Reactivity and Syn–Anti Isomerization of (η^3-Geranyl)- and (η^3-Neryl)palladium Complexes. Evidence for Electronic Control of the Regiochemistry of Nucleophilic Addition

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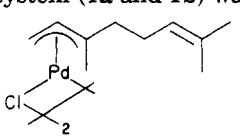
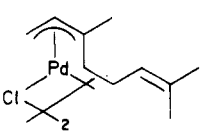
Cationic (η^3-geranyl)- and (η^3-neryl)palladium complexes containing different auxiliary ligands, such as triphenylphosphine, bipyridine, and TMEDA, have been prepared in better than 90% isomeric purity. The fact that the second double bond of the system coordinates more strongly in the geranyl isomer may be used to explain the differences in the regiochemistry of the products from amination of geranyl and neryl complexes. The auxiliary ligands influence the reactivity more strongly than the double bond, which is readily displaced. Triphenylphosphine probably acts as a fair acceptor ligand, as also indicated by ^{13}C NMR, and accelerates amination while TMEDA, which can only act as an electron donor, inhibits amination. The donor–acceptor properties also strongly influence the regiochemistry of amination. It is suggested that triphenylphosphine directs toward the more substituted terminus of the η^3-allyl system due to its acceptor properties.

High stereospecificity, high yields, and tolerance of other functional groups all contribute to make palladium-catalyzed substitution of allylic acetates (Scheme I) a highly useful synthetic reaction.[2] However, the important problem of regiocontrol has been only partly solved. Trost and his co-workers have shown that steric factors are important and an unsymmetric allyl system may be preferentially reacted at the less substituted position by the use of sterically demanding nucleophiles.[2,3] In analogy to acid-catalyzed Markovnikov-type of addition to olefins, it should also be possible to effect preferential reaction at the more substituted position by increasing the electron demands of the metal in the intermediate (η^3-allyl)palladium complex, for instance, by addition of acceptor ligands. Studies of the reactions of (η^3-allyl)palladium complexes in the presence of diethyl diazenedicarboxylate[4] and of (η^3-allyl)molybdenum and -tungsten systems[5] indicate that this concept is correct. Furthermore, extensive work by Schwartz on reductive elimination involving η^3-allyl complexes shows that addition of maleic anhydride (a fair acceptor) has a profound influence on the regiochemistry.[6] During a study of the mechanism and regiochemistry of alkylation of (η^3-allyl)palladium complexes, the geranyl/neryl system (**1a** and **1b**) was used as one of the models.[4a]



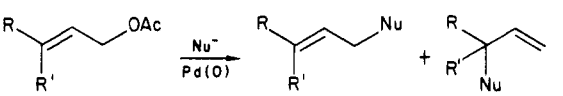
1a



1b

The results were difficult to understand until it was realized that η^3-geranyl/η^3-neryl isomerization is unusually facile and that the two isomers give different product patterns. In fact, it has earlier been observed that geranyl and neryl acetates gave different regioisomers in some alkylation reactions.[3b] A possible explanation seemed to be that the second double bond in these molecules acts as an acceptor ligand and is selectively coordinated in one of the isomers. We therefore decided to investigate the η^3-geranyl/η^3-neryl system in more detail. Here we report the results from amination of these systems with a series of simple amines.

Scheme I



Preparation and Structure of (η^3-Geranyl)palladium Complexes. In order to study the difference in reactivity between geranyl and neryl complexes, it was necessary to prepare these in a pure form. When geranyl chloride, prepared essentially free from isomers from geraniol, was reacted with palladium(0), a 1.1:1 mixture of (η^3-geranyl)- (**1a**) and (η^3-neryl)palladium chloride (**1b**) was formed.[4a] This appears to be the equilibrium composition since the same result is obtained when a mixture of geranyl and neryl chlorides is used as starting material.

The NMR spectrum of the mixture displays two separate sets of signals for chemically equivalent protons (Table I). By double-resonance techniques and by careful integration (the isomers are present in a slightly different abundance) an assignment of the individual resonances to **1a** or **1b** can be made. As with 3-methylbutenyl complexes,[7] the configuration of the isomers was established by observing the nuclear Overhauser effect (NOE) when the 3-methyl protons were irradiated. For one isomer, a 20% enhancement of the signal from the C-2 proton was observed, consistent with the neryl structure **1b**, while for the other isomer only a small enhancement (~4%) was observed in agreement with the geranyl structure **1a**.

In solution and at thermodynamic equilibrium the isomer ratio of η^3-geranyl to η^3-neryl was generally constant and close to 1:1 irrespective of the ligands and counterions. However, treatment of the mixed dimeric chloride complex with silver fluoroborate gave the essentially pure η^3-geranyl isomer. In an even better procedure, using Ag-$(CH_3CN)_4^+BF_4^-$, the pure geranyl complex **2a** could be

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Table I. Selected ^{1}H NMR Data of the Geranyl and Neryl Complexes[a]

	δ (J, Hz)						
compd	H^{1a}	H^{1s}	H^2	H^6	Me^8	Me^9	Me^{10}
1a[b]	2.79 dd	3.54 dd	4.52 dd	5.06 t[c]	1.52 s[c]	1.62 s[c]	0.91 s
1b[b]	2.74 dd	3.50 dd	4.43 dd	4.91 t[c]	1.46 s[c]	1.59 s[c]	1.24 s
2a	3.74 dd	4.47 dd	6.02 dd	5.67 dd	2.07 s[c]	1.85 s[c]	1.47 s
3a[d]	3.31 dd	4.09 dd	5.36 dd	5.15 t[c]	1.65 s[c]	1.72 s[c]	1.31 s
3b[d]	3.19 dd	4.03 dd	5.34 dd	5.03 t[c]	1.61 s[c]	1.69 s[c]	1.53 s
4a	3.39 dd	3.90 dd	5.55 dd	5.01 t[c]	1.56 s[c]	1.67 s[c]	1.40 s
4b	3.26 dd	3.88 dd	5.59 dd	5.00 t[c]	1.56 s[c]	1.64 s[c]	1.24 s
5a	3.75 dd	4.25 dd	5.53 dd	5.20 t[c]	1.61 s[c]	1.70 s[c]	1.38 s
5b	3.63 dd	4.18 dd	5.55 dd	4.99 t[c]	1.52 s[c]	1.58 s[c]	1.73 s
6a	3.15 dd	3.62 dd	5.27 dd	5.11 t[c]	1.61 s[c]	1.71 s[c]	1.22 s
6b	3.04 dd	3.61 dd	5.31 dd	4.95 t[c]	1.57 s[c]	1.67 s[c]	1.44 s
7a	2.96 ddd (9.8)[e]	3.75 dt (8)[e]	5.57 dd	4.79 t[c]	1.45 s[c]	1.61 s[c]	1.29 dd (6.5, 5.4)
7b	2.81 ddd (9.8)[e]	3.75 dt (8)[e]	5.77 dd	4.86 t[c]	1.45 s[c]	1.63 s[c]	1.15 dd (11, 6.3)
8a	3.23 m (10.4)[f]	4.34 m (7.2)[f]	5.44 dd	4.92 t[c]	1.48 s[c]	1.65 s[c]	1.07 t (6.4)
8b	3.17 m (10.3)[f]	4.39 m (7.3)[f]	5.57 dd	4.81 t[c]	1.45 s[c]	1.62 s[c]	1.87 dd (9.8, 8.5)
9a	3.79 dd	4.65 dd	5.73 dd	5.11 t[c]	1.62 s[c]	1.70 s[c]	1.55 s
9b	3.63 dd	4.62 dd	5.80 dd	4.98 t[c]	1.58 s[c]	1.67 s[c]	1.92 s

[a] $CDCl_3$ solution. s = singlet, m = multiplet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, and ddd = double double doublet. $1 < J_{1a1s} < 2.5$ Hz; $7.5 < J_{1s2} < 8.2$ Hz; $12 < J_{1a2} < 14$ Hz. ^{31}P coupling constants are displayed in parentheses. [b] C_6D_6 solution. [c] A fine structure, due to long-range coupling, is also detectable. [d] CD_3CN–$CDCl_3$ (25:75, v/v) solution. [e] Coupling with the trans P nucleus. [f] The coupling with the cis P nucleus is also detectable: $J_P \approx 1.5$ Hz.

isolated in good yield. The structure was established unambiguously by NMR experiments in the following way: First, only one set of signals from chemically equivalent protons is observed. Second, integration shows that only one molecule of acetonitrile is coordinated to the metal. Third, the double bond at the 6-position is coordinated since the C-6 proton and the C-7 methyl proton resonances appear at lower fields than in any of the other cationic complexes, the difference being 0.5–0.9 ppm for the olefinic proton and 0.2–0.5 ppm for the methyl protons. The coordination of the double bond is further indicated by the fact that the four methylene protons at C-4 and C-5 separate sufficiently such that they can all be individually distinguished. The C-5 protons are separated by 0.5 ppm and couple to the olefinic proton at C-6 with remarkably different coupling constants (4 and 11 Hz), which is only consistent with a dissymmetric structure as would result from coordination of one face of the C-6 double bond. Fourth, the complex is mononuclear. Models indicate that a neryl structure could be favored for a mononuclear complex, as also suggested by Verhoeven.[8] It is therefore important to establish that the observed shifts are not due to intermolecular coordination. The nuclearity was established by studying the addition of acetonitrile to complex **2a** in $CDCl_3$ solution in an NMR tube. As the amount of acetonitrile was increased, all ^{1}H resonances of **2a** moved upfield. At the same time, a second set of signals appeared that had constant frequencies independent of the acetonitrile concentration. The spectral changes are consistent with the existence in solution of multiple equilibria as depicted in Scheme II. Complexes **2a** and **3a** were evidently in fast equilibrium since an average spectrum was observed. The second set of signals, the frequencies which are independent of the acetonitrile concentration, may be ascribed to the neryl-type compound **3b**. This complex was evidently in slow (on the NMR time scale) equilibrium with **2a** and/or **3a** as is frequently observed for syn–anti isomerizations (cf. ref 9; see Figure 1).

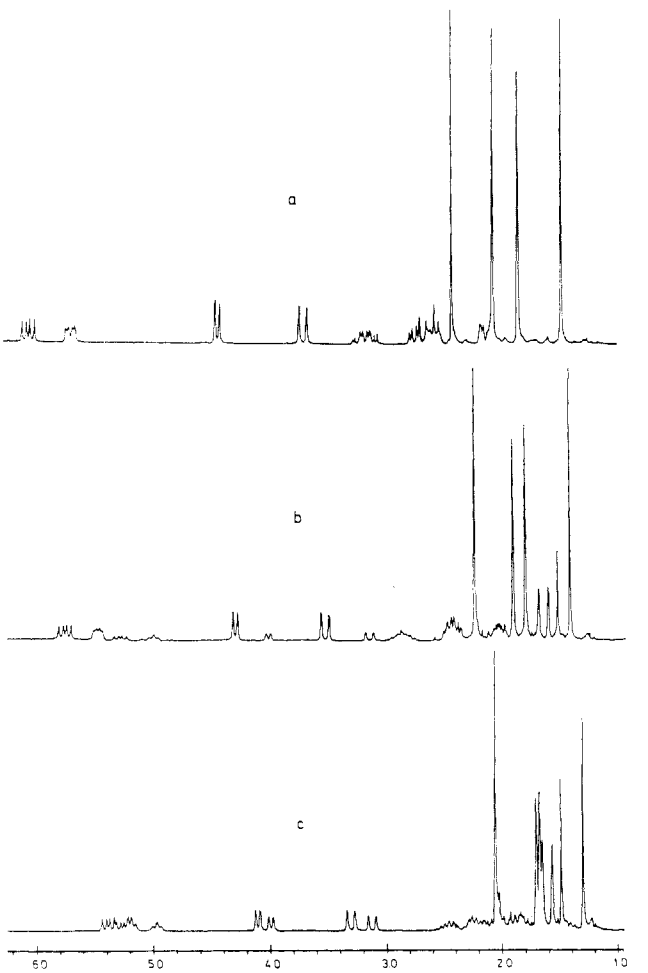

Figure 1. 200-MHz ^{1}H NMR spectra of a 0.090 M solution of **2a** in $CDCl_3$: (a) pure; (b) after addition of 0.125 mmol/mL of CD_3CN; (c) after addition of 0.80 mmol/mL of CD_3CN. For the assignments see Table I.

The equilibrium between **2a** and **3a** can be written in compact form: $(GPdL)_n + nL \rightleftarrows nGPdL_2$, where G denotes geranyl and L acetonitrile. The equilibrium equation

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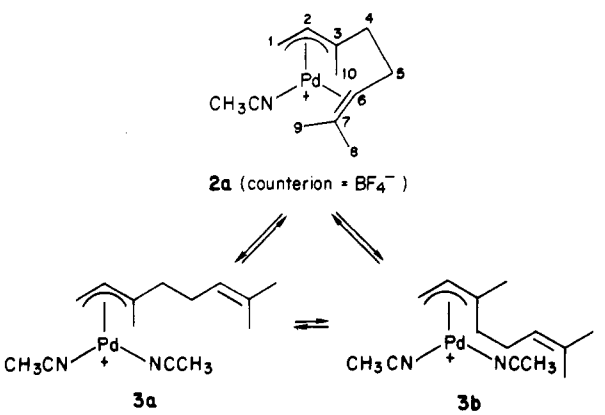
Table II. ^{13}C NMR Data ($CDCl_3$) of the Geranyl and Neryl Complexes[a]

compd	δ (J_P, Hz)										ligand carbons
	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	
1a[b]	55.95	105.16	98.61	40.09	25.61	122.88	132.47	17.68	25.67	20.00	
1b[b]	55.71	106.53	98.61	34.97	26.72	122.88	132.32	17.68	25.56	24.57	
2a	62.89	117.02	117.23	45.00	33.13	115.63	125.96	19.65	27.07	20.06	CN, 123.68; Me, 2.49
5a	58.95	111.87	94.30	38.65	26.34	122.32	133.32	17.68	25.55	20.09	2,2′, 154.63, 153.55; 3,3′, 123.70, 123.49; 4,4, 141.14, 140.72; 5,5′, 127.75, 6,6′, 154.28, 149.63
5b	58.26	113.27	94.75	35.13	26.75	122.32	133.20	17.60	25.40	23.04	2,2′, 154.70, 153.60; 3,3′, 123.77, 123.50; 4,4′, 141.07, 140.77; 5,5′, 127.82; 6,6′, 154.24, 149.68
6a	56.48	111.64	92.08	39.59	26.60	122.28	133.37	17.69	25.65	18.36	NMe, 52.44, 51.26, 50.19, 49.19; NCH_2, 61.09, 59.76
6b	56.48	112.41	91.62	34.10	27.16	122.28	133.04	17.64	25.59	23.25	NMe, 52.51, 51.15, 50.10, 48,87; NCH_2, 61.09, 59.76
7a	66.31 dd (2.3) (27.5)	112.90 t (5.7)	121.93 dd (3.7) (24.8)	38.75 d (3.7)	24.42 dd (4.1) (8.8)	122.44	132.87	17.57	25.54	19.29 d (5.3)	1, 130.86 dd (1.2, 43.3), 129.66 d (40.3); 2, 133.69 d (13) 133.38 d (12.7); 3, 128,89 d (10.5), 128,81 d (10.3); 4, 130.96
7b	66.00 dd (2.3) (27.5)	114.07 t (5.7)	122.12 dd (3.7) (24.7)	34.39 d (4.5)	27.57 dd (4.0) (9.0)	121.98	*c*	17.53	25.54	22.93	1, 131.00 (d) (43), 129.47 d (40); 2, 133.72 d (13), 133.42 d (12.9); 3, 128.30 d (10.5), 128.84 d (10.2); 4, 130.97
8a	61.06 dd (5)	114.42 t (6)	112.63 dd (6)	40.38 d (3.5)	27.84 t (4)	122.11	133.15	17.61	25.58	18.38	CH_2, 28.70 dd (14, 31)8 26.74 dd (14, 32)[d]
8b	61.18 dd (4.2) (29.3)	115.65 t (6.3)	112.81 dd (6.2) (27.3)	33.69 d (4.8)	27.26 t (4.8)	122.12	133.19	17.55	25.53	24.51 d (4.0)	1, 130.76 d (44), 129.57 d (41), 128.61 d (40), 126.92 d (42); 2, 133.88 d (13.5), 132.45 d (13.2), 132.42 d (13), 123.55 d (11), 129.43 d (10.3); 4, 132.55, 131.86, 131.40; CH_2, 28.56 dd (13.8, 31.3), 26.85 dd (13.3, 31.9)
9a[b]	67.49	117.27	117.51	40.79	26.82	121.61	133.67	17.60	25.50	19.38	CC, 118.16, 115.50, 113.77, 112.26; CH_2, 29.57, 23.42, 28.77, 28.13
9b[b]	67.11	118.04	117.20	34.49	27.45	121.64	133.60	17.54	25.45	25.00	C=C, 119.58, 115.20, 113.44, 112.64; CH_2, 29.64, 23.48, 28.77, 28.05

[a] T = 30 ± 2 °C. Chemical shifts referred to the central peak of the $CDCl_3$ triplet settled at δ 77.00. d = doublet, t = triplet, and dd = double doublet. Phosphorus couplings constants (Hz) in parentheses. Digital resolution: 0.75 Hz/point. [b] Since at room temperature the two isomers can only be obtained as equilibrium mixtures, the assignment of the resonances to each isomer was made with the help of selective proton decoupling and/or the slightly different abundance of the two isomers. [c] Not found. Probably overlapped by the phosphine C-2 resonances. [d] The frequencies in the aromatic region were not measured. The C-7 resonance at δ 133.15 was found because of the isomeric impurity of **8a** in the **8b**-^{13}C sample.

Scheme II



can be written as $[GPdL_2]^n/[G_nPd_nL_n] = K_n[L]^n$. The concentration of a hypothetical polymeric complex $[G_nPd_nL_n]$ can be expressed as a function of the formal concentration of the monomeric unit: $[G_nPd_nL_n] = (1/n)[GPdL]$. Inserting this into the equilibrium equation and rearranging gives $[GPdL_2]/[GPdL] = (K_n/n)[L]^n/[GPdL_2]^{n-1}$ or $\log([GPdL_2]/[GPdL]) = \log(K_n/n) + n \log[L] - (n-1) \log[GPdL_2]$. The species $GPdL_2$ (**3a**) and GPdL (**2a**) are in fast equilibrium in solution and give an averaged NMR spectrum.

Since the spectra for the pure species could be determined (that of **3a** by adding a large excess of acetonitrile), their relative concentration and thus $\log[GPdL_2]/([PdL]$ were determined at different acetonitrile concentrations. When this was plotted vs. log [L], a straight line with a slope of 1 was obtained, showing that the complex **2a** must indeed be mononuclear.[10a]

Finally, the stereochemistry of compounds **2a**, **3a**, and **3b** in solution was established by studying NOE and ^{13}C NMR spectra. In the NOE experiments, the 3-methyl group was irradiated. In the average spectrum of **2a** and **3a** only a small increase (~3%) in the intensity of the mean C-2 proton signal was observed. However, the corresponding experiment with **3b** resulted in a greater increase (~18%). The complexes **2a** and **3a** must therefore have a geranyl structure while **3b** has a neryl structure. This is also indicated by the ^{13}C chemical shifts of the C-4 and 3-methyl carbons of **2a**, **3a**, and **3b** and several of their derivatives (Table II). Thus in **2a** and its TMEDA (**6a**), bipyridine (**5a**), and triphenylphosphine (**7a**) complexes, the 3-methyl carbon resonances appear at a field about 3 ppm higher than those of isomers **5b**, **6b**, and **7b**. The reverse is observed for the C-4 resonance. This is completely analogous to the effects observed for geraniol, nerol, and their derivatives.[11] Thus, these results clearly indicate a geranyl structure for **2a** and its derivatives and a neryl

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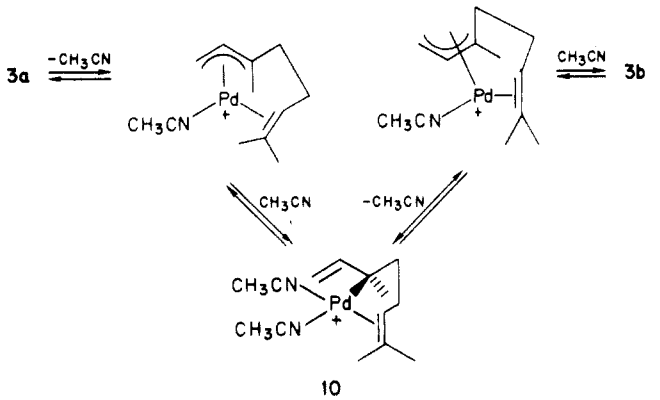
Scheme III



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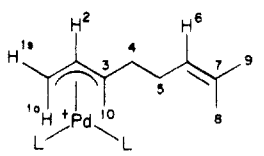
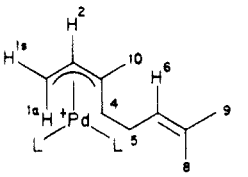
structure for the isomers. This result is strongly supported by the X-ray structure which shows beyond doubt that **2a** has a geranyl structure in the solid state.[10b]



4a, L = pyridine
5a, L_2 = bipyridine
6a, L_2 = TMEDA
7a, L = PPh_3
8a, L_2 = diphos
9a, L_2 = 1,5-cyclooctadiene



4b, L = pyridine
5b, L_2 = bipyridine
6b, L_2 = TMEDA
7b, L = PPh_3
8b, L_2 = diphos
9b, L_2 = 1,5-cyclooctadiene

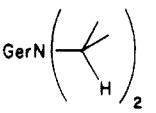
counterion BF_4^-; L_2 =

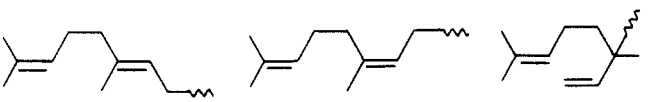
In contrast to acetonitrile, several other ligands produce complexes that are stable to syn–anti isomerization. It was thus possible to take advantage of the geranyl structure of **2a** to prepare a series of other geranyl complexes. For example, addition of >2 equiv of pyridine to **2a** gave the bis(pyridine) complex **4a**. Similarly, triphenylphosphine, bipyridine, TMEDA, and diphos gave complexes **5a**–**8a**. Only the 1,5-cyclooctadiene complex **9a** behaved like the acetonitrile complex **3a** and underwent rapid syn–anti isomerization.

Preparation of η^3-Neryl Complexes. The neryl complexes **4b**–**9b** could initially only be obtained as 1:1 mixtures with the corresponding geranyl complexes by reacting the 1:1 mixture of the chloride complexes **1a** and **1b** with silver fluoroborate followed by the appropriate ligand. However, it was found that on recrystallization of the bipyridine complex **5** the desired neryl isomer **5b** was enriched in the first crop of crystals. The enrichment could be maintained throughout the whole crystallization by adding a small amount of either the bridged chloride complex **1** or the cationic complex **2a** (which both catalyze syn–anti isomerization) to a solution of **5** in ethanol and allowing for slow crystallization. In this way an equal mixture of **5a** and **5b** could be converted to crystals containing ~70% **5b**. By fractional crystallization of this sample about 50% total yield of 90% neryl isomer **5b** could be obtained.

By displacement of the bipyridine ligand, the (η^3-neryl)palladium phosphine complexes **7b** and **8b** were obtained from **5b**.

Syn–Anti Isomerization of (η^3-Geranyl)- and (η^3-Neryl)palladium Complexes. In the early amination experiments the product patterns were difficult to reproduce. The reason was found to be the high aptitude for positional isomerization of the primary products formed by amination at the more substituted terminus C-3 of the η^3-allyl system. However, primary reaction at the less substituted terminus C-1 gave stable products. Since the amination is stereospecific, reaction at C-1 of a geranyl system yields a geranyl product while the neryl system gives a neryl product. However, when either system reacts at C-3, stereochemical integrity is lost and subsequent positional isomerization gives a mixture of geranyl and neryl products, irrespective of the stereochemistry of the starting η^3-allyl complex, e.g., **14c** → **14a** + **14b**. The stereochemistry of the products can thus be used as a probe for primary reaction at C-3 followed by rapid isomerization to the products from reaction at C-1. This is of course only true when syn–anti isomerization (which will also effect geranyl–neryl isomerization) is slow relative to amination. A study of syn–anti isomerization was therefore necessary.

Ger_2NCH_3	Ner_2NCH_3	$LinNHCH_3$
12a	**12b**	**13**
$GerN(CH_3)_2$	$NerN(CH_3)_2$	$LinN(CH_3)_2$
14a	**14b**	**14c**
$GerN^+(CH_3)_3$	$NerN^+(CH_3)_3$	
15a	**15b**	**16**



Ger Ner Lin

It has been observed that a number of different ligands such as phosphines, amines, dienes, and carbon monoxide promote syn–anti isomerization, probably by generating σ-complexes (for a review, see ref 9).

Syn–anti isomerization is obviously also important in the geranyl–neryl system. For instance, the reaction between geranyl chloride and palladium(0) gives a mixture of η^3-geranyl and η^3-neryl complexes,[4a] which on formation of the cationic species gives only the pure η^3-geranyl complex **2a**. The cyclooctadiene complex **9a** also undergoes facile syn–anti isomerization at room temperature. However, with more strongly coordinating ligands, such as triphenylphosphine, bipyridine, and TMEDA, syn–anti isomerization is not observed as long as the reaction mixture is kept at room temperature or below.[12] These results indicate that isomerization may only occur when the internal double bond can coordinate. A possible intermediate is a σ-complex similar to **10**, as suggested also for some systems analogous to the geranyl system (Scheme III).[13] Therefore in the reactions described in Table III, syn–anti isomerizations will not generally be expected to compete with aminations.

Positional Isomerization of the Primary Amination Products. In contrast to syn–anti isomerization, positional isomerization of the amination products turned out to be a severe problem at room temperature. For instance, the reaction between the neryl complex **7b** and di-

(12) (a) A dynamic syn–anti exchange of the terminal η^3-allyl protons is observed in some cases. Examples are addition of pyridine to the diphos complex **8a** (but not to the triphenylphosphine complex **7a**) and addition of less than 2 equiv of triphenylphosphine to the bipyridine complex **5a**. For a related example cf. Powell, J. *Can. J. Chem.* **1973**, *51*, 279.

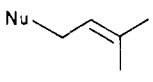
(13) (a) Guthrie, D. J. S.; Spratt, R.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1971**, 935. (b) Hughes, R. R.; Powell, J. *J. Am. Chem. Soc.* **1972**, *94*, 7723.

Table III. Reactivity Data in the Amination Reactions[a]

compd	amine	conditns	approxim half-life	yield,[b] %	isomer distributn[b,c]
2a	$MeNH_2$ (4 equiv)	12 h, rt	nr		
2a	Me_2NH (6 equiv)	8 h, rt	3 h	75%	>95% Ger (**14a**)
2a	Me_3N (3 equiv)	0.5 h, rt	4 min	>90%	>95% Ger (**15a**)
5a	$MeNH_2$ (4 equiv)	24 h, rt	>4 h	30%	75% Ger (**12a**),[d] 25% Ner (**12b**)[d]
5a	Me_2NH (3 equiv)	2 h, rt	10 min	>90%	>98% Ger (**14a**)
5a	Me_3N (3 equiv)	12 h, rt	nr		
5a	i-Pr_2NH (3 equiv)	12 h, rt	nr		
5b	$MeNH_2$ (4 equiv)	12 h, rt	>5 h	<20%	63% Ger (**12a**),[d] 37% Ner (**12b**)[d]
5b	Me_2NH (3 equiv)	4 h, rt	0.5 h	>90%	>95% Ner (**14b**)
5b	Me_3N (3 equiv)	12 h, rt	nr		
7a	$MeNH_2$ (2 equiv)	5 min, rt	<10 s	>90%	63% Lin (**13**), 37% Ger (**12a**)[e,f]
7a	$MeNH_2$ (2 equiv)	20 min, −30 °C, excess PPh_3	<4 min	>90%	70% Lin (**13**), 30% Ger (**12a**)[e,f]
7a	Me_2NH (3 equiv)	5 min, rt	<10 s	>90%	>95% Ger (**14a**)
7a	Me_2NH (3 equiv)	10 min, −30 °C, excess PPh_3	<2 min	>90%	84% Ger (**14a**), 16% Lin (**14c**)
7a	Me_3N (3 equiv)	15 min, rt	<1 min	>90%	>97% Ger (**15a**)
7a	i-Pr_2NH (3 equiv)	3 h, rt	20 min	60%	>97% Ger (**16**), myrcene (**19**) and ocimene byproducts
7b	$MeNH_2$ (3 equiv)	5 min, rt	<10 s	>90%	>90% Lin (**13**), 3% Ner (**12b**)
7b	$MeNH_2$ (3 equiv)	20 min, −30 °C, excess PPh_3	<4 min	>90%	>95% Lin (**13**)
7b	Me_2NH (3 equiv)	5 min, rt	<10 s	>90%	45% Ger (**14a**), 55% Ner (**14b**)
7b	Me_2NH (3 equiv)	10 min, −30 °C, excess PPh_3	<3 min	>90%	86% Lin (**14c**), 14% Ner (**14b**)
7b	Me_3N (3 equiv)	15 min, rt	<2 min	80%	95% Ner (**15b**)
7b	Me_3N (3 equiv)	20 min, −30 °C, excess PPh_3	<5 min	>90%	>97% Ner (**15b**)
7b	i-Pr_2NH (3 equiv)	4 h, rt	40 min	<20%	myrcene (**19**) main product
6a	Me_2NH (3 equiv)	24 h, rt	nr		
6a	Me_3N (3 equiv)	24 h, rt	nr		

[a] rt = room temperature (19–25 °C); nr = no reaction; C (complex) ≃ 0.1 M. [b] The accuracy in the total yields and isomer distributions that are not given as a minimum or maximum value can be estimated to be ±5–10% for the yields and ±3–5% for the abundance of the major isomer. [c] The data for the reaction of the neryl compounds that were used only in 90% isomeric purity are corrected to the result expected from a pure neryl species. This was done by subtracting from the actual isomeric composition the amounts of the products obtained from the geranyl complex (present in 10% abundance), inferred by the known reactivity data of the pure geranyl complexes. [d] Mixed species GerNerNH are most likely also present in the mixture. [e] Note that the percent composition refers to the moles of product formed, not to the moles of complex converted. [f] When the reaction is performed with increasing amounts of $MeNH_2$ ($n > 2$), increasing amounts of the monoalkylated product GerNHMe are also formed, while the percentage of the linalylamine **13** is almost unchanged.

methylamine gave approximately equal amounts of geranyl- (**14a**) and nerylamine (**14b**). Similar results have been observed by Trost and Keinan.[14] However, when the reaction was carried out at −30 °C, we saw (by recording the NMR spectrum of the mixture at intervals) that the linalylamine **14c** was initially formed and it then isomerized to a mixture of **14a** and **14b**. This isomerization was retarded by excess triphenylphosphine. This may explain why in earlier experiments the amination of (η^3-3-methylbutenyl)palladium complexes gave **17** (Nu = Me_2N)



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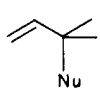


17

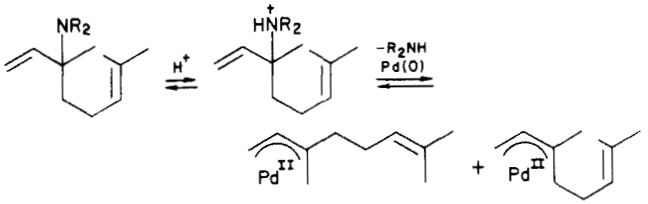
selectively in the presence of excess triphenylphosphine but **18** (Nu = Me_2N) when only 1 equiv was added.[15] This conclusion is supported by the fact that alkylation with anions of dialykyl malonates gives a product pattern which is unchanged by excess triphenylphosphine.[4a] The importance of isomerization of the primary amination product is illustrated by some further experiments.

When dimethylamine and the neryl complex **7b** are reacted at −30 °C and a large excess (>4 equiv) of triphenylphosphine is added to precipitate palladium(0) as $Pd(PPh_3)_4$, the linalylamine **14c** can be isolated in a form about 90% pure. If **14c** is subjected to the ordinary reaction conditions at room temperature or treated with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in the presence of dimethylamine and a small amount of acid, it rapidly isomerizes to a ca. 1:1 mixture of **14a** and **14b**. The isomerization is strongly dependent on the leaving group and the ability of the substrate to coordinate to palladium(0). Thus the nerylamine **14b** does not isomerize at room temperature under the ordinary reaction conditions for amination, probably due to the lower coordination power of the internal double bond.

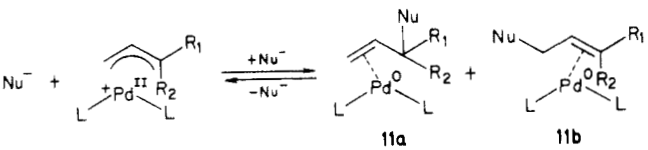
(14) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1979**, *44*, 3451.

(15) Åkermark, B.; Åkermark, G.; Hegedus, L. S.; Zetterberg, K. *J. Am. Chem. Soc.* **1981**, *103*, 3037.

Scheme IV



Scheme V



11a 11b

With a better leaving group than the partly protonated dimethylamine even the neryl system isomerizes as shown by adding dimethylamine to the quarternary ammonium salt **15b** under the ordinary reaction conditions to give again a 1:1 mixture of the geranyl- and nerylamines **14a** and **14b** in a very rapid reaction.

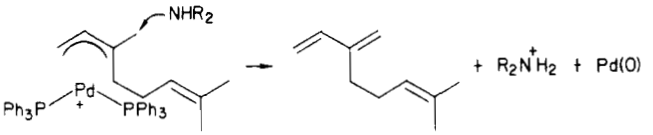
The necessity for protonation may be demonstrated by the relative stability of the linalylamine **14c** to isomerization if no proton souce is available. A mechanism for the isomerization is presented in Scheme IV.

Although positional isomerization is clearly a problem, it can readily be detected since it is accompanied by geranyl–neryl isomerization. This should also apply to other transferable nucleophiles, e.g., alcohols and carboxylates. The geranyl–neryl system is thus very useful for mechanistic studies of the type described here.

Amination of Cationic η^3-Geranyl and η^3-Neryl Complexes. In order to study the relative reactivity and regiochemistry, the geranyl complexes **2a**, **5a**, **6a**, and **7a** and the neryl complexes **5b** and **7b** were reacted with methyl-, dimethyl-, trimethyl-, and diisopropylamine, representing amine nucleophiles of varying nucleophilicity and steric requirements. The results are given in Table III. As would be expected, the preference for reaction at the less substituted terminus of the η^3-allyl system increases as the amine becomes more bulky. The relative overall reactivity of the amines is more difficult to predict. According to theoretical studies and gas phase reactivity, the relative nucleophilicity is $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$.[16] The observed order in the reactions with the geranyl and neryl systems is generally $(CH_3)_2NH > CH_3NH_2 \geq (CH_3)_3N$, demonstrating the sensitivity of the reaction to steric factors. An exception is the chelate complex **2a** that reacts at the relative rates predicted by theory, that is $(CH_3)_3N \gg (CH_3)_2NH \gg CH_3NH_2$.

The auxiliary ligands have a major influence on the reactivity of the complexes which appears to be related to their donor–acceptor properties. The high reactivity of complexes **7** may thus be ascribed to the acceptor properties of triphenylphosphine, as shown by its ability to stabilize palladium(0). All the amines react rapidly with complexes **7** except diisopropylamine, which also gives triene byproducts (Table III). Bipyridine is mainly a donor, and the reactivities of the bipyridine complexes **5** are much lower. Dimethylamine reacts moderately fast, methylamine sluggishly, and trimethylamine not at all. The TMEDA complexes **6** do not react even with dimethylamine. The reaction may be described in a simplified way by Scheme V, which illustrates the suggested influence of the ligands. A ligand such as TMEDA will be expected to selectively stabilize palladium(II) while the phosphines will also stabilize palladium(0). If the transition state for the forward reaction is "product-like" which is in agreement with earlier suggestions,[21-23] it will only be stabilized by the phosphine ligands. These should thus induce high reactivity, which is consistent with the experimental evidence. The influence on reactivity by simple amines (that will be expected to coordinate less strongly than TMEDA) is illustrated by the reactions of the chelate complex **2a**. By NMR it can be shown that the internal double bond is rapidly displaced by trimethylamine, dimethylamine, and methylamine. The two latter compounds also displace the acetonitrile ligand. Therefore bis(amine) complexes appear to be probable intermediates. In fact, the reactivities of the complexes parallel the expected coordinative power of the amines;[24] hence methylamine, which should give the most stable bis(amine)palladium(II) complex, is unreactive whereas dimethylamine reacts fairly slowly and trimethylamine rapidly.

Scheme VI



19

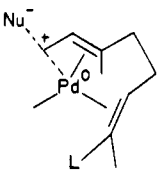
The regiochemistry of the addition is strongly influenced by the ligands. The exclusive donor ligands, that is bipyridine and the simple amines, direct the addition to the less substituted terminus of the η^3-allyl system. However, triphenylphosphine, despite its greater bulk, directs the addition to the more substituted terminus. As suggested earlier[3b,21] one factor could be the relative product stabilities. With bulky ligands such as phosphines a product with a terminal double bond is preferred, giving preferentially **11a**. However, an attractive alternative explanation is that the donor–acceptor properties of the ligands is also an important factor in determining the regiochemistry.

In this context it is interesting to note that the regiochemistry of amination is sometimes dependent on whether the side chain occupies a syn or an anti position. In fact, it has been observed that catalytic alkylation of geranyl and neryl acetate gives different regioisomers.[3b] In the amination of the phosphine complexes **7** the smallest nucleophile, methylamine, reacts mainly at the more substituted positions with both complexes. However, the neryl complex **7b** reacts exclusively at this position to give **13** while the geranyl complex **7a** also gives about 30% of the product from reaction at the less substituted terminus (Table III). The difference is greater in the reactions with dimethylamine in which the geranyl complex gives mainly

(16) Munson, M. S. B. *J. Am. Chem. Soc.* **1971**, *93*, 3914.
(17) (a) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075. (b) Matsushita, H.; Negishi, E. *J. Org. Chem.* **1982**, *47*, 4161.
(18) Åkermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A., manuscript in preparation.
(19) (a) Moberg, C.; Åkermark, B. *J. Organomet. Chem.* **1981**, *209*, 101. (b) Åkermark, B.; Åkermark, g.; Moberg, C. *J. Organomet. Chem.* **1979**, *164*, 97.
(20) Takahashi, U.; Tsukiyama, K.; Sakai, S.; Ishii, Y. *Tetrahedron Lett.* **1970**, 1913.
(21) (a) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416. (b) Adams, R. D.; Chadosh, B. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570.
(22) (a) Sakaki, S.; Nishikawa, M.; Ohyoshi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4062. (b) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.
(23) Döhring, A.; Jolly, P. W. Mynott, R.; Schick, K.-P.; Wilke, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1198.
(24) Chatt, J.; Gamlen, G. A. *J. Chem. Soc.* **1956**, 2371.

14a (from reaction at the less substituted terminus) while **14c** (the product from reaction at the more substituted terminus) dominates for the neryl system. When the nucleophile is trimethylamine, steric factors evidently dominate and both the geranyl and neryl systems give exclusively products from reaction at the less substituted η^3-allyl terminus, i.e., **15a** and **15b**, respectively. On reaction with the even more sterically demanding nucleophile, diisopropylamine, the geranyl complex **7a** gives the expected product **16** from terminal amination, accompanied by a small amount of a mixture of trienes. The neryl complex **7b**, on the other hand, reacts sluggishly to give one triene, myrcene (**19**), as the major product. The conversion of η^3-allyl to the 1,3-diene has been observed before,[17] but the exact mechanism for the reaction is unclear. A possible explanation for the selective formation of myrcene is that deprotonation at the methyl group is sterically favored for the neryl system (Scheme VI). However, steric effects do not explain why the neryl system, which is the less reactive, has a higher susceptibility than the geranyl system for nucleophilic attack at the more substituted η^3-allyl terminus.

Although there is no evidence of ground-state coordination of the internal double bond in complexes **7**, a contribution from a transition state such as **20** (cf. the reaction



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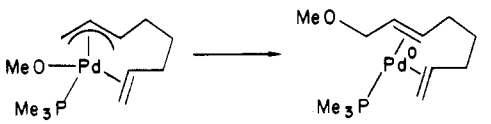
21 → **22**)[23] could be involved, which would explain the



21 **22**

higher reactivity of the geranyl system and also its susceptibility for reaction at the less substituted terminus. This is supported by the fact that the neryl but not the geranyl system gives a product pattern that closely resembles that obtained from the simple 3-methylbutenyl system.[18] Many of the present results appear explainable in terms of the donor–acceptor properties of the auxiliary ligands. An independent measure of these effects was obtained from the ^{13}C NMR spectra. In the TMEDA complexes **6** the chemical shifts are ca. 56 ppm for the less substituted allyl carbon and ca. 92 ppm for the more substituted, i.e., approximately the expected difference between a primary and a tertiary carbon. The corresponding shifts for the bipyridine complexes **5** are ca. 58 and 94 ppm. If the downfield shifts are assumed to parallel increased positive charge, which appears to be a reasonable assumption,[25] the positive charge on carbon is somewhat higher at the η^3-allyl termini of the bipyridine complexes but the relative charge is unaffected. Moderate reactivity and preference for the less substituted terminus on steric grounds were expected and were subsequently proven by experiment. For the triphenylphosphine complexes **7** the shifts are ca. 66 and 122 ppm, which indicates an increase in the positive charge and also a substantial increase in the relative charge at the more substituted terminus. This would be expected to lead to preferential reaction at the more substituted terminus which is in agreement with our experimental results.

Relatively small changes in the electronic properties of the ligands obviously have a strong effect on the reactivity of the η^3-allyl unit. With use of these effects, it should be possible to induce selective reactivity at either of its terminal positions. With a combination of trends in the reactivity and the ^{13}C NMR shifts, we are currently exploring these possibilities.

Experimental Section

General Data. The NMR spectra were recorded on a Bruker WP 200 spectrometer at 200 MHz for ^1H and at 50.3 MHz for ^{13}C. The shifts are expressed as parts per million relative to Me_4Si. GLC was performed on a Pye-Unicam GCD using 5% SE-30 on alkali-washed Chromosorb W stationary phase.

Solvents and chemicals were "reagent grade" materials and were used as received. The mixed geranyl- and nerylpalladium chloride complex (**1a** + **1b**) was prepared as described in an earlier publication.[4]

Tetrakis(acetonitrile)silver tetrafluoroborate was prepared by using a modification of a procedure described in the literature.[26] Silver oxide (10 g, 43 mmol) was suspended in 60 mL of acetonitrile, and concentrated HBF_4 (20.5 g, 37% by weight) was added. After 10 min most of the oxide had dissolved. The solution was filtered and concentrated to 30 mL, and diethyl ether was added. On cooling in a freezer at −20 °C, colorless crystals separated. Recrystallization from acetonitrile–ether and drying in a stream of nitrogen gave tetrakis(acetonitrile)silver tetrafluoroborate (26.7 g, 86%).

(η^3-Geranyl)(acetonitrile)palladium Tetrafluoroborate (2a). The mixed geranyl- and nerylpalladium chloride complex (**1a** + **1b**, 2.0 g, 7.17 mmol) was dissolved in 20 mL of dichloromethane, and solid tetrakis(acetonitrile)silver tetrafluoroborate (2.57 g, 7.17 mmol) was added. Immediate precipitation of silver chloride was observed. After the mixture was stirred for 5 min, the silver chloride was removed by filtration and the solvent was evaporated under vacuum at room temperature to give a pale yellow-green oil. In order to remove excess acetonitrile, the oil was washed twice with 3 mL of benzene, then dissolved in 3 mL of chloroform, and dried under high vacuum. The residue was dissolved again in 3 mL of chloroform, filtered through a small amount of activated charcoal, and dried again to give the pure (η^3-geranyl)(acetonitrile)palladium tetrafluoroborate (**2a**, 2.32 g, 87%) as a yellow-green oil. The pure oil slowly crystallized. If seed crystals are available, it can be recrystallized from dichloromethane–diethyl ether to give pale yellow prisms of pure **2a**, mp 104–109 °C dec. The complex was characterized by its ^1H and ^{13}C NMR spectra (Tables I and II).

(η^3-Geranyl)(2,2′-bipyridine)palladium Tetrafluoroborate (5a). The geranyl complex **2a** (1.00 g, 2.69 mmol) was dissolved in 4 mL of dichloromethane. The solution was cooled to −78 °C, and a small excess of 2,2′-bipyridine (0.46 g, 2.96 mmol) dissolved in 4 mL of cold dichloromethane was added. The mixture was stirred for 10 min and then allowed to warm to room temperature. Most of the solvent was removed under vacuum, and diethyl ether was added to give crystals of better than 98% pure (η^3-geranyl)(2,2′-bipyridine)palladium tetrafluoroborate (**5a**, 1.20 g, 92%), mp 111–113 °C. The complex was crystallized from dichloromethane–diethyl ether or ethanol, containing a small amount of bipyridine, without isomerization. The complex was characterized by its ^1H and ^{13}C NMR spectra (Tables I and II).

(η^3-Neryl)(2,2′-bipyridine)palladium Tetrafluoroborate (5b). Isomerization of **5a** by addition of a small amount of HCl or **1a** + **1b**, or reaction of the mixed chloride complex **1a** + **1b** with tetrakis(acetonitrile)silver tetrafluoroborate followed by bipyridine, gives an approximately 1:1 mixture of the geranyl and

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(26) Gmelin "Handbuch der Anorganische Chemie", 19, *61* (*Ag*) *B6*, 348.

Table IV. Selected ^1H NMR Data (δ in $CDCl_3$) of Geranyl-, Neryl-, and Linalylamines and Geranyl-, Neryl-, and Linalylammonium Salts[a]

$Me_xNCH_2{}^{12}CH^{3}{=}C(Me^{1})CH_2{}^{4}CH_2{}^{5}CH^{6}{=}CMe_2{}^{12}$ $CH_2{}^{12}{=}CH^{3}C(Me^{1})(NMe_x)CH_2{}^{4}CH_2{}^{5}CH^{6}{=}CMe_2{}^{23}$

compd	H^1, H^2	H^3	H^4, H^5	H^6	Me^1	$N(Me)_x$
12a	2.94 d	5.27 t	2.0–2.2 m	5.11 t	1.64 s[b]	2.18 s
12b	2.94 d	5.27 t	2.0–2.2 m	5.11 t	1.73 s[b]	2.18 s
13	5.02 dd	5.68 dd	1.4–1.5 m	5.11 t[b,c]	1.12 s	2.26 s
	5.11 dd		1.8–2.1 m			
14a	2.88 d	5.25 t[b]	2.0–2.2 m	5.10 t,[b] br	1.64 s[b]	2.22 s
14b	2.87 d[b]	5.24 t[b]	2.06[d]	5.11 t,[b] br	1.74 s[b]	2.21 s
14c	5.03 dd	5.83 dd	1.4–1.5 m	5.10 t[b,c]	1.05 s	2.22 s
	5.14 dd		1.8–2.1 m			
15a	3.92 d	5.33 t	2.1–2.2 m	5.02 t,[b] br	1.80 s	3.10 s
15b	3.87 d	5.37 t	2.1–2.3 m	5.06 t,[b] br	1.90 s	3.11 s
16	3.08 d	5.20 t	1.9–2.2 m	5.08 t,[b] br	1.63 s	*e*

[a] s = singlet, d = doublet, t = triplet, dd = double doublet, and br = broad. The chemical shifts of Me^2 and Me^3 are practically constant along the series (1.68 and 1.60 ppm, respectively) and are not listed in the table. [b] A fine structure, due to long-range coupling, is also detectable. [c] Overlapped by other signals. [d] Pseudodoublet. [e] δ 3.05 heptet (NC*H*) and 1.02 d (NCH*Me*$_2$).

neryl complexes **5a** and **5b**. The mixed complex **5a** + **5b** (1.40 g, 2.87 mmol) was dissolved in 16 mL of hot ethanol, a small amount of the mixed chloride complex **1a** + **1b** was added, and the solution was allowed to slowly cool to room temperature. After the mixture was left standing overnight, crystals were collected (1.14 g, 81%) that contained about 70% of the neryl isomer **5b**. Two recrystallizations from ethanol, containing a small amount of bipyridine to prevent isomerization, gave 90% pure (η^3-neryl)(2,2′-bipyridine)palladium tetrafluoroborate **5b**, mp 151–153 °C (0.65 g, 46%). The overall yield can be improved by recycling the material in the mother liquor.

The complex **5b** was characterized by ^1H and ^{13}C NMR (Tables I and II). Anal. Calcd for $C_{20}H_{25}N_2BF_4Pd$: C, 49.36; H, 5.18; N, 5.76. Found: C, 49.36; H, 5.26; N, 5.71.

(η^3-Geranyl)(*N,N,N′,N′*-tetramethylethylenediamine)palladium Tetrafluoroborate (6a). The geranyl complex **2a** (0.370 g, 1.00 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, 0.130 g, 1.12 mmol) were reacted as described for **5a** to give the essentially pure (η^3-geranyl)(*N,N,N′,N′*-tetramethylethylenediamine)palladium tetrafluoroborate (**6a**), mp 106–108 °C (0.420 g, 84%). The complex was characterized by ^1H and ^{13}C NMR (Tables I and II). Anal. Calcd for $C_{16}H_{33}N_2BF_4Pd$: C, 43.02; H, 7.45; N, 6.27. Found: C, 43.16; H, 7.54; N, 6.20.

(η^3-Neryl)(*N,N,N′,N′*-tetramethylethylenediamine)palladium tetrafluoroborate (6b) was only obtained as a 1:1 mixture with the geranyl complex **6a** by isomerization of **6a** in dichloromethane solution containing a catalytic amount of the mixed chloride complex **1a** + **1b**. See Tables I and II for NMR data.

(η^3-Geranyl)bis(triphenylphosphine)palladium Tetrafluoroborate (7a). The geranyl complex **2a** (0.370 g, 1.00 mmol) was dissolved in 3 mL of dichloromethane. The solution was cooled to −78 °C, and triphenylphosphine (0.535 g, 2.04 mmol) in 4 mL of cold dichloromethane was added. The mixture was stirred at −78 °C for 5 min, and the solvent was then rapidly evaporated in vacuo, keeping the temperature below −20 °C. In order to eliminate excess triphenylphosphine, the residue was washed several times with light petroleum and then twice with a 2:1 mixture of light petroleum–diethyl ether. To remove traces of decomposition products (probably palladium(0) complexes), the resulting yellow-pink residue was dissolved in 3 mL of dichloromethane and quickly filtered through a 2-cm column of silica gel in a Pasteur pipette. The solvent was removed from the filtrate to give a pale yellow residue which consisted of essentially pure (η^3-geranyl)bis(triphenylphosphine)palladium tetrafluoroborate (**7a**), mp 120–135 °C dec (0.700 g, 82%), containing <5% of the neryl isomer **7b**. See Tables I and II for ^1H NMR data. Anal. Calcd for $C_{46}H_{47}P_2BF_4Pd$: C, 64.62; H, 5.54; P, 7.24. Found: C, 63.98; H, 5.65; P. 7.08.

Since the mixed (η^3-geranyl)(phosphine)(acetonitrile)palladium tetrafluoroborate complex catalyzes isomerization, excess triphenylphosphine must be used in the ligand exchange reaction. However the excess triphenylphosphine must be removed after the reaction to avoid nucleophilic addition to the η^3-geranyl system and formation of palladium(0) complexes and phosphonium salts that greatly decrease the yield and make the product difficult to purify.

(η^3-Neryl)bis(triphenylphosphine)palladium Tetrafluoroborate (7b). (η^3-Neryl)(bipyridine)palladium tetrafluoroborate (**5b**, isomeric purity 90%, 0.243 g, 0.50 mmol) was dissolved in 3 mL of dichloromethane, the mixture cooled to −78 °C, and triphenylphosphine (0.262 g, 1.00 mmol) in 4 mL of cold dichloromethane was rapidly added. Workup, as described for the geranyl complex, plus two additional washings with diethyl ether gave (η^3-neryl)bis(triphenylphosphine)palladium tetrafluoroborate (**7b**), mp 120–135 °C dec. In $CHCl_3$ solution the pure complexes **7a** and **7b** are stable for several days at room temperature and are stable essentially indefinitely in a freezer but decompose rapidly when contaminated by free triphenylphosphine, bipyridine, or triphenylphosphinepalladium(0) compounds. See Tables I and II for NMR data.

(η^3-Geranyl)[1,2-bis(diphenylphosphino)ethane]palladium tetrafluoroborate (8a) was prepared from complex **2a** (0.370 g, 1.00 mmol) and 1,2-bis(diphenylphosphino)ethane (diphos, 0.410 g, 1.03 mmol) as described for the triphenylphosphine complex **7a**, except that excess diphos was removed simply by washing several times with light petroleum–diethyl ether (1:1). Essentially pure (η^3-geranyl)[1,2-bis(diphenylphosphino)ethane]palladium tetrafluoroborate (**8a**) (0.620 g, 85%) was obtained. See Tables I and II for NMR data.

(η^3-Neryl)[1,2-bis(diphenylphosphino)ethane]palladium tetrafluoroborate (8b) was prepared from complex **5b** (isomeric purity 90%, 0.243 g, 0.50 mmol) and 1,2-bis(diphenylphosphino)ethane (diphos, 0.199 g, 0.50 mmol) as described for the triphenylphosphine complex **7b**. Essentially pure (isomeric purity 90%) (η^3-neryl)[1,2-bis(diphenylphosphino)ethane]palladium tetrafluoroborate (**8b**, 0.314 g, 86%) was obtained. See Tables I and II for NMR data. The compound could be crystallized from CH_2Cl_2–pentane: mp 142–143 °C dec.

Attempted Preparation of (η^3-Geranyl)(1,5-cyclooctadiene)palladium Tetrafluoroborate (9a). The geranyl complex **2a** (0.370 g, 1.00 mmol) was dissolved in 5 mL of dichloromethane, and a substantial excess of 1,5-cyclooctadiene (0.2 mL, 1.6 mmol) was added at room temperature. After being stirred for 5 min, the solution was concentrated to about 2 mL and diethyl ether was added to precipitate a colorless solid (0.400 g, 91%) which was a 1:1 mixture of (η^3-geranyl)(1,5-cyclooctadiene)palladium tetrafluoroborate (**9a**) and the corresponding η^3-neryl isomer **9b**, mp 125–127 °C dec. See Tables I and II for NMR data.

Reactions between η^3-Geranyl and η^3-Neryl Complexes and Amines. Unless otherwise noted, all reactions were performed in an NMR tube using 0.05 mmol of η^3-allyl complex in $CDCl_3$ solution (0.5 mL). Low-temperature experiments instead used $CDCl_3$–CD_2Cl_2 (3:1) as solvent. Excess of the appropriate amine (0.15 mmol) was added with a microsyringe from a stock solution (3–4 mol L^{-1}) in benzene. Yields and approximate rates (half-lives for the starting compounds) are given in Table III. The phosphine complexes **7** were generally generated in situ by addition of 1.9 equiv of triphenylphosphine to the bipyridine complexes **5**.

Control experiments using preformed complexes 7 gave results which were essentially identical with those employing in situ generation.

In most cases the products could be identified in the reaction mixture by ^{1}H NMR (see Table IV), directly or after filtration of precipitate. Approximate total yields were determined by integration of the NMR signals of the crude reaction product and the relative yields by integration of the signals from the isolated amine fraction. In order to determine the yields more accurately, most reactions were repeated on a 0.1-mmol scale. After the appropriate reaction time (see Table III), the solvent and excess amine were evaporated. In the case of methyl-, dimethyl-, and diisopropylamines, 1 mL of water and a few drops of concentrated hydrochloric acid were added to the residue and the mixture was extracted three times with 1.5 mL of hexane, in order to remove the hydrocarbon byproducts, if any. The resulting mixture was then treated with a small amount of solid NaOH and extracted three times with 1.5 mL of hexane. Evaporations of the solvent gave the amine products, the relative amounts of which were determined by ^{1}H NMR.

In the reactions with trimethylamine, the crude, dried reaction products were extracted with water (2 × 1 mL) to give, after evaporation, the essentially pure quarternary ammonium salts.

Isolation of Linalyldimethylamine (14c). The neryl-palladium complex **5b** containing 10% of the isomer **5a** (0.049 g, 0.1 mmol) was dissolved in dichloromethane and cooled to −78 °C, and triphenylphosphine (0.052 g, 0.02 mmol) was added. When all had dissolved, dimethylamine (0.3 mmol) in ca. 100 μL of benzene was added, immediately followed by excess triphenylphosphine (0.100 g, 0.38 mmol). The solution was stirred for 5 min at −78 °C and then warmed to −30 °C. After a few minutes a heavy yellow precipitate of tetrakis(triphenylphosphine)palladium(0) was formed. After addition of hexane (3 mL) the precipitate was removed by filtration and the solvent was evaporated at −20 °C. The amine product was isolated as described above. The yield was essentially quantitative, and the product contained mainly linalyldimethylamine **14c** (80%) but also some neryldimethylamine **14b** (12%) and geranyldimethylamine **14a** (8%).

Using the same procedure but reacting instead the geranyl complex **7a** gave a mixture of geranyldimethylamine **14a** (84%) and linalyldimethylamine **14c** (16%).

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Registry No. **1a**, 89302-63-6; **1b**, 89362-81-2; **2a**, 96328-66-4; **3a**, 96328-68-6; **3b**, 96392-64-2; **4a**, 96328-70-0; **4b**, 96392-66-4; **5a**, 96328-72-2; **5b**, 96392-68-6; **6a**, 96328-74-4; **6b**, 96392-70-0; **7a**, 96328-76-6; **7b**, 96392-72-2; **8a**, 96328-78-8; **8b**, 96392-74-4; **9a**, 96328-80-2; **9b**, 96392-76-6; **12a**, 96348-40-2; **12b**, 96328-59-5; **13**, 96328-60-8; **14a**, 51768-88-8; **14b**, 53652-01-0; **14c**, 96328-61-9; **15a**, 96328-62-0; **15b**, 96328-63-1; **16**, 76027-07-1; **19**, 123-35-3; $Pd(PPh_3)_4$, 14221-01-3; GerNerNH, 96328-64-2; GerNHMe, 63343-64-6; $MeNH_2$, 74-89-5; Me_2NH, 124-40-3; Me_3N, 75-50-3; i-Pr_2NH, 108-18-9; (η^3-geranyl)triphenylphosphine)(acetonitrile)palladium tetrafluoroborate, 96328-82-4; tetrakis(acetonitrile)silver tetrafluoroborate, 93556-88-8; ocimene, 13877-91-3.

Synthesis of Methyl and Hydride Derivatives of Permethylvanadocene and Their Reactions with Carbon Monoxide

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Oxidation of permethylvanadocene with 1 equiv of HCl yields the paramagnetic chlorovanadium(III) complex (η^5-$C_5Me_5)_2VCl$, **2**. This complex can be alkylated with methyllithium to yield the paramagnetic methyl complex (η^5-$C_5Me_5)_2VCH_3$, **3**. Complex **3** undergoes hydrogenolysis under hydrogen pressures of 17–25 atm to yield a paramagnetic monohydride complex (η^5-$C_5Me_5)_2VH$, **4**, which exchanges with a deuterium atmosphere to yield the monodeuteride. Treatment of **4** with carbon monoxide at 1 atm produces the diamagnetic carbonyl hydride complex (η^5-$C_5Me_5)_2V(H)CO$, **6**. Treatment of **3** with excess carbon monoxide at room temperture and 1 atm pressure yields the diamagnetic acetyl carbonyl complex (η^5-$C_5Me_5)_2V[C(O)CH_3](CO)$, **5**. Two intermediates in the conversion were observed spectroscopically by varying the reaction conditions. These were tentatively identified as the diamagnetic methyl carbonyl complex (η^5-$C_5Me_5)_2V(CH_3)CO$, which was observed at low temperature by ^{1}H NMR, and the paramagnetic acetyl complex (η^5-$C_5Me_5)_2VC(O)CH_3$, which was observed by infrared spectroscopy under a deficiency of CO at room temperature.

Introduction

Bis(cyclopentaidenyl)vanadium, or vanadocene, exhibits a rich chemistry which includes coordination of two-electron ligands,[1a] oxidation to V(III) followed by coordination of additional ligands,[1a-c] synthesis of V(III) alkyl complexes,[1d-g] and insertion of CO into the vanadium–alkyl bond of these complexes to form acyl complexes.[1h,i] However, no hydride derivative of vanadocene has ever been prepared.

We have reported the synthesis of permethylvanadocene and its oxidation with ferrocenium ion to yield acetonitrile and carbonyl adducts of vanadium(III).[2] In light of the

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