

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 PdCl₂(MeCN)₂ in MeOH in the presence of NaOAc and PPh₃ 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 NMe₂ 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, C₆H₄(CH₂CH=CH₂)-1-(CHMeNMe₂)-2 can be converted to the *endo*-cyclization product [C₆H₄{CH=CHCH₂CH₂CH(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 η³-allylpalladium complex as a key intermediate and then allow it to react further with PPh₃ to afford a cyclized end product. The X-ray crystal structures of a palladium–allyl complex, *i.e.*, **2i**_{syn}, and a quinolinium derivative, **3a**, are described. Crystal data for **2i**_{syn}: monoclinic, space group *P*2₁/*c*, with *a* = 8.902(1), *b* = 20.587(1), and *c* = 9.702(1) Å, β = 95.52(1)°, *Z* = 4, *R* = 0.038. Crystal data for **3a**: monoclinic, space group *P*2₁/*n* with *a* = 13.032(1), *b* = 6.544(1), and *c* = 13.415(1) Å, β = 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 η²-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 η²-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

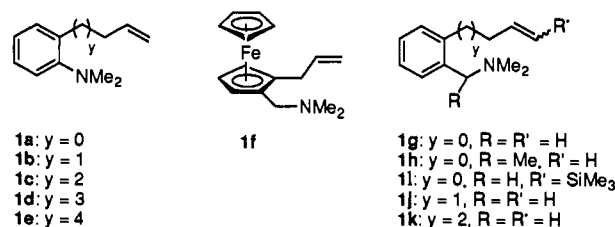


Figure 1. *o*-Alkenyl(tertiary-aminoalkyl)arenes and ferrocene **1a–k**.

common attribute a terminal olefin separated from a NMe₂ group by hydrocarbon chains with different degrees of flexibility.

This paper reports on the reactivity of a specific class of such amino olefins, namely 1,2-disubstituted benzenes, in which there is an (CH₂)_{*y*}CH₂CH=CH₂ substituent positioned ortho to either a dimethylamino (NMe₂) or a (dimethylamino)methyl (CH₂-NMe₂) function. The allyl and amine functions are thus connected by a carbon skeleton chain containing a rigid C sp²–C sp² 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 CH₂ (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-amino-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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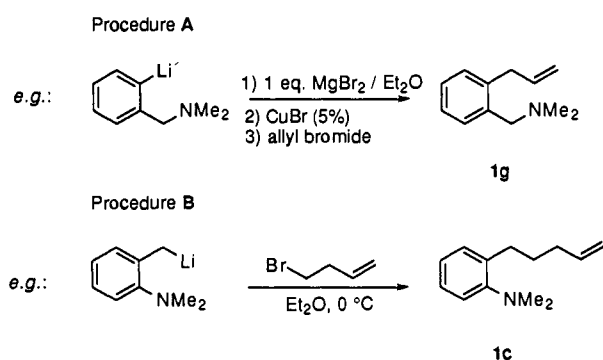
* Abstract published in *Advance ACS Abstracts*, April 15, 1994.

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(3) (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. (b) van Koten, G. *Pure Appl. Chem.* **1990**, *62*, 1155. (c) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567. (d) Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335.

Scheme 1



comparison with those obtained previously¹ for the palladium-mediated heterocyclization reaction of related primary and secondary aminoarenes.

Results

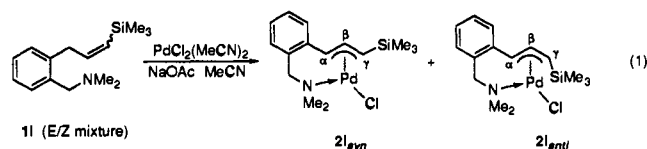
***o*-Alkenyl(tertiary-aminoalkyl)arenes.** The general procedure for the synthesis of the *o*-alkenyl(tertiary-aminoalkyl)arenes is based on a C–C coupling reaction of a (tertiary-aminoalkyl)-substituted aryllithium or benzylolithium compound with an alkenyl bromide, either with (procedure A) or without (procedure B) 1 equiv of MgBr₂ and a catalytic amount of CuBr. The MgBr₂/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 PdCl₂(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 PPh₃.

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 PdCl₂(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^3 -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 ¹³C 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=CHSiMe₃ group, is a mixture of two allylic isomers, **2i_{syn}** and **2i_{anti}**, in a 9:4 ratio (see eq 1) that could be separated by fractional crystallization from diethyl ether

(4) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *Tetrahedron Lett.* **1976**, 223.

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



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 **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 **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 **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)-SiMe₃] allylic unit, a chlorine atom, and the N-donor atom of the intramolecularly coordinating CH₂NMe₂ fragment. The overall (pseudo-four-coordinate) geometry about the palladium center is like that commonly observed in related allylic (d⁸) metal derivatives.⁶ In **2i_{syn}**, the 2-[(dimethylamino)methyl]phenyl and SiMe₃ 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)^o 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 CH₂NMe₂ methylene group.

The second isomer of **2i**, **2i_{anti}**, differs from **2i_{syn}** with respect to the position of the bulky SiMe₃ 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, **2i_{anti}** does not isomerize to **2i_{syn}** (or *vice versa*) even at elevated temperatures (70 °C in CDCl₃), 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 **2i_{anti}** and **2i_{syn}** were formed directly from the respective *Z*- and *E*-isomers of **1i**.

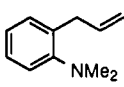
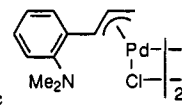
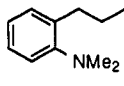
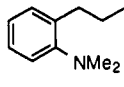
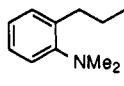
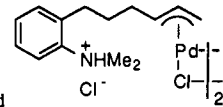
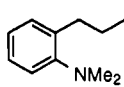
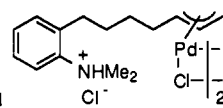
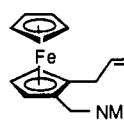
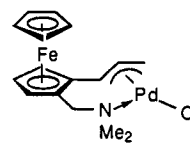
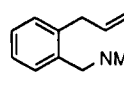
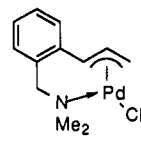
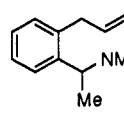
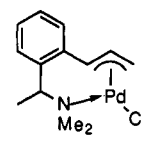
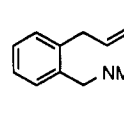
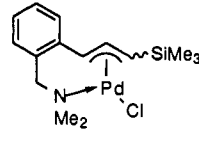
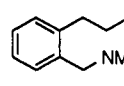
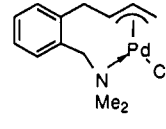
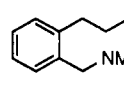
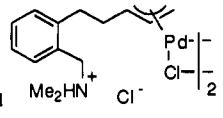
The three complexes **2f–h** are all η^3 -allylpalladium species that exist as only one isomer and whose structures in solution were easily determined by ¹H NMR spectroscopy. In these complexes the methyl groups of the NMe₂ unit afford two signals, *i.e.*, they are diastereotopic, and this confirms amine–palladium 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 PdCl₂(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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(7) (a) Vrieze, K.; Praat, A. P.; Cossee, P. J. *Organomet. Chem.* **1968**, 12, 533. (b) Lukas, L.; Coren, S.; Blom, J. E. J. *Chem. Soc., Chem. Commun.* **1969**, 1303. (c) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, 93, 2642. (d) Heck, R. F. In *Organotransition Metal Chemistry: A mechanistic approach*; Maitlis, P. M.; Stone, F. A. G.; West, R., Eds.; Academic Press: New York and London, 1974; p 81. (e) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, pp 385–446. (f) Ohta, T.; Hosokawa, T.; Murahashi, S. I.; Miki, K.; Kasai, N. *Organometallics* **1985**, 4, 2080. (g) Akermark, B.; Vitagliano, A. *Organometallics* **1985**, 4, 1275. (h) Maassarani, F.; Pfeffer, M.; van Koten, G. *Organometallics* **1989**, 8, 871.

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, MgBr₂, 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 PdCl₂(SMe₂). ^d Obtained when the reaction with PdCl₂(MeCN)₂ is performed in CH₂Cl₂. ^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 ($\gamma = 3$ or 4), and this leads to a dramatic change in their behavior with a palladium(II) salt. Their reactions with PdCl₂(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

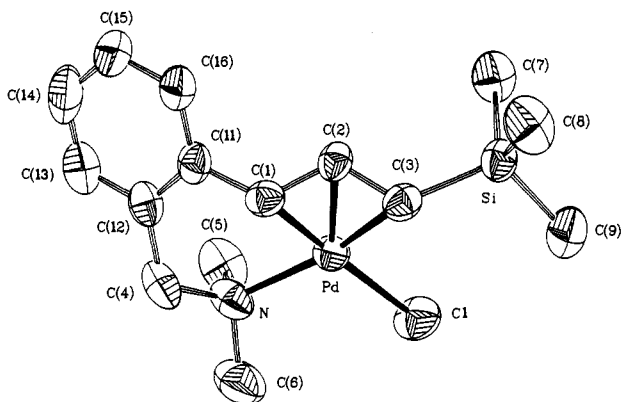


Figure 2. ORTEP drawing of **2i_{syn}** and adopted numbering scheme, with thermal ellipsoids drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex **2i_{syn}**

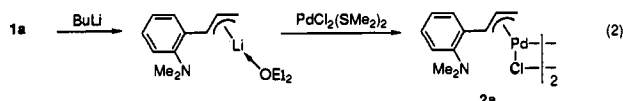
Pd–C(1)	2.086(4)	Pd–Cl	2.372(1)	C(2)–C(3)	1.403(6)
Pd–C(2)	2.114(4)	Pd–N	2.171(4)	C(1)–C(11)	1.482(6)
Pd–C(3)	2.183(5)	C(1)–C(2)	1.404(6)	C(3)–Si	1.872(4)
C(11)–C(1)–C(2)	121.9(4)	C(1)–Pd–Cl	172.6(1)		
C(2)–C(3)–Si	123.8(4)	C(2)–Pd–Cl	136.9(1)		
C(1)–C(2)–C(3)	119.9(4)	C(3)–Pd–Cl	104.3(1)		
N–Pd–Cl	94.07(11)	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 CH₂Cl₂, 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 NEt₃ 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 η³-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 CDCl₃ 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 η³-allyl species (**2d**, **2e**, or **2k**) in a *ca.* 1:4 molar ratio. Furthermore, 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 PdCl₂(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 PdCl₂(Py)₂ (Py = pyridine) and free alkenylaminoarene **1b**. This insoluble intermediate is probably an adduct [PdCl₂(**1b**)], which is the expected precursor to an η³-allylpalladium species.

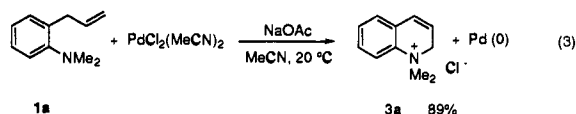
Because of the above evidence for the formation of η³-allylpalladium species from substrates **1d–k**, we believed it to be important to discover whether analogous species derived from **1a–c** were indeed accessible. To this end, amino olefin **1a** was deprotonated with butyllithium to afford an allyllithium derivative, and this was found to transmetalate with PdCl₂(SMe₂)₂ to give

a stable dimeric η³-allylpalladium complex, **2a** (see eq 2). For



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 NMe₂ 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 η³-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 **2i_{syn}** and **2i_{anti}**) identical to that obtained by the direct palladium route described above (eq 1).

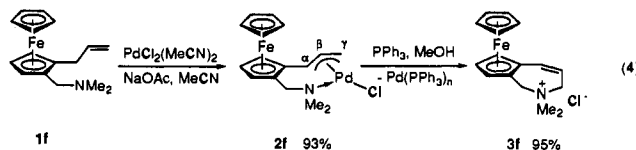
Formation of Heterocyclic Products. When the amino olefin substrates **1a–c** and 1 equiv of PdCl₂(MeCN)₂ were reacted (in MeOH or MeCN) in the presence of sodium acetate, see Experimental Section, a heterocyclization reaction occurred and metallic palladium was formed.⁸ A summary of these reactions 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 heterocyclic product was



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.

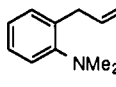
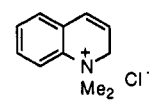
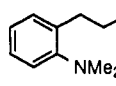
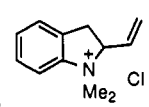
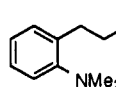
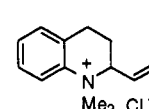
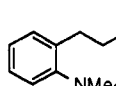
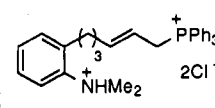
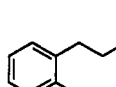
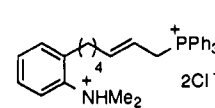
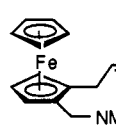
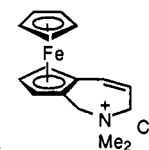
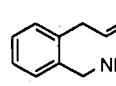
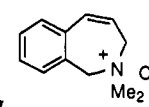
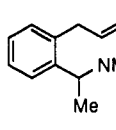
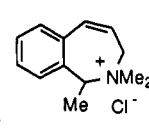
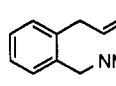
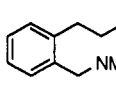
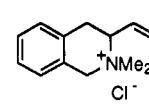
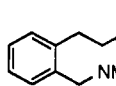
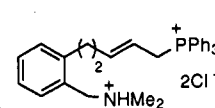
When the amino olefin substrate is an aniline with longer olefinic chains, **1b** (*y* = 1) and **1c** (*y* = 2), the reaction with PdCl₂(MeCN)₂ as described above for **1a** gave high yields of an indolinium derivative **3b** (72%) and a quinolinium derivative **3c** (72%), respectively. With **1b** 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 PdCl₂ 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 η³-allylpalladium complexes **2f–h**, isolated from the reactions of **1f–h** with PdCl₂(MeCN)₂, can be quantitatively depalladated in MeOH by the addition of PPh₃ (eq 4). This new



methodology for the removal of palladium from the product of palladium-mediated coupling reactions^{2c,9} affords insoluble Pd(PPh₃)_n and the seven-membered heterocycles **3f–h**, respectively. Under the same conditions, addition of PPh₃ to η³-allylpalladium

Table 3. Representation of Organic Products

entry	substrate	PPh ₃ ^a	organic product	yield (%) ^b
1		no		89 ^c
2		no		72 ^{c,d}
3		no		72 ^c
4		yes ^e		32 ^c
5		yes ^e		30 ^c
6		yes ^e		98
7		yes		79
8		yes ^e		86
9		yes ^f		
10		yes		90 ^c
11		yes ^e		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 PPh₃ 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., PdCl₂(MeCN)₂ in THF with NEt₃ 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 PPh₃. However,

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

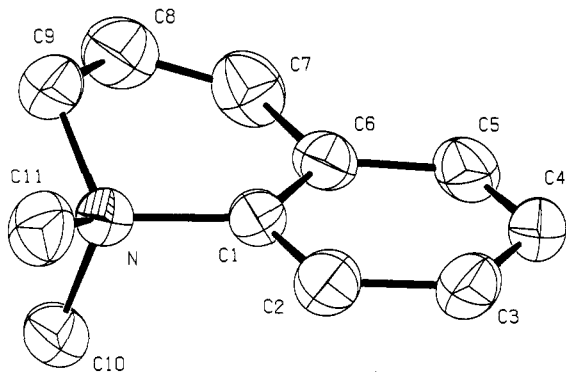
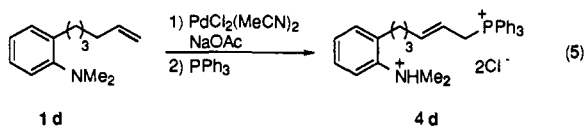


Figure 3. ORTEP drawing of the cation (chloride anion not shown) **3a** and adopted numbering scheme, with thermal ellipsoids drawn at the 50% probability level.

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).



Discussion

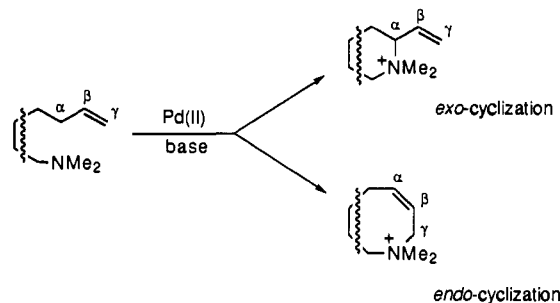
The present results show that controlled intramolecular coupling between an alkene and a tertiary amine can be successfully induced by Pd(II). This reaction, affording cationic heterocycles, has so far clearly escaped general attention, and only a few examples have been reported in the literature.^{2a,b,10} 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 η²-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 NMe₂ unit to an η²-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 η²-coordinated to Pd should be nonproductive in the

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

aminopalladation process. The C–H activation step, which is likely to be mediated by the presence of the intramolecular NMe₂ 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, η³-allylpalladium complexes (**2f–i**) which were shown to be true reaction intermediates, since depalladation, induced with PPh₃, 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, η³-allylpalladium complex **2a**, synthesized *via* a transmetalation route, could be depalladated by PPh₃ to afford the heterocycle **3a**, which is identical to that resulting from the reaction of substrate **1a** with PdCl₂(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 η³-allylpalladium complex. This process, which follows after η¹-N,η²-alkene coordination to the metal, may be related to the well-established synthesis of η³-allylpalladium complexes from alkyl-substituted alkenes and palladium(II).^{7c} Recently we reported a related formation of η¹-N,η³-allylpalladium complexes starting with compounds bearing an intramolecular η¹-N,η²-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 NMe₂ 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 η³-allyl unit.¹¹ This process will depend on the nature of the η³-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 η³-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 NMe₂ grouping onto the η³-allyl moiety. This also underlines the role of PPh₃ in these reactions, since added phosphine displaces by substitution the coordinated tertiary amine

(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.

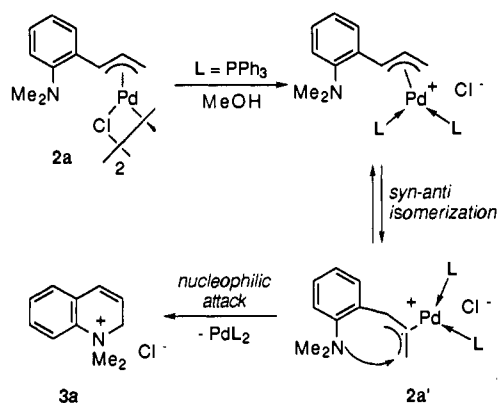
grouping from the palladium center and so generates the tertiary alkylamine nucleophile (see Scheme 3).

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 chemo-selectivity, 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 NMe₂ 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 SiMe₃ 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 SiMe₃ group, respectively), is very stable, and depalladation of this complex to afford organic products could not be induced with PPh₃. 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 PPh₃-induced cyclization reaction, Pd⁰(PPh₃)_n is formed. Recently, Pfeffer *et al.* established that the reaction of the next higher homologue of **1f** (having one extra CH₂ grouping separating the Cp ring and the allyl fragment) with PPh₃ in MeOH produces a 1:2 mixture of the *exo*- and *endo*-cyclized products. In the presence of Pd⁰(PPh₃)_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 Pd⁰-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

Scheme 3



heterocycles *via* intramolecular amination does not take place. With these substrates we do find an initial selective reaction with the palladium(II) salt (when CH₂Cl₂ is used as a solvent) that affords CH₂Cl₂-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 (–NHMe₂⁺) 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.

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 PPh₃ at C_γ to afford phosphonium derivatives (**4d**, **4e**, and **4k**, respectively). This contrasts with the PPh₃ 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 NMe₂ 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

(12) (a) Akermark, B.; Hanson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679. (b) Keinan, E.; Sahai, M. *J. Chem. Soc., Chem. Commun.* **1984**, 648. (c) Chaptal, N.; Colovray-Gotteland, V.; Grandjean, C.; Cazes, B.; Goré, J. *Tetrahedron Lett.* **1991**, *32*, 1795. (d) Friess, B.; Cazes, B.; Goré, J. *Bull. Soc. Chim. Fr.* **1992**, *129*, 273. (e) Granberg, K. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1992**, *114*, 6858.

(13) (a) Grove, D. M.; Kooijman, H.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9916. (b) Pregosin, P. S.; Rügger, H.; Wombacher, F.; van Koten, G.; Wehman-Ooyevaar, I. C. M.; Grove, D. M. *J. Magn. Reson.* **1992**, *30*, 548. (c) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, A.; van Koten, K. *Inorg. Chem.* **1992**, *31*, 5484.

(14) (a) Tamura, R.; Kato, M.; Saegusa, K.; Kakihana, M.; Oda, D. *J. Org. Chem.* **1987**, *52*, 4121. (b) *J. Am. Chem. Soc.* **1993**, *115*, 6609.

(15) (a) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; pp 197–202. (b) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965; p 191.

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 PPh₃ 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 C₃H₅(Me₃Si)Br¹⁹ were prepared by standard literature methods. ¹H (300.13 or 200.13 MHz), ¹³C (75.47 or 50.32 MHz), and ³¹P (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, Université Louis Pasteur, Strasbourg, France.

Synthesis of the α -Alkenyl[(dimethylamino)alkyl]arenes. Procedure A, *o*-(2-Propenyl)-*N,N*-dimethylaniline (1a). A solution of [LiC₆H₄(NMe₂)₂]-1/2(tmeda) (7.87 g, 42.5 mmol) in Et₂O (40 mL) was slowly added to a suspension of anhydrous MgBr₂ (7.91 g, 42.9 mmol) in Et₂O (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 \times 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 MgBr₂ (5.50 g, 30 mmol) was added to a stirred suspension of 2-[(dimethylamino)methyl]ferrocenyllithium¹⁸ (4.89 g, 19.6 mmol) in Et₂O 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 H₂O (50 mL) and extracted with pentane (2 \times 20 mL). The organic layer was dried over MgSO₄ 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, α -(4-Pentenyl)-*N,N*-dimethylaniline (1c). 4-Bromo-1-butene (0.8 mL, 8 mmol) in Et₂O (10 mL) was added dropwise to a suspension of [LiCH₂C₆H₄(NMe₂)₂] (1.1 g, 7.8 mmol) in Et₂O (30 mL) at 0 °C. The mixture was warmed up to room temperature, stirred for 4 h, hydrolyzed with H₂O (20 mL), and extracted with Et₂O (2 \times 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 (CDCl₃) 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, =CH₂); 3.62 (d, 2 H, CH₂, ³J_{HH} = 6.5); 2.78 (s, 6 H, NMe₂). 1b: δ 7.29–7.04 (m, 4 H, Ar); 5.99 (m, 1 H, CH=); 5.11 (m, 2 H, =CH₂); 2.86 (m, 2 H, CH₂); 2.74 (s, 6 H, NMe₂); 2.45 (m, 2 H, CH₂). 1c: δ 7.26–7.02 (m, 4 H, Ar); 5.90 (m, 1 H, CH=); 5.02 (m, 2 H, =CH₂); 2.74 (m, 2 H, CH₂Ar); 2.71 (s, 6 H, NMe₂); 2.17 and 1.81 (2m, 4 H, CH₂). 1d: δ 7.26–6.99 (m, 4 H, Ar); 5.92 (m, 1 H, =CH); 5.04 (m, 2 H, =CH₂); 2.74 (m, 2 H, CH₂); 2.71 (s, 6 H, NMe₂); 2.19 and 1.80 (2m, 4 H, CH₂). 1e: δ 7.26–6.99 (m, 4 H, Ar); 5.86 (m, 1 H, =CH); 5.88 (m, 2 H, =CH₂); 2.73 (m, 2 H, CH₂); 2.70 (s, 6 H, NMe₂); 2.10, 1.68, and 1.47 (3m, 8 H, CH₂). 1f: δ 6.0 (m, 1 H, HC=); 5.06 (m, 2 H, H₂C=); 4.17 (t, 1 H, C₅H₃, ³J_{HH} = 1.8); 4.04 (s, 7H, C₅H₅ + C₅H₃); 3.35 and 3.22 (2d, 2 H, CH₂N, ²J_{HH} = 12.85); 3.10 (m, 2 H, CH₂); 2.10 (s, 6 H, NMe₂). 1g: δ 7.37–7.22 (m, 4 H, Ar); 6.04 (m, 1 H, =CH); 5.08 (m, 2 H, =CH₂); 3.60 (d, 2 H, CH₂, ³J_{HH} = 7.8); 3.45 (s, 2 H, CH₂N); 2.29 (s, 6 H, NMe₂). 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, H₂C=); 3.45 (m, 3 H, CH₂ + HCMe); 2.18 (s, 6 H, NMe₂); 1.27 (d, 3 H, CH₃, 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, CH₂C, ³J_{HH} = 3.0); 3.45 (s, 2 H, CH₂N); 2.30 (s, 6 H, NMe₂); 0.15 (s, 9 H, SiMe₃); (*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, CH₂, ³J_{HH} = 3.7); 2.30 (s, 6 H, NMe₂); 0.27 (s, 9 H, SiMe₃). 1j: δ 7.29–7.15 (m, 4 H, Ar); 5.90 (m, 1 H, HC=); 5.03 (m, 2 H, H₂C=); 3.40 (s, 2 H, CH₂N); 2.80 (m, 2 H, ArCH₂); 2.36 (m, 2 H, CH₂); 2.24 (s, 6 H, NMe₂). 1k: δ 7.32–7.16 (m, 4 H, Ar); 5.90 (m, 1 H, =CH); 5.05 (m, 2 H, =CH₂); 3.41 (s, 2 H, CH₂N); 2.75 (m, 2 H, ArCH₂); 2.26 (s, 6 H, NMe₂); 2.17, 1.71 (2m, 4 H, CH₂).

¹³C NMR (CDCl₃) 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 (NMe₂); 35.0 (CH₂). 1b: δ 152.9, 136.8, 129.5, 126.7, 123.4, 119.6 (Ar); 138.9, 114.5 (C=); 45.3 (NMe₂); 34.6, 30.3 (CH₂). 1c: δ 152.8, 137.3, 129.6, 126.4, 123.3, 119.4 (Ar); 138.9, 114.4 (C=); 45.1 (NMe₂); 33.9, 30.2, 29.9 (CH₂). 1d: δ 152.9, 137.6, 129.6, 126.5, 123.4, 119.5 (Ar); 139.1, 114.4 (C=); 45.3 (NMe₂); 33.8, 30.5, 30.2, 29.1 (CH₂). 1e: δ 152.9, 137.7, 129.6, 126.4, 123.4, 119.5 (Ar); 139.2, 114.3 (C=); 45.3 (NMe₂); 33.9, 30.7, 30.6, 29.4, 29.0 (CH₂). 1f: δ 137.2, 115.4 (C=); 86.8, 82.3 (C₅H₃); 68.9 (C₅H₅); 69.9, 68.0, 66.0 (3 CH, C₅H₃); 57.4 (CH₂N); 45.2 (NMe₂); 32.2 (CH₂). 1g: δ 138.7, 137.0, 130.1, 129.5, 127.2, 125.9 (Ar); 137.4, 115.3 (C=); 61.7 (CH₂N); 45.4 (NMe₂); 36.7 (CH₂). 1j: δ 141.0, 136.7, 130.2, 129.3, 127.1, 125.7 (Ar); 138.5, 114.7 (C=); 61.7 (CH₂N); 45.6 (NMe₂); 35.3, 31.9 (CH₂). 1k: δ 141.7, 136.8, 130.3, 129.4, 127.2, 125.7 (Ar); 138.8, 114.8 (C=); 61.9 (CH₂N); 45.6 (NMe₂); 33.9, 32.0, 30.6 (CH₂).

Synthesis of the η^3 -Allylpalladium Complexes. [PdCl-*syn*- η^3 -{C₃H₄-2-(α -C₆H₄NMe₂)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 Et₂O (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 Et₂O solution to give Li{C₃H₄-2-(α -C₆H₄NMe₂)₂} as its etherate complex (2.6 g, 79%). ¹H NMR (C₆D₆): 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, OCH₂); 2.3 (s, 6 H, NMe₂); 1.05 (t, 6 H, CH₃). A water quench of Li{C₃H₄-2-(α -C₆H₄NMe₂)₂} yields *o*-(1-propenyl)-*N,N*-dimethylaniline and *o*-(2-propenyl)-*N,N*-dimethylaniline in a 1:3 ratio.

A solution of Li{C₃H₄-2-(α -C₆H₄NMe₂)₂}(OEt) (0.23 g, 0.95 mmol) in Et₂O (25 mL) was added dropwise to a suspension of PdCl₂(MeCN)₂ (0.29 g, 0.96 mmol) in Et₂O (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 CHCl₃ (3 mL). Complex 2a was obtained as orange crystals by slow distillation of pentane into this solution (yield 36%). ¹H NMR (CDCl₃): 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 γ H β , ²J_{HH} = 1.1, ³J_{HH} = 5.5); 3.0 (d, 1 H, C γ H α , ³J_{HH} = 11.8); 2.85 (s, 6 H, NMe₂). ¹³C NMR (CDCl₃): 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 (NMe₂).

[PdCl- η^3 -{C₆H₁₀-2-(C₆H₄NMe₂HCl)}] (2d). A solution of 1d (1.05 g, 5.17 mmol) in CH₂Cl₂ (10 mL) was added dropwise to a suspension of PdCl₂(MeCN)₂ (1.35 g, 5.20 mmol) in CH₂Cl₂ (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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(17) Jastrzebski, J. T. B. H.; van Koten, G. *Inorg. Synth.* 1989, 26, 150.

(18) (a) Slocum, D. W.; Rockett, B. W.; Hauser, C. R. *J. Am. Chem. Soc.* 1968, 87, 1241. (b) Note: The lithiated compound can be obtained in high yield within 30 min by treating a solution of (*N,N*-dimethylamino)methylferrocene in hexane at 0 °C with ^tBuLi.

(19) Hosomi, A.; Ando, M.; Sakurai, H. *Chem. Lett.* 1984, 1385.

NMR (CDCl₃ + 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_γH₂); 2.94 (d, 1 H, C_γH₂); 2.78 (m, 2 H, ArCH₂); 2.69 (s, 6 H, NMe₂); 1.86 (m, 4 H, 2CH₂). ¹³C NMR (CDCl₃ + 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, NMe₂); 32.1, 30.3, 30.0 (3 C, CH₂). IR (KBr): 3061 cm⁻¹ (NMe₂H⁺).

[PdCl-η³-[C₇H₁₂-2-(C₆H₄NMe₂HCl)]₂] (2e). This compound was prepared *via* a similar procedure to that described for 2d, starting from 1e (1.04 g) and yielding 2e (0.98 g). ¹H NMR (CDCl₃ + Py-*d*₅): δ 9.55 (br s, +HNMe₂); 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_γH₂); 2.91–2.84 (m, 9 H, C_γ, CH₂, NMe₂); 2.00–1.50 (m, 6 H, CH₂). ¹³C NMR (CDCl₃ + 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, NMe₂); 32.0, 30.6, 30.5, 29.3 (4 C, CH₂). IR (KBr): 3061 cm⁻¹ (NMe₂H⁺).

[PdCl-*syn*-η³-[C₃H₄-2-(C₆H₅FeC₃H₃CH₂NMe₂)] (2f). A solution of 1f (1.2 g, 4.3 mmol) in MeCN (5 mL) was added dropwise to a suspension of PdCl₂(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 CH₂Cl₂ (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 (CDCl₃): 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, C₅H₃); 4.14 (s, 5 H, C₅H₃); 3.93 (d, 1 H, C_γH_{syn}, ³J_{HH} = 7.04); 2.99 (d, 1 H, C_γH_{anti}, ³J_{HH} = 12.30); 3.93, 2.83 (2d, 2 H, CH₂N, ²J_{HH} = 12.47); 2.96, 2.02 (2s, 6 H, NMe₂). Anal. Calcd for C₁₆H₂₀ClFeNPd: C, 45.31; H, 4.72; N, 3.30. Found: C, 45.14; H, 4.79; N, 3.36.

[PdCl-*syn*-η³-[C₃H₄-2-(C₆H₄CH₂NMe₂)] (2g). This complex was prepared *via* a procedure similar to that described for 2f. Recrystallization from a CHCl₃–pentane solution gave 2g (62%) as colorless crystals. ¹H NMR (CDCl₃): 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_γH_{syn}, ³J_{HH} = 7.1); 4.06 (d, 1 H, CH₂N, ²J_{HH} = 12.0); 3.23 (d, 2 H, CH₂N + C_γH_{anti}, *J*_{obsd} = 12.0); 3.09 and 2.11 (2s, 6 H, NMe₂). ¹³C NMR (CDCl₃): 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 (NMe₂); 46.2 (CH₂N). Anal. Calcd for C₁₂H₁₆ClNPd: C, 45.59; H, 5.10; N, 4.43. Found: C, 45.27; H, 5.11; N, 4.42.

[PdCl-*syn*-η³-[C₃H₄-2-(C₆H₄CH(Me)NMe₂)] (2h). This complex was prepared *via* a procedure similar to that described for 2f. Reaction of 1h (0.95 g, 5 mmol) with PdCl₂(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 (CDCl₃): 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_γH_{syn}, ³J_{HH} = 7.0); 3.31 (q, 1 H, MeCH); 3.17 (d, 1 H, C_γH_{anti}, ³J_{HH} = 12.4); 2.96, 2.05 (2s, 6 H, NMe₂); 1.65 (d, 3 H, HCMe). ¹³C NMR (CDCl₃): δ 142.6–127.8 (Ar); 112.9 (C_β); 76.1 (C_α); 72.3 (CHMe); 59.7 (C_γ); 49.1, 48.2 (2s, NMe₂); 20.0 (Me). Anal. Calcd for C₁₃H₁₈ClNPd: C, 47.29; H, 5.50; N, 4.24. Found: C, 47.18; H, 5.59; N, 4.28.

[PdCl-η³-[C₃H₃-γ-SiMe₃-(α-C₆H₄CH₂NMe₂-2)] (2i_{syn}) and (2i_{anti}). (i) *Via Transmetalation Reaction*. A solution of Li{C₃H₃-γ-SiMe₃-(α-C₆H₄CH₂NMe₂-2)} (prepared as described for Li{C₃H₄-2-(α-C₆H₄-NMe₂)}(OEt)₂, *vide supra*) (0.71 g, 2.8 mmol) in Et₂O (20 ml) was added dropwise to a suspension of PdCl₂(SMe₂)₂ in Et₂O (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 (CDCl₃): 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, CH₂N); 3.25 (d, 1 H, C_γH_{anti}, ³J_{HH} = 14.1); 3.10, 2.13 (2s, 6 H, NMe₂); 0.26 (s, 9 H, SiMe₃). ¹³C NMR (CDCl₃): δ 138.3–126.2 (Ar); 117.9 (C_β); 77.7 (C_α); 73.0 (CH₂N); 68.1 (C_γ); 51.6, 46.2 (2s, NMe₂); –0.8 (SiMe₃). *Anti*-trimethylsilyl isomer (2i_{anti}). ¹H NMR (CDCl₃): 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_γH_{syn}, ³J_{HH} = 9.8); 3.98, 3.23 (2d, 2 H, CH₂N); 3.09, 2.12 (2s, 6 H, NMe₂); 0.29 (s, 9 H, SiMe₃). ¹³C NMR (CDCl₃): δ 138.4–126.0 (Ar); 120.6 (C_β); 75.5 (C_α); 73.3 (CH₂N); 68.1 (C_γ); 51.4, 46.1 (2s, NMe₂); 1.7 (SiMe₃).

[PdCl-η³-[C₃H₃-2-(C₆H₄CH₂NMe₂HCl)]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 (CDCl₃ + 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, CH₂N, ²J_{HH} = 13.3); 3.83 (m, 1 H, C_αH); 3.78 (d, 1 H, C_γH₂); 3.28 (td, 1 H, ArCH₂, ³J_{HH} = 12.7, ²J_{HH} = 5.3); 3.00 (m, 1 H, CH₂); 2.94 (d, 1 H, C_γH₂); 2.83 (s, 6 H, NMe₂); 1.89 (m, 2 H, CH₂). ¹³C NMR (CDCl₃ + 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 (NMe₂); 33.4, 31.5 (2 C, CH₂). IR (KBr): 2990 cm⁻¹ (NMe₂H⁺).

Formation of Heterocycles. 2H-*N,N*-Dimethylquinolinium Chloride (3a). A mixture of 1a (0.24 g, 1.5 mmol), PdCl₂(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 CH₂Cl₂, 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 CHCl₃/pentane mixture. Analytically pure compound 3a(PF₆), with PF₆⁻ as counterion instead of Cl⁻, was obtained by treating a water solution of the original product with NH₄PF₆. Crystals were formed from a pentane-layered CH₂Cl₂ solution. ¹H NMR (CDCl₃): δ 8.1–7.3 (m, 4 H, Ar); 6.80 (d, 1 H, H⁴, ³J_{HH} = 9.8); 6.20 (m, 1 H, H³); 4.88 (m, 2 H, H²); 3.97 (s, 6 H, NMe₂). ¹³C NMR (CDCl₃): δ 140.0–119.4 (Ar, C³ and C⁴); 61.4 (C²); 53.5 (NMe₂).

2-Vinyl-*N,N*-dimethylindolinium Chloride (3b). Solutions of 1b (0.42 g, 2.4 mmol) and PdCl₂(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 CH₂Cl₂ (30 mL). After addition of 50 mL of pentane, the product was obtained as a white solid (72%). ¹H NMR (CDCl₃): 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, CH₂); 3.20 (s, 3 H, NMe). ¹³C NMR (CDCl₃): δ 146.5, 131.8, 131.0, 129.7, 126.4, 118.6 (Ar); 129.6 (=CH₂); 127.4 (HC=); 80.8 (CHN); 52.6, 50.1 (NMe); 32.4 (CH₂). Anal. Calcd for C₁₂H₁₆ClN: 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 PdCl₂(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 CH₂Cl₂ (2 × 10 mL). The combined fractions were concentrated to 3–5 mL, and Et₂O was added to precipitate 3c (0.70 g, 72%), which was obtained as a white solid. Analytically pure compound 3c(PF₆), with PF₆⁻ as counterion instead of Cl⁻, was obtained by treating a water solution of 3c with NH₄PF₆. Crystals were formed from a pentane-layered CH₂Cl₂ solution. ¹H NMR 3a (CDCl₃): δ 8.03–7.04 (m, 4 H, Ar); 5.81 (d, 1 H, =CH₂, ³J_{HH} = 16.6); 5.66 (m, 1 H, =HC); 5.40 (d, 1 H, =CH₂, ³J_{HH} = 9.6); 5.07 (m, 1 H, NCH); 3.68, 3.61 (2s, 6 H, NMe₂); 2.85 (t, 2 H, ArCH₂, ³J_{HH} = 7.0); 2.40 (m, 1 H, CH₂); 2.02 (m, 1 H, CH₂). ¹H NMR 3c(PF₆) (acetone-*d*₆): δ 7.66–7.33 (m, 4 H, Ar); 6.01–5.65 (m, 3 H, CH=CH₂); 4.34 (td, 1 H, NCH, ³J_{HH} = 8.0, ³J_{HH} = 3.2); 3.50, 3.38 (2s, 6 H, NMe₂); 3.10 (t, 2 H, ArCH₂, ³J_{HH} = 6.9); 2.48, 2.28 (2m, 2 H, CH₂). ¹³C NMR 3a (CDCl₃): 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 (NMe₂); 23.1, 22.6 (2 CH₂). ¹³C NMR 3c(PF₆) (acetone-*d*₆): δ 142.7, 132.0, 130.7, 130.2, 129.4, 129.2, 127.6, 121.2 (CH=CH₂ and Ar); 75.9 (NCH); 57.1, 53.2 (NMe₂); 23.9, 23.6 (2 CH₂).

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 CH₂Cl₂ (2 × 10 mL). The combined fractions were concentrated, and Et₂O was added to precipitate 3f, which was obtained as an orange solid (0.28 g, 98%). Compound 3f(PF₆), with PF₆⁻ as counterion instead of Cl⁻, was obtained by treating a MeOH solution of 3f with NH₄PF₆, followed by evaporation of the solvent and extraction with CH₂Cl₂. This compound was crystallized from a Et₂O-layered MeOH solution. ¹H NMR 3f (CDCl₃): 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, CH₂); 4.39–4.20 (m, 4 H, C₅H₃ + CH₂N); 4.21 (s, 5 H, C₅H₃); 3.65, 3.27 (2s, 6 H, NMe₂); 3.51 (m, 1 H, CHN). ¹³C NMR 3f (CDCl₃): δ 136.9, 117.9 (HC=); 83.6, 74.2, 71.2, 70.0, 69.4 (C₅H₃); 70.4 (C₅H₃); 64.6, 63.9 (CH₂); 53.0, 50.3 (NMe₂). Anal. Calcd for C₁₆H₂₀F₆FeNP: 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 PdCl₂(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 PPh₃ (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 CH₂Cl₂ (2 × 10 mL). After concentration of the combined CH₂Cl₂ solutions, a precipitate was obtained by addition of Et₂O. The compound **3g** was obtained as white crystals (0.48 g, 2.29 mmol, 79%) from a slow diffusion of pentane into a CH₂Cl₂ solution. Analytically pure compound **3g**(PF₆), with PF₆⁻ as counterion instead of Cl⁻, was obtained by treating a water solution of **3g** with NH₄PF₆. Crystals were formed from a pentane-layered CH₂Cl₂ solution. ¹H NMR (CDCl₃): 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, ArCH₂); 3.70 (d, 2 H, NCH₂); 3.62 (s, 6 H, NMe₂). ¹³C NMR (CDCl₃): δ 140.3 (ArC=); 137.8, 132.0, 130.4, 129.3, 129.2 (Ar); 122.5 (=C); 65.7 (ArCH₂); 60.8 (NCH₂); 51.2 (NMe₂). Anal. Calcd for C₁₂H₁₆NPF₆: 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 (CDCl₃): 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, CH₂, ²J_{HH} = 17.6, ³J_{HH} = 5.4); 3.92 (br d, 1 H, CH₂); 3.74, 3.27 (2s, 6 H, NMe₂); 1.63 (d, 3 H, CH₃). Anal. Calcd for C₁₃H₁₈ClN: 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 Et₂O-layered CH₂Cl₂ solution. ¹H NMR (CDCl₃): δ 7.26–7.12 (m, 4 H, Ar); 5.96 (dd, 1 H, H₂C=, ³J_{HH} = 16.7, ²J_{HH} = 16.7, ²J_{HH} = 1.6); 5.67 (dd, 1 H, H₂C=, ³J_{HH} = 9.6); 5.85 (m, 1 H, HC=); 5.21, 4.85 (2d, 2 H, NCH₂, ²J_{HH} = 15.5); 5.01 (m, 1 H, HCN); 3.58, 3.20 (2s, 6 H, NMe₂); 3.26, 3.20 (dd, 2 H, CH₂, ³J_{HH} = 5.1 and 9.0, ²J_{HH} = 18.5). ¹³C NMR (CDCl₃): δ 128.8–126.5 (Ar and vinyl); 69.8 (NCH); 63.3 (NCH₂); 51.8, 45.5 (NMe₂), 30.3 (CH₂). MS: *m/z* 188 (M⁺), 173, 146, 104. Anal. Calcd for C₁₃H₁₈ClN: 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-(triphenylphosphino)-4-hexene Hydrochloride (4d). PPh₃ (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 CH₂Cl₂ (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 (CDCl₃): 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, CH₂P, ²J_{HP} = 14.5, ³J_{HH} = 7.0); 3.24 (br s, 6 H, NMe₂); 2.91 (m, 2 H, CH₂Ar); 2.14 (m, 2 H, CH₂C=); 1.57 (m, 2 H, CH₂). ¹³C NMR (CDCl₃): δ 142.1 (d, 1 C, CH, ³J_{PC} = 13.3); 140.9–117.5 (24 C, Ar); 115.0 (1 C, =CH, ²J_{PC} = 8.8); 47.8 (s, 2 C, NMe₂); 32.2, 30.5, 30.1 (3 s, CH₂); 27.8 (d, 1 C, CH₂, ¹J_{HP} = 49.6). ³¹P NMR (CDCl₃): δ 20.5 (P⁺). MS for M = [C₃₂H₃₆NP]⁺: *m/z* = 465 (M⁺), 464 ([M - H]⁺), 262 (PPh₃⁺).

1-(N,N-Dimethylanilino-2)-7-(triphenylphosphino)-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 (CDCl₃): 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, CH₂P, ³J_{HP} = 14.3, ³J_{HH} = 6.8); 3.26 (d, 6 H, NMe₂); 2.99, 1.97, 1.45 (3 m, 8 H, 4 CH₂). ¹³C NMR (CDCl₃): 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, NMe₂); 32.6, 31.4, 31.0, 28.1 (4 C, CH₂); 27.9 (d, CH₂P, ¹J_{PC} = 49.2). ³¹P NMR (CDCl₃): δ 20.6 (P⁺). MS for M = [C₃₃H₃₈NP]⁺: *m/z* = 479 (M⁺), 478 ([M - H]⁺), 262 (PPh₃⁺).

1-(N,N-Dimethylammonio)methylphenyl-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 (CDCl₃): 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, CH₂, ³J_{HH} = 5.8); 4.24 (dd, 2 H, CH₂P, ³J_{HP} = 14.6); 2.82 (m, 2 H, CH₂); 2.80 (d, 6 H, NMe₂, ³J_{HH} = 4.7); 2.16 (m, 2 H, CH₂). ¹³C NMR

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	ω/2θ	ω/2θ
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 > 2.5σ(I))	2713	1654
Refinement		
no. of refined reflectns/ 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 = 1/σ ² (F)	w = 1/σ 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

(CDCl₃): 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 (CH₂N); 42.2 (NMe₂); 34.3, 31.5 (2 C, CH₂); 27.8 (d, 1 C, CH₂P, ¹J_{PC} = 50.5). ³¹P NMR (CDCl₃): δ 20.0 (P⁺). MS for M = [C₃₂H₃₆NP]⁺: *m/z* 465 (M⁺), 464 ([M - H]⁺), 262 (PPh₃⁺).

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°. Numerical 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-86²¹ 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.

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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 PLATON²⁵ (including the ellipsoid plot). Final coordinates are given in the supplementary material.

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(26) We thank the reviewers for their critical comments and some interesting suggestions.

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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 $\text{Pd}(\text{PPh}_3)_4$ 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 **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.