C_6H_4CH_2NMe_2$-2)}] ($2i_{syn}$) and ($2i_{anti}$).

(i) Via Transmetalation Reaction. A solution of Li{C_3H_3-γ-$SiMe_3$-(α-$C_6H_4CH_2NMe_2$-2)} (prepared as described for Li{C_3H_4-2-(α-C_6H_4-NMe_2)}(OEt_2), *vide supra*) (0.71 g, 2.8 mmol) in Et_2O (20 ml) was added dropwise to a suspension of $PdCl_2(SMe_2)_2$ in Et_2O (40 mL). The reaction mixture was stirred overnight. After centrifugation, the orange supernatant was separated from the black precipitate and concentrated *in vacuo* to a volume of *ca.* 10 mL. Fractional crystallization gave 0.34 g (0.87 mmol) of the *syn*-trimethylsilyl isomer ($2i_{syn}$) and 0.23 g (0.58 mmol) of the *anti*-trimethylsilyl isomer ($2i_{anti}$) (total yield, 52%).

(ii) Via Direct Palladation Reaction. The reaction procedure is the same as that described earlier for the synthesis of **2f**. Complex **2i** was formed as a mixture of the *syn* and *anti* isomers in a ratio of 4.5:2 and in a total yield of 75%. *Syn*-trimethylsilyl isomer ($2i_{syn}$). ^1H NMR ($CDCl_3$): δ 7.57–7.21 (m, 4 H, Ar); 5.55–5.42 (m, 1 H, HC_β); 4.59 (d, 1 H, C_αH, $^3J_{HH}$ = 9.9); 4.01 and 3.22 (2d, 2 H, CH_2N); 3.25 (d, 1 H, $C_\gamma H_{anti}$, $^3J_{HH}$ = 14.1); 3.10, 2.13 (2s, 6 H, NMe_2); 0.26 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 138.3–126.2 (Ar); 117.9 (C_β); 77.7 (C_α); 73.0 (CH_2N); 68.1 (C_γ); 51.6, 46.2 (2 s, NMe_2); –0.8 ($SiMe_3$). *Anti*-trimethylsilyl isomer ($2i_{anti}$). ^1H NMR ($CDCl_3$): δ 7.52–7.23 (m, 4 H, Ar); 5.95 (m, 1 H, HC_β); 4.65 (d, 1 H, C_αH, $^3J_{HH}$ = 10.6); 4.03 (d, 1 H, $C_\gamma H_{syn}$, $^3J_{HH}$ = 9.8); 3.98, 3.23 (2d, 2 H, CH_2N); 3.09, 2.12 (2s, 6 H, NMe_2); 0.29 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 138.4–126.0 (Ar); 120.6 (C_β); 75.5 (C_α); 73.3 (CH_2N); 68.1 (C_γ); 51.4, 46.1 (2s, NMe_2); 1.7 ($SiMe_3$).

[PdCl-η³-{C_5H_8-2-($C_6H_4CH_2NMe_2HCl$)}]₂ (2k). This compound was prepared *via* a procedure similar to that described for **2d**. Starting with **1k** (0.90 g, 3.47 mmol) yielded 0.89 g of a precipitate which could be assigned as **2k**. ^1H NMR ($CDCl_3$ + Py-d_5): δ 10.75 (br s, 1 H, NH^+); 8.00–7.16 (m, 4 H, Ar); 5.55 (dt, 1 H, HC_β, $^3J_{HH}$ = 11.7, $^3J_{HH}$ = 6.9); 4.57, 4.47 (2d, 2 H, CH_2N, $^2J_{HH}$ = 13.3); 3.83 (m, 1 H, C_αH); 3.78 (d, 1 H, $C_\gamma H_2$); 3.28 (td, 1 H, $ArCH_2$, $^3J_{HH}$ = 12.7, $^2J_{HH}$ = 5.3); 3.00 (m, 1 H, CH_2); 2.94 (d, 1 H, $C_\gamma H_2$); 2.83 (s, 6 H, NMe_2); 1.89 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$ + Py-d_5): δ 141.1, 131.5, 130.1, 129.6, 128.2, 127.1 (Ar); 111.6 (C_β); 80.1 (C_α); 59.7, 56.2 (C_γ); 41.6 (NMe_2); 33.4, 31.5 (2 C, CH_2). IR (KBr): 2990 cm^{-1} (NMe_2H^+).

Formation of Heterocycles. 2H-*N,N*-Dimethylquinolinium Chloride (3a). A mixture of **1a** (0.24 g, 1.5 mmol), $PdCl_2(MeCN)_2$ (0.30 g, 1.16 mmol), and sodium acetate (0.15 g, 1.5 mmol) in MeCN (50 mL) was heated at reflux for 6 h. The metallic palladium was removed by centrifugation, and the solvent was evaporated *in vacuo*. Extraction with CH_2Cl_2, followed by evaporation of the solvent *in vacuo*, yielded **3a** as an off-white solid (89% yield). This compound can be purified by recrystallization from a 1:1 $CHCl_3$/pentane mixture. Analytically pure compound **3a**(PF_6), with PF_6^- as counterion instead of Cl^-, was obtained by treating a water solution of the original product with NH_4PF_6. Crystals were formed from a pentane-layered CH_2Cl_2 solution. ^1H NMR ($CDCl_3$): δ 8.1–7.3 (m, 4 H, Ar); 6.80 (d, 1 H, H^4, $^3J_{HH}$ = 9.8); 6.20 (m, 1 H, H^3); 4.88 (m, 2 H, H^2); 3.97 (s, 6 H, NMe_2). ^{13}C NMR ($CDCl_3$): δ 140.0–119.4 (Ar, C^3 and C^4); 61.4 (C^2); 53.5 (NMe_2).

2-Vinyl-*N,N*-dimethylindolinium Chloride (3b). Solutions of **1b** (0.42 g, 2.4 mmol) and $PdCl_2(MeCN)_2$ (0.60 g, 2.3 mmol) in MeOH (25 mL) were mixed and stirred for 4 days. Metallic palladium was separated by centrifugation, and the volatiles were removed *in vacuo*. The residue was extracted with CH_2Cl_2 (30 mL). After addition of 50 mL of pentane, the product was obtained as a white solid (72%). ^1H NMR ($CDCl_3$): δ 8.02 (m, 1 H, Ar); 7.24 (m, 3 H, Ar); 6.04 (m, 1 H, HC=); 5.87 (d, 1 H, $^3J_{HH}$ = 16.8, $=CH_{trans}$); 5.60 (d, 1 H, $^3J_{HH}$ = 9.7, $=CH_{cis}$); 4.88 (m, 1 H, CHN); 3.62 (s, 3 H, NMe); 3.31 (d, 2 H, $^3J_{HH}$ = 8.3, CH_2); 3.20 (s, 3 H, NMe). ^{13}C NMR ($CDCl_3$): δ 146.5, 131.8, 131.0, 129.7, 126.4, 118.6 (Ar); 129.6 (=CH_2); 127.4 (HC=); 80.8 (CHN); 52.6, 50.1 (NMe); 32.4 (CH_2). Anal. Calcd for $C_{12}H_{16}ClN$: C, 68.73; H, 7.69; N, 6.68. Found: C, 68.64; H, 7.58; N, 6.49.

***N,N*-Dimethyl-1,2,3,4-tetrahydro-2-vinylquinolinium Chloride (3c).** A solution of **1c** (0.82 g, 4.34 mmol) in MeOH (10 mL) was added dropwise to a suspension of $PdCl_2(MeCN)_2$ (1.12 g, 4.32 mmol) in MeOH (40 mL). After 5 min, a solution of sodium acetate (0.40 g, 4.88 mmol) in MeOH (10 mL) was added. The mixture was stirred at room temperature for 6 h. The suspension was filtered over Celite and the filtrate concentrated *in vacuo*. The resulting residue was extracted with CH_2Cl_2 (2 × 10 mL). The combined fractions were concentrated to 3–5 mL, and Et_2O was added to precipitate **3c** (0.70 g, 72%), which was obtained as a white solid. Analytically pure compound **3c**(PF_6), with PF_6^- as counterion instead of Cl^-, was obtained by treating a water solution of **3c** with NH_4PF_6. Crystals were formed from a pentane-layered CH_2Cl_2 solution. ^1H NMR **3a** ($CDCl_3$): δ 8.03–7.04 (m, 4 H, Ar); 5.81 (d, 1 H, $=CH_2$, $^3J_{HH}$ = 16.6); 5.66 (m, 1 H, =HC); 5.40 (d, 1 H, $=CH_2$, $^3J_{HH}$ = 9.6); 5.07 (m, 1 H, NCH); 3.68, 3.61 (2s, 6 H, NMe_2); 2.85 (t, 2 H, $ArCH_2$, $^3J_{HH}$ = 7.0); 2.40 (m, 1 H, CH_2); 2.02 (m, 1 H, CH_2). ^1H NMR **3c**(PF_6) (acetone-, d_6): δ 7.66–7.33 (m, 4 H, Ar); 6.01–5.65 (m, 3 H, $CH=CH_2$); 4.34 (td, 1 H, NCH, $^3J_{HH}$ = 8.0, $^3J_{HH}$ = 3.2); 3.50, 3.38 (2s, 6 H, NMe_2); 3.10 (t, 2 H, $ArCH_2$, $^3J_{HH}$ = 6.9); 2.48, 2.28 (2m, 2 H, CH_2). ^{13}C NMR **3a** ($CDCl_3$): δ 142.2, 131.0, 129.7, 129.1, 129.0, 129.0, 126.9, 122.2 (C= and Ar); 73.7 (NCH); 58.2, 53.5 (NMe_2); 23.1, 22.6 (2 CH_2). ^{13}C NMR **3c**(PF_6) (acetone-d_6): δ 142.7, 132.0, 130.7, 130.2, 129.4, 129.2, 127.6, 121.2 (CH=CH_2 and Ar); 75.9 (NCH); 57.1, 53.2 (NMe_2); 23.9, 23.6 (2 CH_2).

Azepinium Derivative 3f. Triphenylphosphine (1.2 g, 4 mmol) was added to a suspension of **2f** (0.38 g, 0.9 mmol) in MeOH (15 mL). After 1 h, the reaction mixture was filtered and the solvent removed *in vacuo*. The residue was extracted with CH_2Cl_2 (2 × 10 mL). The combined fractions were concentrated, and Et_2O was added to precipitate **3f**, which was obtained as an orange solid (0.28 g, 98%). Compound **3f**(PF_6), with PF_6^- as counterion instead of Cl^-, was obtained by treating a MeOH solution of **3f** with NH_4PF_6, followed by evaporation of the solvent and extraction with CH_2Cl_2. This compound was crystallized from a Et_2O-layered MeOH solution. ^1H NMR **3f** ($CDCl_3$): δ 6.91 (d, 1 H, HC=, $^3J_{HH}$ = 10.14); 5.81 (m, 1 H, HC=); 4.67, 4.64 (2br s, 2 H, CH_2); 4.39–4.20 (m, 4 H, C_5H_3 + CH_2N); 4.21 (s, 5 H, C_5H_5); 3.65, 3.27 (2s, 6 H, NMe_2); 3.51 (m, 1 H, CHN). ^{13}C NMR **3f** ($CDCl_3$): δ 136.9, 117.9 (HC=); 83.6, 74.2, 71.2, 70.0, 69.4 (C_5H_3); 70.4 (C_5H_5); 64.6, 63.9 (CH_2); 53.0, 50.3 (NMe_2). Anal. Calcd for $C_{16}H_{20}F_6FeNP$: C, 44.98; H, 4.68; N, 3.28. Found: C, 44.94; H, 4.74; N, 3.36.

Azepinium Derivative 3g. A solution of **1g** (0.45 g, 2.90 mmol) in MeOH (10 mL) was added dropwise to a suspension of $PdCl_2(MeCN)_2$ (0.76 g, 2.92 mmol) in MeOH (30 mL). After 5 min, a solution of sodium acetate (0.25 g, 3.05 mmol) in MeOH (10 mL) was added. The reaction mixture was stirred for 2 h at room temperature, after which PPh_3 (3.15 g, 12 mmol) was added as a solid, and the reaction mixture was stirred for another 2 h. After this period, the suspension was filtered, and the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (2 × 10 mL). After concentration of the combined CH_2Cl_2 solutions, a precipitate was obtained by addition of Et_2O. The compound **3g** was obtained as white crystals (0.48 g, 2.29 mmol, 79%) from a slow diffusion of pentane into a CH_2Cl_2 solution. Analytically pure compound **3g**(PF_6), with PF_6^- as counterion instead of Cl^-, was obtained by treating a water solution of **3g** with NH_4PF_6. Crystals were formed from a pentane-layered CH_2Cl_2 solution. ^1H NMR **3g** ($CDCl_3$): δ 7.67–7.31 (m, 4 H, Ar); 7.21 (d, 1 H, CH, $^3J_{HH}$ = 10.6); 6.27 (td, 1 H, CH, $^3J_{HH}$ = 6.4); 4.37 (s, 2 H, $ArCH_2$); 3.70 (d, 2 H, NCH_2); 3.62 (s, 6 H, NMe_2). ^{13}C NMR **3g** ($CDCl_3$): δ 140.3 (ArC=); 137.8, 132.0, 130.4, 129.3, 129.2 (Ar); 122.5 (=C); 65.7 ($ArCH_2$); 60.8 (NCH_2); 51.2 (NMe_2). Anal. Calcd for $C_{12}H_{16}NPF_6$: C, 45.15; H, 5.05; N, 4.39. Found: C, 44.98; H, 5.06; N, 4.43.

Azepinium Derivative 3h. This compound was prepared *via* a procedure similar to that described for **3f**, starting from **2h** (0.74, 2.24 mmol) and affording **3h** in 86% yield. ^1H NMR ($CDCl_3$): δ 7.63–7.24 (m, 4 H, Ar); 6.77 (d, 1 H, =CH, $^3J_{HH}$ = 12.0); 5.83 (m, 1 H, =CH); 5.07 (q, 1 H, HCMe, $^3J_{HH}$ = 6.9); 4.84 (dd, 1 H, CH_2, $^2J_{HH}$ = 17.6, $^3J_{HH}$ = 5.4); 3.92 (br d, 1 H, CH_2); 3.74, 3.27 (2s, 6 H, NMe_2); 1.63 (d, 3 H, CH_3). Anal. Calcd for $C_{13}H_{18}ClN$: C, 69.79; H, 8.11; N, 6.26. Found: C, 69.64; H, 8.15; N, 6.21. ***N,N*-Dimethyl-1,2,3,4-tetrahydro-3-vinylisoquinolinium Chloride (3j).** This compound was prepared *via* a procedure similar to that described for **3g**, starting from **1j** and yielding **3j** as a white solid by crystallization from a Et_2O-layered CH_2Cl_2 solution. ^1H NMR ($CDCl_3$): δ 7.26–7.12 (m, 4 H, Ar); 5.96 (dd, 1 H, H_2C=, $^3J_{HH}$ = 16.7, $^2J_{HH}$ = 16.7, $^2J_{HH}$ = 1.6); 5.67 (dd, 1 H, H_2C=, $^3J_{HH}$ = 9.6); 5.85 (m, 1 H, HC=); 5.21, 4.85 (2d, 2 H, NCH_2, $^2J_{HH}$ = 15.5); 5.01 (m, 1 H, HCN); 3.58, 3.20 (2s, 6 H, NMe_2); 3.26, 3.20 (dd, 2 H, CH_2, $^3J_{HH}$ = 5.1 and 9.0, $^2J_{HH}$ = 18.5). ^{13}C NMR ($CDCl_3$): δ 128.8–126.5 (Ar and vinyl); 69.8 (NCH); 63.3 (NCH_2); 51.8, 45.5 (NMe_2), 30.3 (CH_2). MS: *m/z* 188 (M^+), 173, 146, 104. Anal. Calcd for $C_{13}H_{18}ClN$: C, 69.79; H, 8.11; N, 6.26. Found: C, 69.28; H, 8.27; N, 6.12.

Formation of the Phosphonium Compounds. 1-(*N,N*-Dimethylanilino-2)-6-(triphenylphosphinio)-4-hexene Hydrochloride (4d). PPh_3 (5.42 g, 20.7 mmol) was added to a suspension of **2d** (1.09 g) in MeOH (40 mL). A yellow precipitate was formed after 2 h of stirring of the mixture at room temperature. The reaction mixture was filtered, and the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (20 mL) and the solution concentration. Addition of the THF gave a pale yellow precipitate. The compound **4d** (0.89 g, 32% yield from **1d**) was obtained by filtration. ^1H NMR ($CDCl_3$): δ 12.15 (br s, 1 H, HN^+); 7.98–7.05 (m, 19 H, Ar); 6.00 (m, 1 H, HC=); 5.36 (m, 1 H, =CH); 4.55 (dd, 2 H, CH_2P, $^2J_{HP}$ = 14.5, $^3J_{HH}$ = 7.0); 3.24 (br s, 6 H, NMe_2); 2.91 (m, 2 H, CH_2Ar); 2.14 (m, 2 H, CH_2C=); 1.57 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 142.1 (d, 1 C, CH, $^3J_{PC}$ = 13.3); 140.9–117.5 (24 C, Ar); 115.10 (1 C, =CH, $^2J_{PC}$ = 8.8); 47.8 (s, 2 C, NMe_2); 32.2, 30.5, 30.1 (3 s, CH_2); 27.8 (d, 1 C, CH_2, $^1J_{HP}$ = 49.6). ^{31}P NMR ($CDCl_3$): δ 20.5 (P^+). MS for for M = $[C_{32}H_{36}NP]^+$: *m/z* = 465 (M^+), 464 ([M − H]$^+$), 262 (PPh_3^+).

1-(*N,N*-Dimethylanilino-2)-7-(triphenylphosphinio)-5-heptene Hydrochloride (4e). This compound was prepared *via* a procedure similar to that described for **4d**, starting from **2e** (0.98 g) and yielding **4e** (0.79 g, 30% yield from **1e**). ^1H NMR ($CDCl_3$): δ 12.2 (1 H, HN^+); 7.76–7.19 (m, 19 H, Ar); 5.84 (m, 1 H, CH); 5.28 (m, 1 H, CH); 4.48 (dd, 2 H, CH_2P, $^3J_{HP}$ = 14.3, $^3J_{HH}$ = 6.8); 3.26 (d, 6 H, NMe_2); 2.99, 1.97, 1.45 (3 m, 8 H, 4 CH_2). ^{13}C NMR ($CDCl_3$): δ 142.8 (d, 1 C, CH, $^3J_{PC}$ = 13.2); 140.9–117.1 (24 C, Ar); 113.9 (d, CH, $^2J_{PC}$ = 9.8); 47.9 (s, NMe_2); 32.6, 31.4, 31.0, 28.1 (4 C, CH_2); 27.9 (d, CH_2P, $^1J_{PC}$ = 49.2). ^{31}P NMR ($CDCl_3$): δ 20.6 (P^+). MS for M = $[C_{33}H_{38}NP]^+$: *m/z* = 479 (M^+), 478 ([M − H]$^+$), 262 (PPh_3^+).

1-((*N,N*-Dimethylammonio)methyl)phenyl-2)-5-(triphenylphosphonio)-3-pentene Hydrochloride (4k). This compound was prepared *via* a procedure similar to that described for **4d**, starting from **2k** (0.89 g) and yielding **4k** (0.57 g, 35% yield from **1k**). ^1H NMR ($CDCl_3$): δ 11.28 (1br s, 1 H, NH^+); 7.85–6.89 (m, 19 H, Ar); 6.09 (td, 1 H, CH, $^3J_{HH}$ = 20.8, $^3J_{HH}$ = 6.5); 5.24 (td, 1 H, CH, $^3J_{HH}$ = 6.5); 4.33 (d, 2 H, CH_2, $^3J_{HH}$ = 5.8); 4.24 (dd, 2 H, CH_2P, $^3J_{HP}$ = 14.6); 2.82 (m, 2 H, CH_2); 2.80 (d, 6 H, NMe_2, $^3J_{HH}$ = 4.7); 2.16 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 141.5 (d, 1 C, CH, $^3J_{PC}$ = 13.3); 141.2–117.1 (24 C, Ar); 115.0 (CH, $^2J_{PC}$ = 9.4); 56.7 (CH_2N); 42.2 (NMe_2); 34.3, 31.5 (2 C, CH_2); 27.8 (d, 1 C, CH_2P, $^1J_{PC}$ = 50.5). ^{31}P NMR ($CDCl_3$): δ 20.0 (P^+). MS for M = $[C_{32}H_{36}NP]^+$: *m/z* 465 (M^+), 464 ([M − H]$^+$), 262 (PPh_3^+).

Table 5. Crystal Data and Details of the Structure Determination for **2i**$_{syn}$ and **3a**

	2i$_{syn}$	**3a**
	Crystal Data	
empirical formula	$C_{15}H_{24}ClNPdSi$	$C_{11}H_{14}ClN$
formula weight	388.32	195.69
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	8.902(1)	13.032(1)
b (Å)	20.587(1)	6.544(1)
c (Å)	9.702(1)	13.415(1)
β (deg)	95.520(10)	114.72(1)
V (Å^3)	1769.8(3)	1039.2(2)
Z	4	4
D_{calc} (g cm^{-3})	1.457	1.251
F(000) (electrons)	792	416
μ(Mo Kα) (cm^{-1})	12.4	3.2
crystal size (mm)	0.43 × 0.30 × 0.25	0.08 × 0.40 × 0.40
	Data Collection	
temperature (K)	295	295
radiation (Å)	Mo Kα (Zr), 0.710 73	Mo Kα (Zr), 0.710 73
θ_{min}, θ_{max}, (deg)	1.0, 28.5	0.1, 27.5
scan type	$\omega/2\theta$	$\omega/2\theta$
scan Δω, (deg)	0.7 + 0.35 tan θ	0.6 + 0.35 tan θ
horizontal, vertical aperture (mm)	3.0, 6.0	3.0, 6.0
reference reflections	−1 0 −2; 1 2 0 (no decay)	1 0 −3; 2 −1 0 (3% decay)
data set (*h*; *k*; *l*)	−11:11; 0:26; −13:0	−16:16; 0:8; −17:17
total data, unique data	4229, 4097	6115, 2380
observed data ($I > 2.5\sigma(I)$)	2713	1654
	Refinement	
no. of refined reflctns/ params	2173, 207	1654, 162
final *R*, R_w, *S*	0.038, 0.040, 1.23	0.042, 0.046, 0.49
weighting scheme	$w = I/\sigma^2(F)$	$w = 1/\sigma^2(F)$
max and av shift error	0.080, 0.003	0.005, 0.001
min and max resd dens (e Å^{-3})	−0.84, 0.69	−0.20, 0.23

X-ray Structure Determination of 2i$_{syn}$. X-ray data were collected for a yellow block-shaped crystal glued on top of a capillary on an ENRAF-NONIUS CAD4 diffractometer. The cell parameters were determined from setting angles of 25 SET4 reflections in the range 10° < θ < 16°. Numeral details are given in Table 5. Data were corrected for Lorentz polarization and absorption (DIFABS,[20] correction range 0.74–1.19). The structure was solved by Patterson techniques with SHELXS-86[21] and refined by full-matrix least-squares methods on *F* with SHELX76.[22] The three allylic H atoms as well as the benzylic H atoms on C(4) were found from a difference Fourier map and their positions refined. The remaining H atoms were taken into account at calculated positions (C–H = 0.98 Å). All non-hydrogen atoms were refined with anisotropic displacement parameters. Convergence was reached at *R* = 0.038. Scattering factors were taken from Cromer and Mann,[23] corrected for anomalous dispersion (ref 24). Geometrical calculations, including the illustration, were done with PLATON.[25] Final coordinates are given in the supplementary material.

X-ray Structure Determination of 3a. X-ray data were collected on an ENRAF-NONIUS CAD4 diffractometer for an orange crystal sealed in a Lindemann glass capillary. Unit cell dimensions were derived from the setting angles of 25 reflections in the range 9° < θ < 20°. Numerical details are given in Table 5. A total of 6115 reflections were scanned.

(20) Walker, M.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(21) Sheldrick, G. M. *SHELXS-86. Program for crystal structure determination*; Univ. of Göttingen: Göttingen, Federal Republic of Germany, 1986.
(22) Sheldrick, G. M. *SHELX76. Program for crystal structure determination*; Univ. of Cambridge: Cambridge, England, 1976.
(23) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
(24) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Data were corrected for Lorentz polarization and a small linear decay of 3% and averaged (R_{av} = 0.047) into a unique set of 2380 reflections. The structure was solved by direct methods (SHELXS-86)[21] and refined on F by full-matrix least-squares methods (SHELX76)[22] to a final R = 0.042. All positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. Scattering factors were taken from Cromer and Mann.[23] Geometrical calculations were done with PLATON[25] (including the ellipsoid plot). Final coordinates are given in the supplementary material.

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(25) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
(26) We thank the reviewers for their critical comments and some interesting suggestions.

Note added in proof: Compounds such as **3g** and **3h** (see Table 3) were obtained by the reaction of the α-OAc derivatives of **1g** and **1h**, respectively, with a catalytic amount of $Pd(PPh_3)_4$ in MeCN. See: Grellier, M.; Pfeffer, M.; van Koten, G. *Tetrahedron Lett.*, in press.

Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, all H-atom parameters, bond lengths, and bond angles for $\mathbf{2i}_{syn}$ and **3a** (5 pages); listings of observed and calculated structure factors (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.