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Palladium-Catalyzed Telomerization of Dienes and Tertiary Allylic Amines. A Novel Reaction Involving Cleavage of the Carbon–Nitrogen Bond

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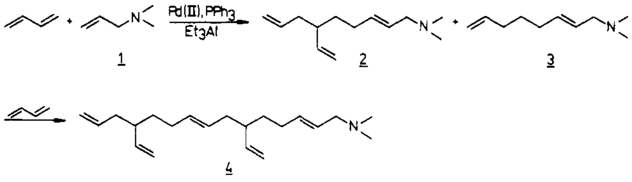
Tertiary allylic amines react with 1,3-butadiene or isoprene in the presence of dichlorobis(triphenylphosphine)palladium(II) and triethylaluminum to give *N,N*-dialkyl-6-allyl-2,7-octadienylamines together with *N,N*-dialkyl-2,7-octadienylamines. The formation of the latter compounds is largely suppressed when palladium chloride anchored to a phosphinated styrene–divinylbenzene polymer is used. The reaction involves the cleavage of the carbon–nitrogen bond of the allylic amines, and it is assumed that Al(III) in addition to reducing Pd(II) to Pd(O) promotes this cleavage.

Introduction

Considerable interest has been devoted to the telomerization of conjugated dienes and various nucleophiles such as alcohols,[1,2] water,[3] carboxylic acids,[1,4] ammonia,[5,6] primary[1] and secondary amines,[4,6-8] hydrazones,[9,10] and active methylene compounds[11] catalyzed by palladium(II) and palladium(0) reagents. The 2,7-octadienyl derivatives that have been isolated in high yields from many of these reactions are useful synthons that have been used for the syntheses of natural products.[12,13] We recently found that palladium(0)–ligand complexes also catalyze the telomerization of dienes and tertiary allylic amines,[14] and herewith our studies of this useful reaction are described.

Results

1,3-Butadiene reacts with *N,N*-dimethyl-2-propenylamine (**1a**) in the presence of catalytic amounts of dichlorobis(triphenylphosphine)palladium(II) and triethylaluminum to give *N,N*-dimethyl-6-(2-ethenyl)-2,8-nonadienylamine (**2**) with an *E*/*Z* ratio of ca. 14:1 along with a small amount of *N,N*-dimethyl-2,7-octadienylamine (**3**).



The product **2** is formed by cleavage of the carbon–nitrogen bond of the allylic amine and the regioselective addition of the amine function and the allylic residue to the 1- and 6-positions of a butadiene dimer, respectively. The reaction is analogous to telomerizations of dienes and other nucleophiles, such as secondary amines, except that an allylic group is replacing a proton. When a large excess of 1,3-butadiene is used in the reaction, the allylic amine **2** slowly reacts further to give telomer **4** (^{1}H NMR and MS), which probably is formed in the same way as **2**. Trace amounts of even higher oligomers of unknown structure are formed as well.

The yield of compound **2** is strongly dependent on the reaction conditions. The reaction is sensitive to moisture and molecular oxygen. An essentially quantitative yield, based on the amine **1a**, was obtained by using a catalyst prepared from palladium chloride, triphenylphosphine, and triethylaluminum with a Pd/P/Al ratio of 1:3:4 to 1:3:10. Higher or lower Pd/P ratios resulted in lower yields. Even when the catalyst is prepared in this way, the reaction is still somewhat unpredictable. In some cases only a small amount of the octadienylamine **3** or no telomer at all was observed. In spite of considerable efforts to find the source for this variation, no satisfactory explanation has been found. The conditions for preparing the catalyst, especially the temperature, seem to have a major influence on the outcome of the reaction. After the catalyst had been prepared at about −70 °C, the reaction mixture was allowed to stir at ambient temperature for several hours and was then heated at about 60 °C.

When the catalyst was prepared from dichlorobis(triphenylphosphine)palladium(II) and triethylaluminum, the yield of product **2** was somewhat lower, but the results were reproducible. Treatment of 30 mmol of 1,3-butadiene with 5 mmol of the allylic amine **1a** in the presence of 0.1 mmol of catalyst gave a 90:10 mixture of the amines **2** and **3** in a total yield of 79% (isolated yield after extraction and Kugelrohr distillation) and ca. 14% of amine **4** after 16 h at 20 °C, followed by 3 h at 60 °C. Under the same conditions, a 4.5-fold excess of 1,3-butadiene resulted in the formation of 67% of a 90:10 mixture of products **2** and **3** and ca. 20% of product **4**. When only 0.005 mmol of catalyst was used, ca. 35% of a 84:16 mixture of compounds **2** and **3** was formed after 14 h at 20 °C, followed by 8 h at 60 °C.

Since optimum conditions for the reaction were obtained with a P/Pd ratio of 3:1, attempts were made to improve the yield of amine **2** by using dichlorobis(triphenylphosphine)palladium(II) together with 1 equiv of triphenylphosphine. However, reactions with catalysts prepared in this way resulted in lower yields of the desired telomer. With the bidentate phosphine bis(1,2-di-

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phenylphosphine)ethane, used together with palladium chloride or in a preformed complex with palladium chloride, lower yields (ca. 10–15%) of amine **2** were obtained. A lack of dimerization of 1,3-butadiene when bidentate phosphines are used has previously been observed.[15]

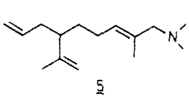
The total yield of the undesired telomer **3** usually ranged from 5 to 10%, even with catalysts that produced low yields of the telomer **2**. When the reaction was followed by GLC, it was found that compound **3** was formed in the initial part of the reaction and the total yield of this telomer then remained constant.

The formation of amine **3** is, however, largely suppressed when a polymer-supported catalyst prepared from a 2% cross-linked Merrifield resin and dichlorobis(benzonitrile)palladium(II) is used. This catalyst has also been found to give a higher *E*/*Z* ratio (>49:1) of **2**. Treatment of 25 mmol of 1,3-butadiene with 5 mmol of *N*,*N*-dimethyl-2-propenylamine in the presence of this polymer-supported catalyst containing ca. 0.04 mmol of Pd and with a P/Pd ratio of 3.5:1 gave 61% of a 98.5:1.5 mixture of amines **2** and **3** after 18 h at 20 °C, followed by 4 h at 60 °C. A somewhat lower yield, 48%, of a 98.5:1.5 mixture of compounds **2** and **3** was formed under the same conditions using 75 mmol of 1,3-butadiene, 5 mmol of amine, and a catalyst containing 0.01 mmol of Pd. Large amounts of higher telomers, mainly compound **4**, were formed in these reactions. The amounts correspond essentially to complete conversion of the allylic amine.

Triethylaluminum reduces Pd(II) to Pd(0), but in addition Al(III) probably acts as a Lewis acid in the reaction, as shown by the lack of formation of amine **2** using tetrakis(triphenylphosphine)palladium(0) as a catalyst. Attempts have been made to use butyllithium and ethylmagnesium bromide in place of triethylaluminium. In the former case only oligomers of butadiene were formed, probably in a reaction catalyzed only by butyllithium.[16] From the latter reaction no products were isolated.

Isoprene reacts analogously to 1,3-butadiene, although slightly higher reaction temperatures and/or longer reaction times are required. Compound **5** and two isomers, probably **6** and **7**, were formed in a ratio of 80:14:6 (*E*/*Z* ratios not determined) along with ca. 10% of terpene amines, of which **8** and **9** are the major isomers, in a total isolated yield of 63%. Optimum conditions for the reactions were 19 h at 20 °C followed by 50 h at 60 °C or 25 h at 80 °C. A higher reaction temperature (100 °C) gave a somewhat lower yield of the products. In these reactions, no variation of the isomeric distribution with time or with temperature was observed. From reactions with *cis*- and *trans*-1,3-pentadiene no analogous telomers were detected.

Substituted allylic amines can be used in place of the amine **1a**, although the yields of the less desireable telomer **3** are usually higher. From *N*,*N*-dimethyl-2-methyl-2-propenylamine and 1,3-butadiene a 87:13 mixture of amines **10** (*E*/*Z* ratio ca. 12:1) and **3** were formed in a total yield of 47%, together with higher telomers, which are probably analogous to compound **4**. *N*,*N*-Dimethyl-*trans*-2-butenylamine on reaction with 1,3-butadiene gave a 38:37:25 mixture of compounds **11** (as a 1:1 mixture of two diasteromers), **12**, and **3** in a total yield of 28%, whereas only compound **3** (50%) was isolated from the reaction with *N*,*N*-dimethyl-3-methyl-2-butenylamine. The fate of the lost allyl group is unknown.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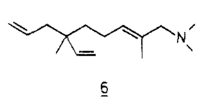
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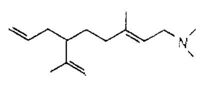
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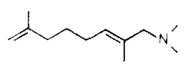
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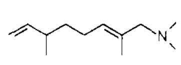
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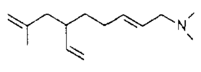
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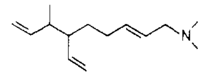
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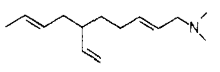
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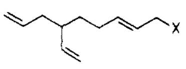
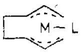

13 a X=Cl
b X=OAc
c X=CN
d X=OH

Other allylic substrates such as 2-propenylacetate and 2-propenenitrile react analogously to tertiary allylic amines with butadiene when palladium chloride is replaced by palladium acetate or palladium acetylacetonate. These reactions were, however less regioselective, the yields of the telomers were lower, and the results were often difficult to reproduce. When telomers with other functional groups than amines are desired, these are more conveniently prepared by standard reactions starting from the amines. The allylic chloride **13a** was obtained in 85% yield by reaction of the amine **2** with ethyl chloroformate. Compound **13a** could in turn be transformed into the acetate **13b** (85%) or into the nitrile **13c** (96% by NMR) by reaction with potassium acetate and sodium cyanide, respectively. Hydrolysis of the acetate afforded the alcohol **13d** (85%).

Discussion

It is generally accepted that nickel-catalyzed telomerizations of conjugated dienes and nucleophiles proceed via bis(η^3-allyl) metal complexes **14**.[17] Such complexes have repeatedly been suggested to be also involved in palladium-catalyzed telomerizations.[12] Strong support for this hypothesis comes from the recent isolation of the (η^1,η^3-octadienyl)palladium complex **15** and its reaction with methanol to give a 2,7-octadienyl ether.[18] This reaction was investigated by NMR, and it was shown to involve the coordination of the alcohol to palladium, followed by proton transfer from oxygen to palladium.

Bimetallic complexes **16** have also been suggested as intermediates in palladium-catalyzed telomerizations,[1] and further support for a bis(palladium) species in the palladium-catalyzed reaction of isoprene with ammonia has recently been presented.[6]



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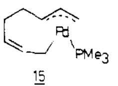

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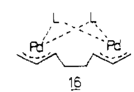

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The telomerization of conjugated dienes with tertiary allylic amines has a close analogy to reactions with primary and secondary amines in which the allylic group is replaced by a proton. The reactions show the same regioselectivity as demonstrated by the formation of *N*,*N*-diethyl-6-deuterio-2,7-octadienylamine from 1,3-butadiene and *N*-deuterio-*N*,*N*-diethylamine.[19] Although experimental evidence presently is lacking, it seems appropriate to assume that these reactions follow similar mechanisms.

The Lewis acid and palladium(0) probably assist in the cleavage of the carbon–nitrogen bond of the allylic amine. The palladium(0) is assumed to coordinate to the double bond and the aluminum atom to nitrogen. Reactions involving the cleavage of the carbon–nitrogen bond of allylic amines have previously been observed in similar systems. Upon reaction with catalytic amounts of Pd(II) and triethylaluminum, *N*,*N*-dialkyl-3-(1,7-octadienyl)amines rearrange to *N*,*N*-dialkyl-2,7-octadienylamines.[20] Disproportionation of 2-propenylamine to ammonia, bis(2-propenyl)amine, and tris(2-propenyl)amine has been observed by using the same catalytic system.[21,22] Dienes are formed from tertiary allylic amines bearing δ protons using palladium(0) and protic acids as catalysts.[23] A (η^3-allyl)palladium complex, formed by oxidative addition of the protonated allylic amine to Pd(0), has been suggested as an intermediate in this elimination. Furthermore, it has been recently reported that *N*,*N*-diethyl-2-propenylamine reacts with a stoichiometric amount of $Zn[Co(CO)_4]_2$, a complex involving both a transition metal and a main-group metal, to give a (η^3-allyl)cobalt carbonyl complex and zinc(II) amide.[24] The ability of the Lewis acid to coordinate to the palladium atom of a (η^3-allyl)palladium complex, analogous to nickel complexes,[25] may also be of importance.

A few other cases are previously known where one carbon atom and one heteroatom are added to a butadiene dimer. In these cases cyclic compounds are formed by the addition of carbon–heteroatom double bonds to the 3- and 6-positions of bis(allyl)palladium complexes. Ketones react with 1,3-butadiene to give divinyltetrahydropyrans,[26] isocyanates react to give divinyl-δ-valerolactams,[27] and carbon dioxide to give a δ-lactone.[28] Olefins, on the other hand, are known to insert into the carbon–palladium bond of the bis(η^3-allyl)palladium complex.[17]

We have previously observed that on reaction of secondary amines with an excess of 1,3-butadiene in the presence of dichlorobis(triphenylphosphine)palladium(II), C_{16} amines are slowly formed. Octadienylamines are probably intermediates in these reactions, since C_{16} amines are formed in palladium-catalyzed reactions of octadienylamines with 1,3-butadiene as well.[29] The formation of small amounts of higher telomers has also been observed in a few other cases, such as in the palladium-catalyzed telomerization of isoprene and secondary amines,[7] and under certain conditions high yields of C_{16} adducts from butadiene and alcohols have been obtained.[30] It is not clear whether these higher oligomers are formed by insertion of a double bond into the carbon–palladium bond of a bis(allyl)palladium complex, or whether they are formed by cleavage of the carbon–heteroatom bond of the initial octadienyl adduct, analogous to the reactions described here.

Experimental Section

All reactions involving organometallic reagents were performed under purified nitrogen. The syntheses of tertiary allylic amines and their reactions with 1,3-dienes were performed in oven-dried Fisher & Porter autoclaves (aerosol compatibility vessel purchased from Fisher & Porter). 1,3-Butadiene, 3-chlorobutene, dimethylamine, *N*,*N*-dimethyl-2-propenylamine, ethyl chloroformate, isoprene, and 3-methyl-3-butenyl bromide were obtained from Fluka. 2-Methyl-2-propenyl chloride, triethylaluminum and triphenylphosphine were obtained from Merck. Isoprene was refluxed over sodium, distilled from $NaBH_4$, passed through a column containing a mixture of powdered KOH, powdered anhydrous $CaSO_4$, and SiO_2 (230–400 mesh) (1:1:1 by volume), and finally distilled and stored under nitrogen with molecular sieves (4 Å). Triethylaluminum was dissolved in dry toluene (20% solutions) before use and stored under nitrogen. Toluene (PA grade) and methylene chloride were dried over $CaCl_2$ and distilled from $CaCl_2$ before use. Dimethyl sulfoxide (Me_2SO) was distilled and dried with molecular sieves (4 Å). Dichlorobis(triphenylphosphine)palladium(II) was prepared from disodium tetrachloropalladate and triphenylphosphine and dichlorobis[ethylenebis(diphenylphosphine)]palladium(II) according to Sanger.[31] Polymer-supported palladium complexes were prepared by reaction of a commercial chloromethylated styrene–2% divinylbenzene resin (Fluka) containing 2.3 mmol of Cl/g with lithium diphenylphosphide in tetrahydrofuran (distilled from benzophenone ketyl) followed by reaction with dichlorobis(benzonitrile)palladium(II) in benzene (reflux 2 h).

NMR spectra were recorded on a Bruker WP-200 FT spectrometer ($CDCl_3$ as solvent and Me_4Si as internal standard). IR spectra were recorded on a Perkin-Elmer 257 spectrometer. Analytical GLC was performed on a Varian Aerograph Series 1400 instrument using a 1.8 m × 3 mm steel column packed with 20% Apiezon L + 10% KOH on Chromosorb W (for amines) and on a Pye GCD chromatograph using a 1.2 m × 2 mm glass column of 5% SE 30 on Chromosorb W. Preparative GLC was performed on a PYE-104 instrument using a 1 m × 6 mm glass column of 20% Apiezon L + 10% KOH on Chromosorb W. Mass spectra were run on an LKB 9000 instrument. A syringe pump from Sage Instruments, Model 355, was used. Microanalyses were performed by Analytical Laboratories, Engelskirchen, Germany.

Synthesis of Tertiary Allylic Amines. General Procedure. Dimethylamine (2.2 equiv) was distilled into a Fisher & Porter autoclave (vessel size 250 mL) equipped with a magnetic stirrer at −78 °C. The allylic halide (1 equiv) was added, the cooling bath (dry ice–EtOH) was removed, and the mixture was allowed to warm to ambient temperature and to stir for 48 h. The reaction mixture was extracted with an excess of saturated sodium hydroxide, the organic layer was separated, and the excess dimethylamine was removed by distillation. The residue was distilled twice from sodium hydroxide to a vessel containing molecular sieves (4 Å) and stored under nitrogen.

***N*,*N*-Dimethyl-2-methyl-2-propenylamine (1b).** Reaction of dimethylamine (19 g, 422 mmol) and 2-methyl-2-propenyl chloride (17.1 g, 190 mmol) afforded 13.5 g (72%) of **1b**: ^1H NMR (200 MHz, $CDCl_3$) δ 1.75 (s, 3 H), 2.18 (s, 6 H), 2.79 (s, 2 H), 4.84 (m, 2 H).

***N*,*N*-Dimethyl-3-methyl-2-butenylamine (1c).** Reaction of dimethylamine (8.6 g, 191 mmol) and 3-methyl-2-butenyl bromide (12.7 g, 86 mmol) afforded 4 g (41%) of **1c**: ^1H NMR (200 MHz, $CDCl_3$) δ 1.65 (s, 3 H), 1.74 (s, 3 H), 2.21 (s, 6 H), 2.86

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(d, 2 H, J = 6.1 Hz), 5.24 (m, 1 H).

***N,N*-Dimethyl-2-butenylamine (1d) and *N,N*-Dimethyl-1-methyl-2-propenylamine (1e).** Treatment of dimethylamine (12 g, 266 mmol) with 3-chloro-1-butene (10.8 g, 120 mmol) gave 6.8 g (57%) of a mixture of 1d (74%) and 1e (26%). Amine **1d**: ^{1}H NMR (200 MHz, $CDCl_3$, mixture): δ 1.69 (d, 3 H, J = 6.4 Hz), 2.20 (s, 6 H), 2.83 (d, 2 H, J = 5.9 Hz), 5.4–5.9 (m, 2 H). Amine **1e**: ^{1}H NMR (200 MHz, $CDCl_3$, mixture) δ 1.4 (d, 3 H, J = 6.6 Hz), 2.23 (s, 6 H), 2.8–2.95 (m, 1 H), 5.02–5.15 (m, 2 H), 5.4–5.9 (m, 1 H).

General Procedure for the Reactions of 1,3-Dienes with Tertiary Allylic Amines. $PdCl_2(PPh_3)_2$ was placed in a Fisher & Porter autoclave (vessel size 90 mL) equipped with a magnetic stirrer. The autoclave was flushed with nitrogen and cooled to −78 °C (dry ice–EtOH bath). The other reagents were added to the autoclave under a nitrogen atmosphere in the following order: the 1,3-diene, the tertiary allylic amine, toluene, and finally triethylaluminum as a 20% solution in toluene (dropwise over 1–2 min). After the cooling bath was removed, the slurry was stirred for 16–21 h at ambient temperature, followed by 3–49 h at 60–90 °C (depending on the diene and amine). The mixture was diluted with diethyl ether (ca. 50 mL) and extracted with 2 M HCl (2 × 50 mL); the aqueous phase was washed with diethyl ether (2 × 50 mL), made alkaline with saturated sodium hydroxide, and extracted with diethyl ether (3 × 50 mL). After the organic phase was dried ($MgSO_4$), the solvent was removed under reduced pressure (water aspirator) and the crude product was distilled under reduced pressure in a Kugelrohr apparatus.

Reaction of 1,3-Butadiene and 1a. A mixture of $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), 1,3-butadiene (1.63 g, 30.2 mmol), the amine **1a** (425 mg, 5 mmol), toluene (1 mL), and Et_3Al (1 mmol) was stirred at ambient temperature for 16 h and then heated at 60 °C for 3 h. Kugelrohr distillation at 45–90 °C (ca. 0.5–1 torr) gave a 9:1 mixture of **2**[32] and **3**[33] (745 mg, 79%). Increasing the temperature to ca. 170 °C gave **4** (ca. 14%).

Compound 2: MS (70 eV), *m/e* (relative intensity) 193 (16), 192 (50), 178 (40), 152 (100), 150 (39). Anal. Calcd for $C_{13}H_{23}N$: C, 80.76; H, 11.99; N, 7.25. Found: C, 80.78; H, 11.90; N, 7.07.

Compound 4: ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.17–1.57 (m, 4 H), 1.8–2.2 (m, 10 H), 2.20 (s, 6 H), 2.83 (d, 2 H), 4.87–5.08 (m, 6 H), 5.3–5.9 (m, 7 H); MS (70 eV), *m/e* (relative intensity) 301 (8), 300 (18), 260 (40), 152 (100), 150 (60). Anal. Calcd for $C_{21}H_{35}N$: C, 83.64; H, 11.71; N, 4.65. Found: C, 83.54; H, 11.67; N, 4.59.

Reaction of Isoprene and 1a. Stirring a mixture of $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), isoprene (1.36 g, 20 mmol), the amine **1a** (425 mg, 5 mmol), toluene (1 mL), and Et_3Al (1 mmol) at ambient temperature for 19 h and then at 80 °C for 49 h afforded a mixture of **5** (72%), **6** (13%), and **7**, (5%) along with **8** and **9** (10%) in a total yield of 63%.

Compound 5: ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.3–1.5 (m, 2 H), 1.62 (s, 6 H), 1.8–2.2 (m, 5 H), 2.15 (s, 6 H), 2.75 (s, 2 H), 4.64–4.80 (m, 2 H), 4.9–5.07 (m, 2 H), 5.26 (b t, 1 H, J = 7 Hz), 5.6–5.83 (m, 1 H). Anal. Calcd for $C_{15}H_{27}N$: C, 81.37; H, 12.30; N, 6.33. Found: C, 81.42; H, 12.22; N, 6.38.

Compound 6: ^{1}H NMR (200 MHz, $CDCl_3$, mixture with **7**) δ 0.97 (s, 3 H), 1.25–1.4 (m, 2 H), 1.62 (s, 3 H), 1.8–2.2 (m, 4 H), 2.14 (s, 6 H), 2.73 (b s, 2 H), 4.95–5.09 (m, 4 H), 5.18–5.33 (m, 1 H), 5.62–5.88 (m, 2 H).

Compound 7: ^{1}H NMR (200 MHz, $CDCl_3$, mixture with **6**) δ 1.4–1.55 (m, 2 H), 1.62 (s, 6 H), 1.82–2.2 (m, 5 H), 2.21 (s, 6 H), 2.87 (d, 2 H, J = 7 Hz), 4.66–4.8 (m, 2 H), 4.86–ca. 5 (m, 2 H), 5.18–5.33 (m, 1 H), 5.62–5.88 (m, 1 H).

Reaction of 1,3-Butadiene and 1b. A mixture of $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), 1,3-butadiene (1.5 g, 27.8 mmol), the amine **1b** (450 mg, 4.54 mmol), toluene (1 mL), and Et_3Al (1 mmol) was stirred at ambient temperature for 16 h and then heated at 60 °C for 5.75 h. A 87:13 mixture of **10** and **3** (491 mg, 52%) was obtained.

Compound 10: ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.15–1.58 (m, 2 H), 1.68 (s, 3 H), 1.9–2.2 (m, 5 H), 2.20 (s, 6 H), 2.84 (d, 2 H, J = 5.4 Hz), 4.62–4.76 (2 H, m), 4.9–5.02 (m, 2 H), 5.38–5.64 (m, 3 H). Singlets at δ 1.71 and 2.22 and a doublet at δ 2.92 probably originate from the cis isomer of **10** (ca. 8%). Anal. Calcd for $C_{14}H_{25}N$: C, 81.08; H, 12.16; N, 6.76. Found: C, 81.20; H, 12.21; N, 6.69.

Reaction of 1,3-Butadiene and 1c. Stirring a mixture of $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), 1,3-butadiene (1.85 g, 34.2 mmol), the amine **1c** (375 mg, 3.32 mmol), toluene (1 mL), and Et_3Al (1 mmol) at ambient temperature for 21 h and then heating at 90 °C for 7 h afforded 254 mg (50%) of **3**.

Reaction of 1,3-Butadiene and the Mixture of 1d and 1e. Reaction of $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), 1,3-butadiene (1.62 g, 30 mmol), a mixture of amines **1d** and **1e** (500 mg, 5 mmol), toluene (1 mL), and Et_3Al (1 mmol) at ambient temperature for 21 h, followed by 70 °C for 6 h, afforded 290 mg (28%) of a 38:37:25 mixture of **11**, **12**, and **3**.

Compound 11: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 and 0.97 (two d of equal intensity originating from the two diasteromers, 3 H, J = 6 Hz), 1.1–1.65 (m, 2 H), 1.78–2.28 (m, 5 H), 2.20 (s, 6 H), 2.84 (d, 2 H, J = 5.5 Hz), 4.88–5.09 (m, 4 H), 5.36–5.82 (m, 4 H); MS, *m/e* (relative intensity) 207 (10), 206 (35), 192 (23), 152 (100), 150 (28). Anal. Calcd for $C_{14}H_{25}N$: C, 81.08; H, 12.16; N, 6.76. Found: C, 80.97; H, 12.05; N, 6.86.

Compound 12: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.2–1.7 (m, 2 H), 1.64 (d, 3 H, J = 4.5 Hz), 1.8–2.2 (m, 5 H), 2.20 (s, 6 H) 2.84 (d, 2 H, J = 5.5 Hz), 4.88–5.03 (m, 2 H), 5.27–5.67 (m, 5 H); MS, *m/e* (relative intensity) 207 (25), 206 (54), 192 (32), 152 (100), 150 (93). Anal. Calcd for $C_{14}H_{25}N$; C, 81.08; H, 12.16; N, 6.76. Found: C, 80.98; H, 12.18; N, 6.74.

Reaction of 1,3-Butadiene and 1a Using the Polymer-Supported Palladium Complex. A mixture of polymer-bound $PdCl_2(PPh_3)_n$ (100 mg, 0.01 mmol of Pd, P/Pd ratio 3.5:1), 1,3-butadiene (4.05 g, 75 mmol), the amine **1a** (425 mg, 5 mmol), toluene (1 mL), and Et_3Al (1 mmol) was reacted at ambient temperature for 18 h and then heated at 60 °C for 4 h. A 98.5:1.5 mixture of **2** and **3** (463 mg, 48%) was obtained. The ^{1}H NMR spectrum of **2** prepared in this way is identical with that of **2** prepared using the homogenous catalyst, except that peaks originating from the cis isomer are absent.

6-(2-Ethenyl)-2,8-nonadienyl Chloride (13a). To a solution of ethyl chloroformate (1.0 g, 9.3 mmol) in 10 mL of dry CH_2Cl_2 a solution of the amine **2** (1.48 g, 7.7 mmol) in 5 mL of dry CH_2Cl_2 was added over a 1-h period with a syringe pump at ambient temperature. After the solution was stirred for an additional hour, the solvent was removed in vacuo (water-aspirator pressure). The residue was flash chromatographed on a SiO_2 (230–400 mesh) column using pentane as the eluant to afford 1.2 g (85%) of pure **13a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.2–1.6 (m, 2 H), 1.9–2.2 (m, 5 H), 4.02 (d, 2 H, J = 6.1 Hz), 4.9–5.1 (m, 4 H), 5.45–5.9 (m, 4 H); IR (film) 680 cm^{-1}.

6-(2-Ethenyl)-2,8-nonadienyl Acetate (13b). To a solution of the chloride **13a** (1.52 g, 8.27 mmol) in 20 mL of dry Me_2SO was added potassium acetate (3.16 g, 32.25 mmol). After the mixture was stirred at ambient temperature for 1.5 h, followed by 1.5 h at 60 °C, 20 mL of water was added and the mixture was then extracted with 3 × 30 mL of pentane. The combined organic phase was dried ($MgSO_4$) and the solvent removed in vacuo to yield 1.46 g (85%) of **13b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.2–1.6 (m, 2 H), 1.9–2.2 (m, 5 H), 2.06 (s, 3 H), 4.51 (d, 2 H, J = 6.25 Hz), 4.9–5.1 (m, 4 H), 5.45–5.9 (m, 4 H) (a doublet at δ 4.61 probably originates from the cis isomer); IR (film) 1740 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.94; H, 9.68; O, 15.38. Found: C, 74.83; H, 9.62; O, 15.21.

6-(2-Ethenyl)-2,8-nonadienol (13d). To a solution of the acetate **13b** (187 mg, 0.90 mmol) in 4 mL of methanol was added 0.6 mL of 2 M sodium hydroxide. The mixture was refluxed for 50 min, 5 mL of brine was added, and the methanol was removed in vacuo (water-aspirator pressure). The residue was extracted with pentane (3 × 10 mL), the organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure to yield 127 mg (85%) of **13d**: ^{1}H NMR (200 MHz, $CDCl_3$) 1.2–1.6 (m, 2 H), 1.55 (b s, 1 H), 1.9–2.2 (m, 5 H), 4.09 (b s, 2 H), 4.9–5.07 (m, 4 H), 5.47–5.87 (m, 2 H). The singlet at δ 1.55 disappears after shaking the solution with D_2O.

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(32) ^{1}H NMR and ^{13}C NMR spectra are reported in ref 14.

(33) Identical (GLC, MS, NMR) with an authentic sample.