

Palladium-Assisted Amination of Olefins. A Mechanistic Study

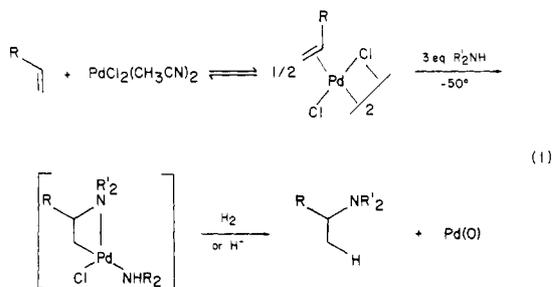
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Abstract: The mechanism of the palladium-assisted amination of olefins has been studied by low-temperature NMR and ultraviolet spectroscopy, conductivity measurements, and stoichiometry and exchange studies. The specific sequence of steps followed strongly depends on the nature of the amine. With dimethylamine, the sequence consists of cleavage of the chloride bridge by the amine to give a single olefin-palladium-amine complex (2). This undergoes amination of the olefin and concomitant cyclization to form the chelating β -aminoalkylpalladium complex (3) directly and dimethylammonium hydrochloride. In contrast, with diethylamine, the initially formed olefin-palladium-amine complex undergoes amination to form a discrete zwitterionic complex (6). This reacts slowly with additional added amine to give the chelating β -aminoalkylpalladium complex (7).

Palladium-assisted attack of nucleophiles on olefins is a long-known, synthetically useful procedure, and it is the basis of a number of commercially important processes. Early studies centered on the use of oxygen nucleophiles such as water, alcohols, and acetate and resulted in the development of the Wacker process, for the conversion of ethene to acetaldehyde, and the related conversions of olefins to vinyl acetates, vinyl ethers, and acetals.² Because of their industrial importance, extensive mechanistic studies of the reactions of oxygen nucleophiles with palladium-bound olefins have been carried out. In spite of this, the area is still subject to much controversy.³⁻⁶

Although nucleophilic attack on palladium-coordinated chelating olefin complexes was a general process,⁷ the use of nitrogen and carbon (carbanion) nucleophiles with monoolefin-palladium(II) complexes met with considerably less success until 1974, when the palladium-assisted amination of monoolefins was developed.⁸ This process required 3 equiv of amine to go to completion, and had to be carried out at low temperature (-50°C) to prevent competitive displacement of the olefin from the metal (eq 1). This amination was successfully extended to intramo-



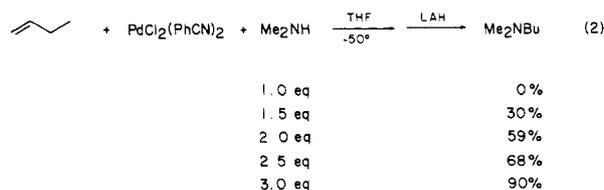
lecular versions, including the palladium(II)-catalyzed cyclization of *o*-allylanilines to 2-alkylindoles^{9,10} and the cyclization of ω -

olefinic tosamides to *N*-tosylated enamines.¹¹ From these amination studies came the realization that the palladium-olefin species reactive toward nucleophiles had amines as auxiliary ligands. This realization permitted the development of the palladium-assisted alkylation of olefins by carbanions.^{12,13}

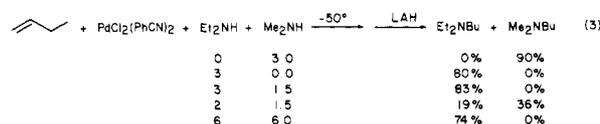
Most of this synthetic work was directed by mechanistic assumptions about the amination process. However, much of the data resulting from these synthetic studies were inconsistent with the working mechanistic hypothesis. Thus, a detailed mechanistic investigation of the palladium-assisted amination of olefins was undertaken. The results of this study are reported below.

Results and Discussion

Three equivalents of amine are required for complete amination of the metal-bound olefin. No amination has occurred after addition of 1 equiv of amine, and a substantial amount of, but not complete, amination has occurred after addition of 2 equiv (eq 2).



Furthermore, with diethylamine as the initial nucleophile, until 3 equiv have been added, the aminated intermediate is labile, and can undergo exchange with added dimethylamine. After 3 equiv of diethylamine have been added no exchange with subsequently added dimethylamine occurs (eq 3).



For a better understanding of these observations, a series of NMR studies was undertaken. A 0.08 M solution of PdCl₂(PhCN)₂ in THF-*d*₈ was placed in a 10-mm NMR tube, 1-butene was added as a gas, the tube was cooled to -50°C in the probe of a 360-MHz NMR instrument, and the NMR spectrum was monitored during the sequential addition of dimethylamine in THF-*d*₈. With no added dimethylamine, the spectrum is that of

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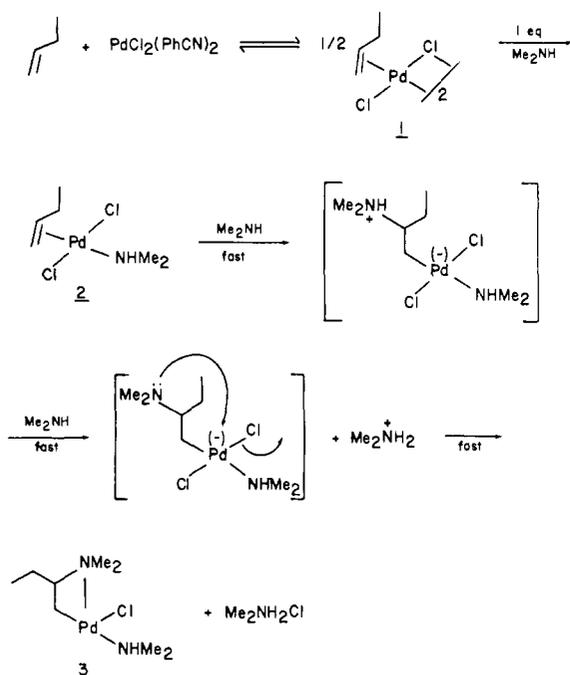
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Scheme I



$[(\pi\text{-}1\text{-butene})\text{PdCl}]_2$ (**1**) rapidly exchanging with free excess butene, as expected [δ 1.30 (br s, 3, CH_3), 2.02 (m, 2, CH_2), 5.00 (m, 2, $=\text{CH}_2$), 6.21 (m, 1, $\text{CH}=\text{}$)]. Upon addition of 1 equiv of dimethylamine, the signals due to exchanging olefin disappear and are replaced by those of free (excess) butene and bound butene in the form of $(\pi\text{-}1\text{-butene})\text{Pd}(\text{Me}_2\text{NH})\text{Cl}_2$ (**2**) [δ 1.40 (t, 3, CH_3), 1.95, 2.28 (m, 2, CH_2), 2.48 (s, 3, $\text{N}-\text{CH}_3$), 2.50 (s, 3, $\text{N}-\text{CH}_3$), 4.8 (m, 2, $=\text{CH}_2$), 6.15 (m, 1, $=\text{CH}$)]. No other species are detectable by NMR. Upon addition of the second equivalent of dimethylamine, the spectrum corresponds to a mixture of complex **2** and a new, aminated product, the cyclic, chelating β -aminoalkylpalladium complex **3** [δ 0.00 (dd, 1, CHPd), 0.75 (t, 3, CH_3), 0.84 (m, 1, CHPd), 1.25, 1.50 (m, 2, CH_2), 3.60 (m, 1, CHN), 3.0 (m, 12, NCH_3)]. Finally, upon addition of the third equivalent of amine, all olefin complex **2** is consumed and only β -aminoalkylpalladium complex **3** is present. (This material has been isolated and purified at low temperatures, and its NMR spectrum corresponds to that observed in the above experiment.) Reduction of this complex gives a high yield of butyldimethylamine. These spectra correspond to the sequence of steps shown in Scheme I. Olefin complex **1** reacts with the first equivalent of amine in a bridge-splitting reaction to produce amino olefin complex **2**. Thus after the first equivalent of amine has been added, no amination of the olefin has occurred, as is observed in eq 2. As additional amine is added a rapid amination of the olefin, deprotonation of the zwitterionic complex, and cyclization to form **3** occurs. Since the deprotonation is rapid, 3 equiv of amine are consumed to form 1 equiv of complex **3**. Hence, amination is still incomplete after a total of 2 equiv of amine has been added, and some olefin complex **2** remains. Addition of the third equivalent of amine converts the remainder of **2** to **3** and completes the amination.

This sequence of NMR measurements was repeated with ethylene as the olefin and diethylamine as the nucleophile. A 0.01 M solution of the preformed ethylene-palladium chloride complex in $\text{THF-}d_8$ was placed in an NMR tube and 1 equiv of gaseous ethylene was added. Diethylamine was then added at -55°C and NMR spectral changes were monitored. As above, prior to addition of any amine, only $[(\pi\text{-ethylene})\text{PdCl}]_2$ (**4**) rapidly exchanging with free ethylene is observed (δ 5.22, s). Upon addition of 1 equiv of amine, the signals due to exchanging olefin disappear and are replaced by free (excess) ethylene and coordinated ethylene in the form of $(\pi\text{-ethylene})\text{Pd}(\text{Et}_2\text{NH})\text{Cl}_2$ (**5**) [δ 1.56 (t, 6, CH_3), 2.41 (m, 2, CH_2N), 3.04 (m, 2, CH_2N), 5.20 (s, 4, $\text{CH}_2=\text{CH}_2$)]. Upon addition of 2 equiv of diethylamine, signals from olefin

Scheme II

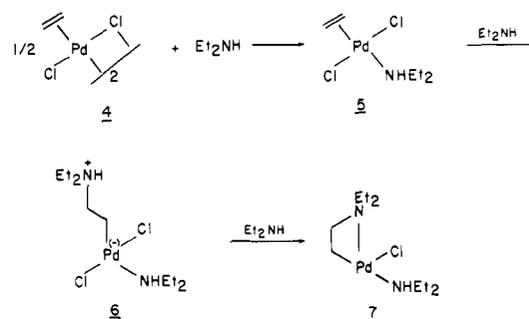


Table I. Amination of 1-Decene with Dimethylamine

expt	mmol of $(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2$	mmol of Me_2NH	base	yield, %
1	0.10	0.30		90.1
2	0.10	0.20		58.7
3	0.10	0.20	<i>i</i> -Pr ₂ NH (28 μL , 0.20 mmol)	92.1
4	0.10	0.20	Na_2CO_3 (21 mg, 0.20 mmol)	67.0
5	0.10	0.20	NaH (5 mg, 0.20 mmol)	65.4
6	0.10	0.20	1-(dimethylamino)pyridine (15 mg, 0.12 mmol)	65.4
7	0.10	0.20	NaOEt (8.2 mg, 0.12 mmol)	68.9

complex **5** are replaced by those of zwitterionic complex **6**, resulting from amination of this olefin [δ 1.43 (m, 12, CH_3), 3.27 (m, 2, CH_2N), 2.75 (m, 4, CH_2N , $\text{CH}_2\text{CH}_2\text{N}$), 3.26 (m, $\text{CH}_3\text{CH}_2\text{N}$)]. This stands in sharp contrast to the complex resulting from amination with dimethylamine (**3**), which rapidly undergoes deprotonation and cyclization. In the absence of excess amine, complex **6** is stable and does not cyclize. Upon addition of the third equivalent of diethylamine, deprotonation and cyclization to complex **7** occurs [δ 0.20 (t, 2, CH_2Pd), 1.52 (t, 6, CH_3), 1.57 (t, 6, CH_3), 2.50 (m, 4, CH_2N), 2.63 (m, 4, CH_2N), 3.99 (t, 2, $\text{CH}_2\text{CH}_2\text{N}$)]. These spectra correspond to the sequence of steps shown in Scheme II. The first step is the same as with dimethylamine, a rapid bridge-splitting reaction to form **5**. Amination then occurs to form the stable zwitterionic complex **6**, which does not cyclize. Apparently this complex is reactive toward amine exchange, since addition of dimethylamine at this stage results in introduction of a dimethylamino group into the olefin in place of the diethylamino group (eq 3). Addition of the third equivalent of diethylamine effects deprotonation and cyclization to form the β -aminoalkyl complex **7**. Once this complex forms, no amine exchange is observed.

The importance of a third equivalent of base is nicely demonstrated by the amination of 1-decene with 2 equiv of dimethylamine, followed by addition of a non-nucleophilic base (Table I).

This same reaction has been followed by UV-vis spectroscopy, and the features detailed in Scheme II were confirmed. Stepwise addition of 0.0625-equiv portions of diethylamine to a 0.0004 M solution of $[(\text{ethylene})\text{PdCl}]_2$ in THF at -50°C results in monotonic spectral changes in the spectrum up to the addition of 1 equiv of amine/Pd. Application of the graphical method of Coleman¹⁴ indicates that only two absorbing species are present in the solution, the starting complex **4** and complex **5**. The rate of this bridge-splitting reaction is too fast to measure on the stopped-flowtime scale ($k > 10^8 \text{ s}^{-1}$). Further addition of amine also shows monotonic spectral changes until an $\text{Et}_2\text{NH}/\text{Pd}$ ratio of 2 is reached. Again, the graphical method of Coleman¹⁴ indicates that only two species are present during this stage of the reaction as well, complexes **5** and **6**. Addition of excess amine leads to no further immediate change in the spectrum since at this low concentration, deprotonation and cyclization to form **7** are slow, and only observed after several hours.

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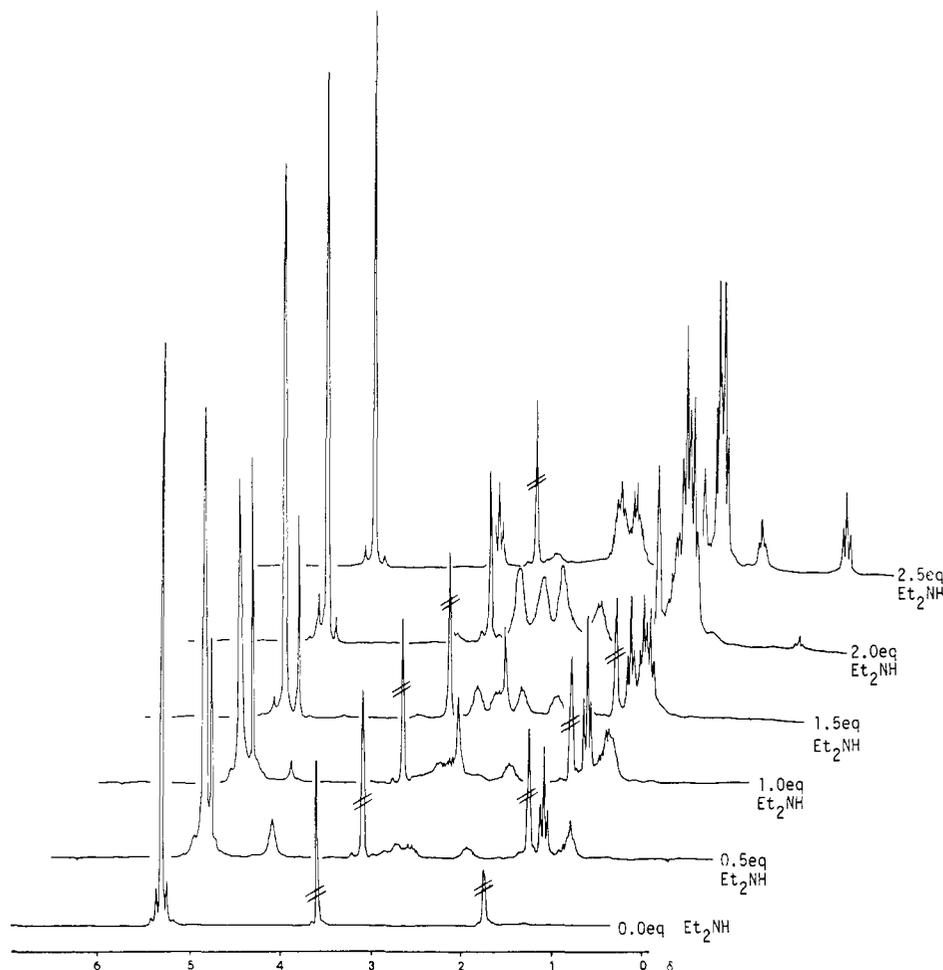


Figure 1. Amination of $[(\text{ethene})\text{PdCl}_2]_2$ by Et_2NH .

Since the bridge-splitting reaction (generation of **5**) is immeasurably fast,¹⁵ and the cyclization (**6** \rightarrow **7**) is very slow, the rate of the amination step (**5** \rightarrow **6**) could be conveniently measured by observing the spectral changes between 260 and 400 nm for the single reaction observed (**5** \rightarrow **6**) when the starting ethylene complex is treated with excess diethylamine. A plot of k_{obsd} (the concentration of excess amine), corrected for the small amount of amine consumed in the bridge-splitting reaction, gives a straight line with an intercept of zero. The slope of this line gives the rate constant k at -50°C in THF as solvent for the amination reaction (**5** \rightarrow **6**) as $k = 540 \pm 30 \text{ M}^{-1} \text{ s}^{-1}$. The same value is obtained when the olefin complex is in excess over the free amine. The rate law can be written as: $d[\mathbf{6}]/dt = k[\mathbf{5}][\text{Et}_2\text{NH}]$.

Repetition of the NMR study at a higher concentration of palladium-olefin complex [0.04 M] revealed additional complexity in the reaction mechanism (Figure 1). Treatment of $\text{PdCl}_2(\text{PhCN})_2$ with 2.5 equiv of ethene in $\text{THF}-d_8$ at -50°C gave a spectrum which had a single olefin peak at δ 5.30, corresponding to ethylene rapidly exchanging with the ethylene-palladium complex. Integration and comparison to the peak area due to benzonitrile (from the starting palladium complex) showed the presence of 2.5 equiv of ethylene. Addition of 0.5 equiv of diethylamine produced complex **5** as above, but only 0.35 equiv was detected, by integration of both the coordinated ethylene peak and the coordinated diethylamine peaks. In addition, a new, broad set of peaks [δ 1.28 (br t), 3.2 (br m)] corresponding to the remainder (0.15 equiv) of the added diethylamine appeared. The peak due to the exchanging ethylene also contained this missing 0.15 equiv of ethylene. This suggests that two different amine-

palladium-olefin species are formed at these higher concentrations, and one of these is undergoing some exchange process which broadens the diethylamine and the ethylene peaks. Addition of the next 0.5 equiv of diethylamine (1.0 equiv total) produces more of both species. By integration there now is 0.5 equiv of complex **5** and 0.5 equiv of the unidentified exchanging amine-olefin-palladium complex. Addition of the next 0.5 equiv of amine (1.5 equiv total) causes substantial changes in the system. All peaks due to the "exchanging" species disappear, and the NMR spectrum corresponds to a 1:1 mixture of complex **5** and complex **6**. Thus, whatever this unidentified species is, it forms during the addition of the first equivalent of amine and is consumed by the time 1.5 equiv have been added. Addition of the remaining 1.5 equiv of diethylamine in 0.5-equiv portions gives spectra identical with those obtained in the experiment at higher dilution discussed above.

Related studies of the reaction of π -allylpalladium halides with amines had shown that these chloro-bridged dimers underwent an unsymmetrical bridge-splitting reaction in THF to produce complex ion pairs of the type $[(\pi\text{-allyl})\text{Pd}(\text{amine})_2]^+[(\pi\text{-allyl})\text{PdCl}_3]^-$ in which the π -allyl groups rapidly exchanged.¹⁶ Since these species are ionic they were detected by conductance measurements, and characterized by NMR spectroscopy and X-ray diffraction studies. To determine if the unidentified exchanging species in the above experiments might be a similar complex ion pair, the conductivity profile for the reaction of dimethylamine with $[(\pi\text{-1-butene})\text{PdCl}_2]$ (0.15 M) in THF at -50°C was examined. As Figure 2 shows, the conductivity increases steadily up to a point at which 1 equiv of amine/Pd has been added, then sharply drops over addition on the next 0.5 equiv of amine. After this point, there is no further change (NOTE! $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ is

(15) A referee has pointed out that THF may split the halogen bridge upon dissolution of the olefin complex and that the addition of amine results in displacement of coordinated THF rather than bridge splitting. The experimental data do not permit distinction between these two possibilities.

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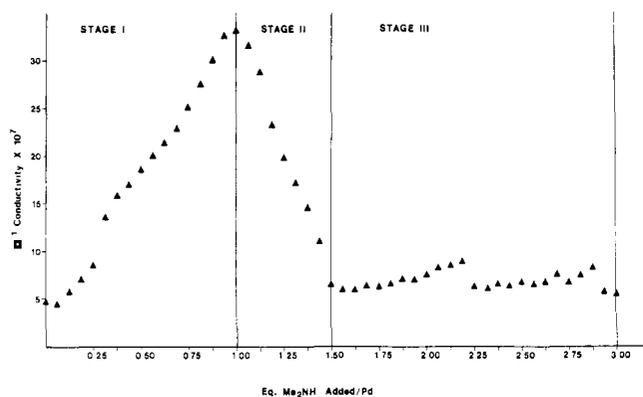
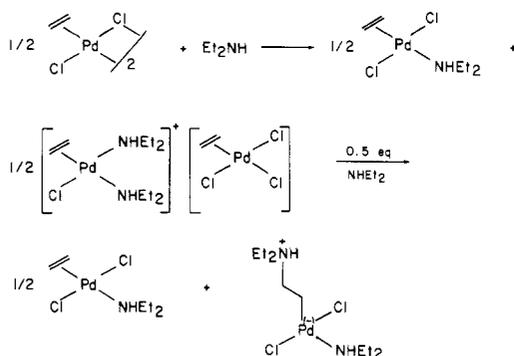


Figure 2. Conductivity profile for the reaction of dimethylamine with $[(\pi\text{-}1\text{-butene})\text{PdCl}]_2$ in THF at -50°C .

Scheme III



insoluble under these conditions and does not conduct). The same reaction using diethylamine and ethylene could not be carried out due to insolubility of the intermediate complexes at concentrations sufficient to permit conductivity measurements (0.1 M). However, the reaction of diethylamine with $[(\pi\text{-}1\text{-butene})\text{PdCl}]_2$ (0.04 M, a slightly more soluble system) showed a similar conductance profile. This conductance profile exactly parallels the NMR results presented above, for which the "exchanging" complex is produced to a maximum over the addition of the first equivalent of amine but is consumed completely during its addition of the next 0.5 equiv of amine. Thus, the "exchanging" complex seen in the NMR may be the charged complex detected by conductance measurements and at higher concentrations. Scheme III may more accurately describe the early stages of the amination reaction. The exact nature of this ionic (conducting) species and its importance to the overall amination reaction have not been established, and the conductivity data are not to be overinterpreted. Although the conductance profiles for amination by both dimethylamine and diethylamine are virtually identical, *no* NMR evidence for an exchanging species is seen with dimethylamine, while with diethylamine this species may account for one-half of the palladium in the early stages of the reactions. Additionally, the conductivities measured were all very low. Regardless, both systems result in rapid, high-yield amination of olefins, albeit by slightly different routes.

Experimental Section

Materials. For the spectrometric studies tetrahydrofuran (THF, Merck Uvasol) was used and for the kinetic work THF (Merck P.A.), distilled once. The NMR studies were done in THF- d_8 (99% Stohler Isotope Chemicals) used as received. For the chemical experiments, THF was distilled from potassium-benzophenone prior to use. Di(μ -chloro)dichloro(diethene)dipalladium(II) was prepared according to Kharasch.¹⁷ Anal. ($\text{C}_4\text{H}_8\text{Cl}_4\text{Pd}_2$): C, H, Cl, Pd. Bis(diethylamine)(dichloro)palladium(II) was prepared from palladium chloride (Baker) and excess diethylamine, (BDH) distilled once, by refluxing for 5 h. Anal. ($\text{C}_8\text{H}_{22}\text{Cl}_2\text{N}_2\text{Pd}$): C, H, Cl, N, Pd. Trichloro(ethene)palladium(II) anion was prepared in solution by adding 1 equiv per palladium of tetrabutylammonium chloride to an ca. 2×10^{-4} M solution of di(μ -chloro)dichloro(diethene)dipalladium(II) in THF at -50°C .

Determination of Stoichiometry. Bis(benzonitrile)palladium(II) chloride (0.30 g, 0.78 mmol) was dissolved in THF (5 mL), degassed with argon, and excess gaseous 1-butene was added via a balloon attached to the stopcock of the flask. This mixture was stirred at 0°C for 20 min, then cooled to -55°C in a dry ice/acetonitrile bath. The desired amount (1–3 equiv) of dimethylamine solution (2.46 M in THF) was added dropwise to the stirred olefin-palladium chloride solution, and the resulting mixture was stirred at -55°C for 40 min. Lithium aluminum hydride (60 mg, solid) was added, and the mixture was allowed to warm to 25°C . Water (0.5 mL) was carefully added to quench the excess lithium aluminum hydride. When hydrogen evolution stopped, toluene (20 μL) was added as an internal GLC standard, a portion of the resulting solution was removed and centrifuged, and the clear supernatant was analyzed by GLC (10 ft, 5% Apiezon N, 85°C). The yields reported in eq 2 were obtained in this manner.

Amine-Exchange Experiments. In a typical procedure bis(benzonitrile)palladium dichloride (0.600 g, 1.56 mmol) was dissolved in 5 mL of THF. After 10 min, the temperature was decreased to -10°C and 10 mL of 1 M 1-butene/THF solution was added. The brown solution was stirred for 20 min, then the temperature was further decreased to -50°C . After 15 min the appropriate amount of amine (i.e., neat Et_2NH , or 2.50 M $\text{Me}_2\text{NH}/\text{THF}$) was added. In the exchange cases this was followed after 20 min by a second addition of the "exchange" amine. After another 25 min at -50°C , LiAlH_4 (60 mg, 1.5 mmol) was added and the temperature was slowly raised to 25°C ; water and toluene (40 μL as internal GLC standard) were added and the mixture was analyzed on GLC as above.

Amination in the Presence of an Added Base. Bis(benzonitrile)palladium dichloride (38.4 mg, 0.10 mmol) was dissolved in 2 mL of THF in a glass tube equipped with a screw cap. The solution was cooled to -5°C and 1-decene (57 μL , 0.30 mmol) was added. After the mixture was cooled to -60°C the appropriate amount of a freshly titrated solution of dimethylamine in THF (2.38 M) was added. After 40 min, the base was added. After 0.5 min, the temperature was quickly raised to -30°C and the reaction was quenched by addition of LiAlH_4 (10 mg, 0.25 mmol) and the cooling was removed. After 50 min, 200 μL of water and internal standard (10 μL of tetradecane) were added and the yields determined by GLC. The results are presented in Table I.

NMR Experiments. (1) Butene-Dimethylamine Reaction. The amination reaction was followed by ^1H NMR. In a typical ^1H NMR procedure dichlorobis(benzonitrile)palladium(II) (96 mg, 0.25 mmol) was dissolved in 3 mL of THF- d_8 in a 10-mm NMR tube. The solution was cooled to -50°C , and 8 mL of gaseous 1-butene was injected via a long-needle syringe. The NMR tube was placed into a centrifuge rubber insert filled with dry ice. Stirring was achieved by placing the insert into a vortex stirrer. With stirring, $\text{Me}_2\text{NH}/\text{THF}-d_8$ (2.76 M, 91 μL , 0.25 mmol) was added slowly through long thin polyethylene tubing connected to a 100- μL syringe. The NMR tube was thereafter transferred to a dry ice cooled bath with absolute ethanol before insertion into the NMR probe. After execution of a sufficient number of scans the above addition procedure was repeated until a total of 1.00 mmol of Me_2NH ($\text{Me}_2\text{NH}/\text{Pd} = 4$) had been added. (All spectra are available as supplementary material.)

(2) Ethene-Diethylamine Reaction. In a typical ^1H NMR procedure (Bruker WP 200) bis(benzonitrile)palladium dichloride (7.7 mg, 0.02 mmol) was dissolved in 0.5 mL of THF- d_8 in a 5-mm NMR tube. At -78°C ethylene (1.8 mL gas, 0.08 mmol) was slowly added via a long-needle syringe. Mixing to a homogeneous solution was achieved with a vortex stirrer while the NMR tube was surrounded by dry ice. The NMR tube was cooled by a bath with dry ice and acetone before insertion into the NMR probe. Integration showed that 0.05 mmol of ethylene had been dissolved (i.e., molar ratio of ethylene/palladium = 2.5).

Addition of Et_2NH was performed in portions as $\text{Et}_2\text{NH}/\text{THF}-d_8$ (0.5 M, 40 μL , 0.01 mmol) increasing the molar ratio of $\text{Et}_2\text{NH}/\text{palladium}$ with 0.5 equiv per addition. Each addition was followed by vortex stirring and NMR recording. The reaction was studied up to a molar ratio of 3.

Preparation of β -Amino- α -Alkylpalladium(II) Complexes. (a) Chloro(2-dimethylaminobutyl)(dimethylamine)palladium(II) (3). Dichlorobis(benzonitrile)palladium(II) (384 mg, 1.0 mmol) was dissolved in 5 mL of THF. At -15°C 1-butene was added from a balloon. The solution was slowly cooled to -60°C . Slow addition (~ 2.5 min) of $\text{Me}_2\text{NH}/\text{THF}$ (2.0 M, 2.5 mL, 5 mmol) turned the originally clear, brown solution to a white heterogeneous mixture. After the mixture was stirred at -60°C for 15 min, the cold mixture was transferred via a cannula through a short, septum-covered, cooled alumina oxide packed column to remove $\text{Me}_2\text{NH}_2\text{Cl}$. Dropwise addition of 7 mL of pentane to the cooled, light, clear solution induced precipitation of product. Cannula transfer of the cold mixture to a cooled, septum-covered fritted filter, washing twice with cold pentane, and evacuation in the cold yielded a white crystalline

Table II. Spectrophotometric Equilibrium Measurements ($t = -50$ °C)

solution	$10^4 C_{\text{Et}_2\text{NH}_2}$ M	$10^4 C_{\text{Pd}}$ M	ϵ, cm^{-1}		
			340 nm	360 nm	390 nm
0	0	4.62			
1	0.25	4.60	0.0968	0.0649	0.0497
2	0.53	4.60	0.1050	0.0740	0.0560
3	0.79	4.60	0.1120	0.0834	0.0610
4	1.04	4.58	0.1190	0.0933	0.0671
5	1.29	4.56	0.1250	0.1030	0.0720
6	1.54	4.56	0.1320	0.1110	0.0785
7	1.81	4.54	0.1380	0.1210	0.0850
8	2.05	4.52			
9	2.32	4.52	0.1500	0.1340	0.0960
10	2.57	4.50	0.1560	0.1450	0.1040
11	2.81	4.50	0.1610	0.1520	0.1090
12	3.05	4.48	0.1660	0.1600	0.1150
13	3.29	4.48	0.1710	0.1680	0.1180
14	3.55	4.46	0.1740	0.1760	0.1230
15	3.79	4.46	0.1820	0.1860	0.1320
16	4.05	4.44	0.1830	0.1940	0.1370

solution	$10^4 C_{\text{Et}_2\text{NH}_2}$ M	$10^4 C_{\text{Pd}}$ M	ϵ, cm^{-1}		
			345 nm	380 nm	405 nm
17	4.29	4.43	0.1760	0.1610	0.0963
18	4.52	4.42	0.1910	0.1580	0.0916
19	4.78	4.41	0.2130	0.1520	0.0888
20	5.26	4.39	0.2330	0.1450	0.0817
21	5.77	4.36	0.2630	0.1380	0.0749
22	6.24	4.34	0.2880	0.1310	0.0684
23	6.67	4.32	0.3140	0.1260	0.0621
24	7.16	4.30	0.3430	0.1180	0.0558
25	7.73	4.28	0.3610	0.1140	0.0495
26	8.34	4.25	0.3610	0.1070	0.0472

^a ϵ denotes the absorptivity.

product, which showed remarkable thermal stability when crystalline. Thus the filter could be weighed at slightly above 0 °C (indicating around 284 mg of product and a yield in the 90% area). The white crystals could be handled at room temperature for a short time without noticeable decomposition. Storage over night in the freezer resulted in decomposition as did addition of acetone or other solvents at room temperature.

¹H NMR (360 MHz) (CDCl_3) δ 0.10 (dd, $J = 10, 6$ Hz, 1, CHPd), 0.75 (t, $J = 7.3$ Hz, 3, CH_3C), 0.88 (t, $J = 7.6$ Hz, CHPd), 1.25, 1.46 (m, 2, $\text{CH}_3\text{CH}_2\text{C}$), 2.2–2.5 (m, 12, CH_3N), 3.61 (m, 1, CHN).

(b) **Chloro(2-diethylaminoethyl)(diethylamine)palladium(II) (7)**. The complex was prepared exactly as above, except ethylene and diethylamine were used in place of butene and dimethylamine. ¹H NMR spectrum (200 MHz) ($\text{THF}-d_6$) δ 0.199 (t, $J = 8.10$ Hz, 2, CH_2Pd), 1.52 (t, $J = 7.0$ Hz, 6, $\text{CH}_3\text{CH}_2\text{N}$), 1.57 (t, $J = 7.0$ Hz, 6, $\text{CH}_3\text{CH}_2\text{N}$), 2.43 (m, 4, CH_2N), 2.64 (m, 4, CH_2N), 4.00 (t, $J = 8.10$ Hz, 2, $\text{CH}_2\text{CH}_2\text{NPd}$).

Conductivity Measurements. Dichlorobis(benzonitrile)palladium(II) (0.90 g, 2.35 mmol) was dissolved in degassed THF (16 mL) and stirred under an atmosphere of 1-butene (balloon) for 10 min at 0 °C. A YSI No. 3402 cell ($K = 0.1$) connected to a YSI 31 bridge was immersed in the solution, which was then cooled to -50 °C in a dry ice/acetone bath. A solution of dimethylamine (3.4 M in THF) was added in 50- μL increments (0.0725 equiv), and the conductance was measured after each addition. A steady increase was noted up to the addition of 1 equiv of amine/eq of Pd. As soon as this point was passed, a precipitate

formed, and the conductivity dropped.

UV Spectroscopic Procedures. Low-temperature (ca. -50 °C) UV and visible absorption spectra were recorded with a Cary 15 spectrometer equipped with a thermostated closed flow titration vessel connected to a flow-through cell (Hellma 170-Q5) with optical path length 0.100–5.00 cm.¹⁸ The amine was added from a piston burette.

In a typical procedure, a known volume, e.g., 30 mL of THF, was transferred with a pipet to the inner vessel of the thermostat. The temperature was lowered to ca. -50 °C and a background (solvent) spectrum was recorded from, e.g., 500 nm to solvent cutoff, 205 nm for 0.100 cm, and 270 nm for the 5.00-cm cell. The wavelength was then set at a fixed value and the stability checked for about 30 min. If moisture was deposited on the cell, an increase in absorbance could be observed. Provided that no change occurred, 30 mL of a THF solution of the appropriate palladium complex was introduced with a pipet. The spectrum was recorded when the temperature of the solution was stable which took about 3 min. In the amination experiments, a small volume, e.g., 0.1 mL, of amine solution was then added and the spectrum recorded after about 5 min.

The spectrum of dichlorobis(diethylamine)palladium(II) was recorded between 205 and 300 nm with use of a 2×10^{-4} M solution in a 0.100 cm cell between 285 and 500 nm using a 1 mM solution of a 5.00 cm cell. The spectrum did not change even after addition of a large excess of amine, up to 230 mM.

The spectrum of the tetrabutylammonium ion pair of trichloro(ethene)palladium(II) was recorded between 205 and 500 nm at ca. 2×10^{-4} M concentration in THF in a 0.100-cm cell.

Spectrophotometric Equilibrium Measurements. The spectra of the solutions listed in Table II were recorded at -47 to -53 °C. For the range 205 to 350 nm 0.100-cm cells were used, and for the range 315 to 500 nm a 5.00-cm cell was used.

Kinetic Measurements. For the kinetic runs, a Hi-Tech Scientific Limited Stopped-flow Spectrometer SF-3L equipped with a 1-cm cell, connected with a control unit SF 30C, was used. According to the specifications the deadtime of the instrument was 7 ms. The stopped-flow experiments at -50 °C were performed under pseudo-first-order conditions, generally using excess added amine but in a few cases with excess olefin–palladium complex.

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Registry No. 2, 92314-31-3; 3, 92314-30-2; 4, 12122-75-7; 6, 92345-41-0; 7, 55640-48-7; $\text{CH}_2=\text{CHCH}_2\text{CH}_3$, 106-98-9; $(\text{PhCN})_2\text{PdCl}_2$, 14220-64-5; Me_2NH , 124-40-3; Et_2NH , 109-89-7; Et_2NBu , 4444-68-2; Me_2NBu , 927-62-8; PdCl_2 , 7647-10-1; $(\text{Et}_2\text{NH})_2\text{PdCl}_2$, 18955-12-9; $(\text{CH}_2=\text{CH}_2)\text{PdCl}_2$, 34664-23-8.

Supplementary Material Available: ¹H NMR spectra of 1, 2, and 3, UV-vis spectra of Pd complexes 4–7, and titration curves for data in Table II (11 pages). Ordering information is given on any current masthead page.

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